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UTJECAJ SILE OPTEREĆIVANJA NA REZULTATE MJERENJA TVRDOĆE REFERENTNOG TVRDOMJERA 5030 TKV

INFLUENCE OF LOAD ON HARDNESS MEASUREMENT RESULTS OF REFERENCE HARDNESS MACHINE 5030 TKV

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Sažetak: Kod etalonskih uređaja za tvrdoću jedna od utjecajnih veličina na rezultat mjerenja je ostvarivanje odgovarajućeg opterećenja. Ako se pogleda osnovni izraz za izračun vrijednosti tvrdoće po metodi Vickers jasno je uočljivo da ista pored ostalog ovisi o vrijednostima sile opterećivanja i ubrzanja zemljine sile teže na mjestu instalacije etalonskog tvrdomjera. U ovom radu je istraživano kako stvarno izmjerene vrijednosti sile opterećivanja i ubrzanja sile teže utječu na rezultate izmjerene tvrdoće. Ispitivanja su provedena na referentnom etalonskom tvrdomjeru 5030TKV za metodu HV10. Za ispitivanja sila opterećivanja korišteni su posrednički etaloni sile s mjernom nesigurnošću < 0,01% a za utvrđivanje ubrzanja sile teže relativni gravimetar rezolucije $1 \cdot 10^{-8}$ ms^{-2}. Nakon ovih mjerenja provedeno je indirektno umjeravanje etalonskog tvrdomjera referentnim etalonskim pločicama te doneseni određeni zaključci.

Ključne riječi: tvrdoća, referentni etalonski tvrdomjer, sila, ubrzanje sile teže,

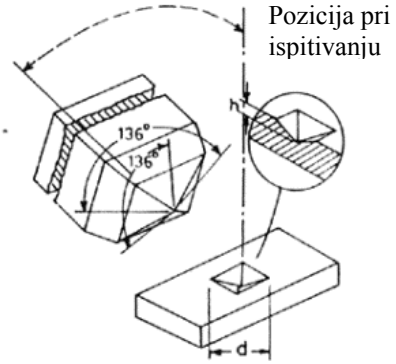
Abstract: In standard hardness testers, one of the values that affect the measurement result is the achievement of adequate load. Considering the basic expression for hardness calculation according to the Vickers method it is clear that, apart from other things, it depends on the load force values and gravitational acceleration at the point of standard hardness tester installation. This paper studies how the actually measured values of the loading force and gravitational acceleration affect the results of the measured hardness. The studies were carried out on a reference hardness machine 5030TKV for the HV10 method. For the testing of loading forces the intermediate force standards were used with the uncertainty of measurement of <0,01%, and relative gravimeter of $1 \cdot 10^{-8}$ ms^{-2} resolution was used to determine the gravitational acceleration. These measurements were followed by indirect calibration of the standard hardness machine using reference standard plates. Finally, certain conclusions have been provided.

Key words: hardness, reference standard hardness machine, force, gravitational acceleration

1. UVOD

Po definiciji tvrdoća je otpornost materijala prema prodiranju drugog, znatnije tvrđeg tijela. Ispitivanje tvrdoće je vjerojatno najčešće uporabljeno ispitivanje nekog mehaničkog svojstva, unatoč tome što mehanička svojstva utvrđena ispitivanjem tvrdoće nisu fizikalno jednoznačne veličine. Ispitivanje tvrdoće tek neznatno oštećuje površinu ispitivanog predmeta pa se općenito može svrstati među nerazorna ispitivanja. Osnovni princip mjerenja kod većine metoda je mjerenje veličine ili dubine otiska što ga indentor, opterećen nekom silom, načini u ispitivanom materijalu.

Vickers metoda je standardna metoda mjerenja tvrdoće metala, posebno onih s vrlo tvrdom površinom. Izumljena je 1920-ih godina od strane inženjera tvrtke Vickers, Ltd., Velika Britanija, kao alternativna metoda mjerenja tvrdoće materijala. Kod Vickersove metode kao indentor se koristi četverostrana piramida s vršnim kutom između nasuprotnih stranica od 136° (slika 1).



Slika 1: Dijamantna piramida kao indentor za Vickers metodu i načinjeni otisak

Po definiciji, tvrdoća po Vickersu približna je onoj Brinellovoj, a izračunava se izrazom:

$$HV = \text{Konstanta} \times \frac{\text{Ispitna sila}}{\text{Površina otiska}} \tag{1}$$

Konstanta je dobivena iz slijedećeg izraza:

$$\text{Konstanta} = \frac{1}{g_{\text{n}}} = \frac{1}{9{,}80665} \approx 0{,}102 \tag{2}$$

Tako matematički izraz za izračun vrijednosti Vickersove tvrdoće poprima oblik [1]:

$$HV = 0{,}102 \frac{2\,F \sin\frac{136^{\circ}}{2}}{d^2} \approx 0{,}1891 \frac{F}{d^2} \tag{3}$$

gdje je F, N sila, a d, mm^2 srednja vrijednost dijagonale otiska nakon rasterećenja. Uobičajene vrijednosti sila kod Vickersove metode prikazane su u tablici 1.

Provjera sila opterećivanja provodi se, kad je god to moguće, u tri različita položaja sustava za opterećivanje. Provjera mora biti provedena pomoću uređaja za provjeru sile koji mora ispunjavati kriterije klase 0,5 prema normi HRN EN ISO 376 [2]. Ako se koristi neki drugi postupak njegova mjerna nesigurnost mora biti najmanje jednaka onom ostvarenom s uređajem klase 0,5. Svaka izmjerena sila ne smije prekoračiti dozvoljene vrijednosti od nazivne sile [3]:

a) za konvencionalnu i semimikro tvrdoću ± 0,1 %,
b) za mikrotvrdoću ± 0,5 %.

Tablica 1: Vrijednosti sila opterećivanja za Vickersovu metodu [1]

Konvencionalna tvrdoća[1)]		Semimikrotvrdoća		Mikrotvrdoća[2)]	
Oznaka	Ispitna sila *F*, N	Oznaka	Ispitna sila *F*, N	Oznaka	Ispitna sila *F*, N
HV 5	49,03	HV 0,2	1,961	HV 0,01	0,09807
HV10	98,07	HV 0,3	2,942	HV 0,015	0,147
HV 20	196,1	HV 0,5	4,903	HV 0,02	0,1961
HV 30	294,2	HV 1	9,807	HV 0,025	0,2452
HV 50	490,3	HV 2	19,61	HV 0,05	0,4903
HV 100	980,7	HV 3	29,42	HV 0,1	0,9807

[1)] Ispitne sile >980,7 N smiju se primjenjivati
[2)] Ispitne sile za mikro tvrdoću su preporučljive

Za svaku silu i za svaki položaj sustava za opterećivanje potrebno je provesti niz od barem tri mjerenja.

2. EKSPERIMENTALNI DIO

Za ispitivanja utjecaja sile opterećivanja na izmjerene vrijednosti tvrdoće korišten je referentni etalonski tvrdomjer 5030TKV koji je izrađen u tvrtki INDENTEC, Velika Britanija, a odgovarajuće opterećenje ostvaruje se utezima preko polužnog sustava (slika 2). Polužni sustavi za mjerenja sile u najboljim svjetskim institutima ostvaruju nesigurnost mjerenja sile ≤0,01 % što u potpunosti zadovoljava zahtjeve na opterećenje kod etalonskih tvrdomjera sukladno normi EN ISO 6507-3. No kako je po definiciji sila $\boldsymbol{F = m \cdot g}$, da bi se postiglo odgovarajuće pojedino opterećenje masom utega, provedena su gravimetrijska mjerenja (ubrzanje sile teže) na mjestu instalacije etalonskog tvrdomjera 5030TKV i na temelju tih vrijednosti provedena je izrada utega odgovarajuće mase.
Za provedbu gravimetrijskih mjerenja primijenjen je relativni gravimetar CG-3M AutoGrav kanadske tvrtke Scintrex, koji je trenutno jedan od najsuvremenijih relativnih gravimetra (slika 3).

Slika 2: Referentni etalonski tvrdomjer 5030TKV

Slika 3: Relativni gravimetar Scintrex CG-5

To je kvarcni, mikroprocesorski kontroliran i visoko automatiziran instrument. Radni domet gravimetra je preko 7000 mGal-a (1 mGal = 10^{-5} ms^{-2}), što obuhvaća područje cijele Zemlje, bez potrebe za resetiranjem, a standardna rezolucija gravimetra je 1 μGal-a (1 μGal = 10^{-8} ms^{-2}). Niveliranjem je dobivena nadmorska visina na mjestu instalacije tvrdomjera **114,267 m**, koja je kasnije korištena pri obveznim redukcijama gravimetrijskih mjerenja. Obradom i izjednačenjem dobivena je vrijednost ubrzanja sile teže od: $\boldsymbol{g}$ **= 9,80663337 ms^{-2} ± 4,2 10^{-8} ms^{-2}**. Ova vrijednost ubrzanja sile teže korištena je za proračun mase utega preko kojih se ostvaruje određena vrijednost opterećenja za sustav opterećivanja kod etalonskog tvrdomjera.

Ispitivanje sile je provedeno u četiri različite pozicije ispitnog stola za metodu HV10 s dva različita posrednička etalona za istu silu opterećivanja. Primijenjena su dva etalona iz razloga što oni imaju različitu konstrukciju te mjernu sposobnost što može utjecati na dobivene rezultate mjerenja. Oba etalona sile su umjerena kao posrednički etaloni na mjernoj točki 100 N. U tablici 2 su prikazani mjeriteljski uvjeti i mjerne karakteristike etalona sile.

Tablica 2: Mjeriteljski uvjeti umjeravanja sile opterećivanja za metodu HV10

Okolišni uvjeti	Temperatura	Tlak	Vlažnost
	21 °C ± 0,5 °C	1035 hPa	55 % rel.

Mjerno pojačalo MGC-plus		**Prijenosni etaloni sile**		
Mjerno područje:	0,00000 – 2,00000 mV/V	Dinamometar Z30	Mjerno područje:	20 – 100 N
			Nul signal	-0,00124 mV/V
Najbolja mjerna sposobnost:	≤ 0,00005 mV/V		Priključak	6 - žilni
			Mjerna nesigurnost	0,0030 %
Očitavač:	AB12	Dinamometar U1	Mjerno područje:	100 – 500 N
Rezolucija:	0,00001 mV/V		Nul signal:	0,00187 mV/V
Noseća frekvencija :	225 Hz		Priključak:	6 - žilni
			Mjerna nesigurnost:	0,015 %

U tablici 3 su prikazane vrijednosti nazivne sile (F) i referentna vrijednost očitanja za tu silu (X_{REF}) za opterećenje HV10, rezultati pet mjerenja sila (X_i) na svakoj poziciji te izračunate vrijednosti odstupanja (q), ponovljivosti (b) te proširene mjerne nesigurnosti (U). Procjena i proračun mjerne nesigurnosti je provedena sukladno dokumentu [4].

Tablica 3: Rezultati ispitivanja sila opterećivanja za metodu HV10

Mjerna pozicija	F, N	X_{REF}, mV/V	X_1, mV/V	X_2, mV/V	X_3, mV/V	X_4, mV/V	X_5, mV/V	q, % q_{max}	q, % q_{min}	b, %	U, %
Poz. 1	98,07	0,40005	0,40028	0,40023	0,40022	0,40028	0,40027	0,057	0,042	0,015	0,049
Poz. 2			0,40015	0,4003	0,40016	0,40029	0,40027	0,062	0,025	0,037	0,051
Poz. 3			0,40024	0,40032	0,40039	0,40038	0,40024	0,085	0,047	0,037	0,051
Poz. 4			0,40032	0,40038	0,40026	0,40024	0,40028	0,082	0,047	0,035	0,050
Poz. 1	98,07	1,96199	1,96235	1,96258	1,96255	1,96251	1,96247	0,030	0,018	0,012	0,018
Poz. 2			1,96301	1,96318	1,96304	1,96304	1,96294	0,060	0,048	0,012	0,018
Poz. 3			1,96287	1,96295	1,96285	1,96270	1,96263	0,049	0,032	0,016	0,019
Poz. 4			1,96238	1,96254	1,96268	1,96240	1,96276	0,039	0,020	0,019	0,020

Nakon ispitivanja sila opterećivanja provedeno je indirektno umjeravanje etalonskog tvrdomjera a rezultati su prikazani u tablici 4. Na temelju ovih rezultata procijenit će se utjecaj sila na vrijednosti izmjerene tvrdoće.

Tablica 4: Indirektno umjeravanje referentnog etalonskog tvrdomjera 5030 TKV primarnim etalonskim pločicama

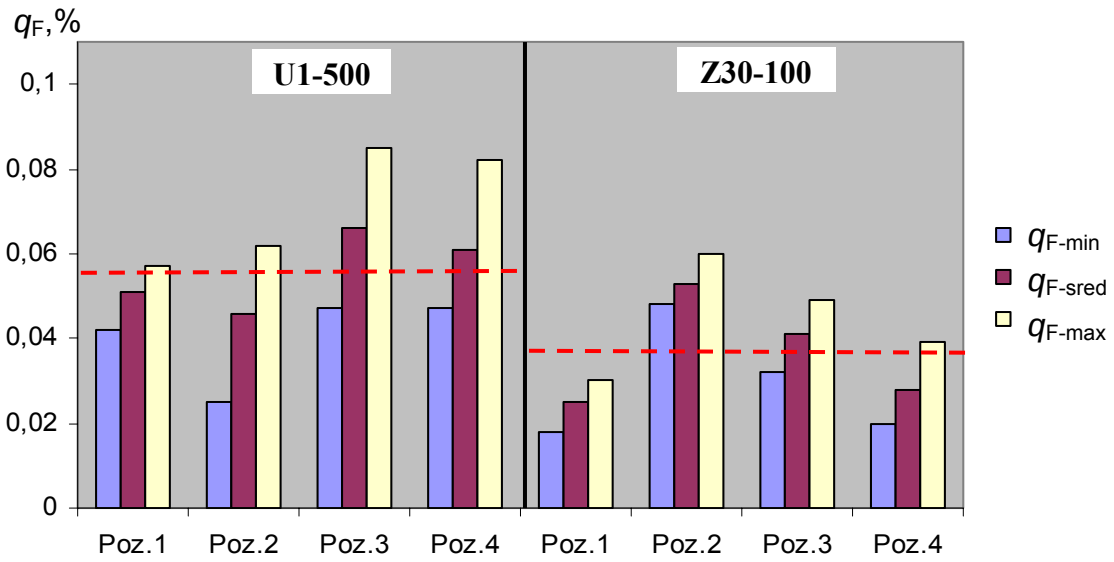
Mjeriteljski uvjeti						
Okoliš				Etalonski tvrdomjer		
Temperatura:	22 ºC ± 0,5 ºC			Oznaka:	5030TKV; CCD_LSFSB	
Tlak:	1035 hPa			Rezolucija:	0,000 1 mm	
Primarne etalonske pločice		**Rezultati mjerenja**				
Oznaka:	IN28256G	1	2	3	4	5
Vrijednost :	272,2	$272{,}79_{min}$	$273{,}41_{max}$	273,38	272,82	273,08
Srednja vrijednost						**273,10 HV10**
Proširena mjerna nesigurnost						**1,66 HV10**
Oznaka:	IN4519G	1	2	3	4	5
Vrijednost :	457,4	456,21	455,57	456,95	$455{,}08_{min}$	$457{,}7_{max}$
Srednja vrijednost						**456,32 HV10**
Proširena mjerna nesigurnost						**2,97 HV10**
Oznaka:	IN60150G	1	2	3	4	5
Vrijednost :	807,9	804,16	807,61	$803{,}05_{min}$	$810{,}96_{max}$	805,96
Srednja vrijednost						**806,17 HV10**
Proširena mjerna nesigurnost						**5,65 HV10**

3. ANALIZA REZULTATA

Na temelju rezultata iz tablice 3 s obzirom na primijenjeni posrednički etalon sile za opterećenje HV10 ustanovljene su slijedeće srednje vrijednosti sile opterećivanja:

- F_{HV10} = 98,107 N primjenom etalona sile Z30 i
- F_{HV10} = 98,125 N primjenom etalona sile U1.

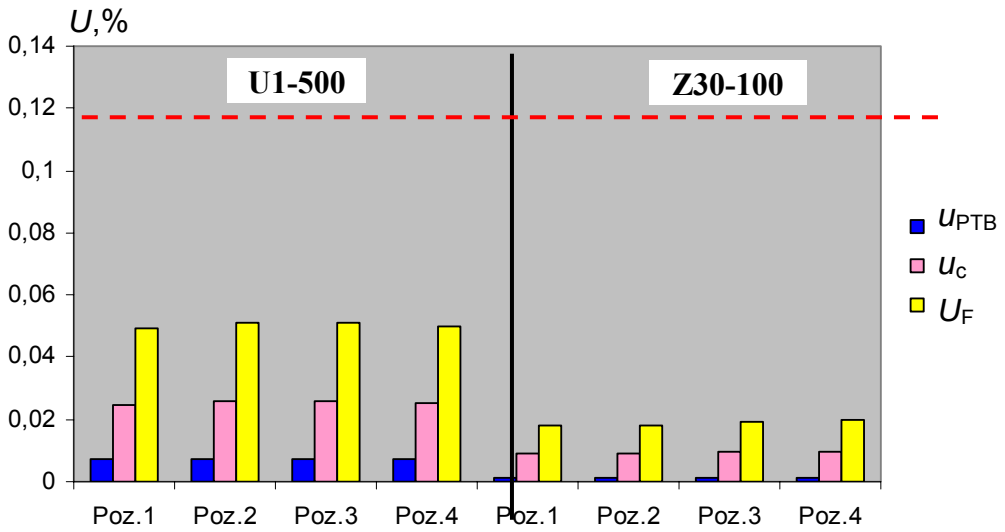
Obje vrijednosti su unutar ±0,1 % odstupanja od normirane (98,07 N) i u slučaju kada se odstupanju pribroji i vrijednost proširene mjerne nesigurnosti. Da bi se mogli donijeti konkretniji zaključci potrebno je provesti analizu odstupanja sila te analizu mjernih nesigurnosti ispitivanja sila. Analiza odstupanja je prikazana dijagramski na slici 4, a analiza mjernih nesigurnosti na slici 5. U prvom dijelu dijagrama prikazana su odstupanja sila dobivena umjeravanjem posredničkim etalonom U1 nazivne sile 500 N, a u drugom dijelu umjeravanjem posredničkim etalonom Z30 nazivne sile 100 N. To znači da su mjerenja sila provedena na mjernoj točci 20 % nazivne sile za etalon U1 i 100 % nazivne sile kod etalona Z30.



Slika 4: Odstupanja sila opterećivanja za metodu HV10 primjenom novog modela provjere sila

Iz dijagramskog prikaza jasno je da kod primjene etalona U1 dolazi do većeg rasipanja vrijednosti sila, ali i povećanja odstupanja pri povećanju udaljenosti između indentora i ispitnog stola ili pri rotaciji etalona kod svakog mjerenja.

Ako se uzme srednja vrijednost $\bar{q}_F$ za sve četiri pozicije, što je prikazano na dijagramima isprekidanom crvenom linijom, uočljivo je da je ona nešto viša primjenom posredničkog etalona U1. Razlog tomu moguće je objasniti raspodjelom mjernih nesigurnosti umjeravanja sila opterećivanja prikazanih na slici 5. Uspoređujući vrijednosti nesigurnosti u_{PTB}, što predstavlja nesigurnost umjeravanja u primarnim etalonima sile u PTB-u, Njemačka, jasno je da etalon nazivne sile 100 N ima bolju mjernu sposobnost što izravno utječe na odstupanje i nesigurnost umjeravanja sila opterećivanja HV10. Isti trend je i kod standardne nesigurnosti umjeravanja sila opterećivanja (u_c).



Slika 5: Udjeli pojedinih mjernih nesigurnosti pri umjeravanju sila za metodu HV10 primjenom različitih etalona sile

Razmatrajući dobivene rezultate odstupanja sile opterećenja (tablica 3) i niske vrijednosti procijenjenih i proračunatih nesigurnosti provedena je korekcija sila opterećivanja. Oba posrednička etalona sile pokazala su da je sila nešto veća od vrijednosti 98,07 N, te je izvršena korekcija sile i za stvarnu vrijednost sile uzeta je vrijednost F_{HV10} = 98,107 N. Razmatrajući izraze (2) i (3) vidljivo je da se dvije komponente ovih izraza mogu zamijeniti točnijim vrijednostima a to su:

- sila F_{HV10} = 98,107 N i
- ubrzanje sile teže g = 9,80663337 ms^{-2}.

Uvrštavanjem ovih vrijednosti u izraze (2) i (3) za izračunavanje tvrdoće dobivene su druge vrijednosti tvrdoće. Pri provedbi indirektne metode umjeravanja etalonskog tvrdomjera primijenjene su standardne i stvarno izmjerene vrijednosti za izračun tvrdoće, a rezultati su prikazani u tablici 5.

Tablica 5: Rezultati umjeravanja primarnim etalonskim pločicama s i bez primijenjene korekcije F i g

Primarna etalonska pločica		Pokazivanje etalonskog tvrdomjera				
Oznaka	Tvrdoća primarne etalonske pločice HV_{PEP}	Korekcija	Izmjerena vrijednost tvrdoće $\overline{HV}$ HV	Proširena mjerna nesigurnost U_{HTM} HV	Odstupanje etalonskog tvrdomjera $\lvert\bar{b}\rvert$ HV	Maksimalno odstupanje etalonskog tvrdomjera ΔH_{HTMmax} HV
IN28256G	272,2 HV10	bez	273,10	1,66	0,90	**2,56**
		s	273,19	1,66	0,99	**2,65**
IN45199G	457,4 HV10	bez	456,32	2,97	1,08	**4,05**
		s	456,48	2,97	0,92	**3,89**
IN60150G	807,9 HV10	bez	806,17	5,65	1,73	**7,39**
		s	806,44	5,65	1,46	**7,11**

Iz ovih rezultata je vidljivo da su vrijednosti tvrdoće s uvedenom korekcijom vrijednosti sile opterećivanja i ubrzanja sile teže nešto povećane što se je moglo odmah i pretpostaviti jer je stvarno izmjerena sila veća od normirane vrijednosti. To povećanje vrijednosti tvrdoće za metodu HV10 maksimalno iznosi oko 0,3HV10. Primijenjena korekcija nije imala utjecaja na procjenu i proračun mjerne nesigurnosti umjeravanja indirektnom metodom. Kod izračuna odstupanja i maksimalnog odstupanja etalonskog tvrdomjera također je došlo do promjena vrijednosti.

4. ZAKLJUČAK

Istraživanja sila opterećivanja na sustavu 5030TKV za metodu HV10 su pokazala da izbor prijenosnih etalona sila za provjeru sila opterećivanja može doprinijeti smanjenju mjerne nesigurnosti. Stoga je neophodna primjena posredničkih etalona sile s proširenom mjernom nesigurnošću njihova umjeravanja ≤0,05 %. Primjenom ovih etalona sile kod referentnog etalonskog tvrdomjera 5030TKV moguće je postići proširenu mjernu nesigurnost umjeravanja sila opterećivanja ≤ 0,07 % (uz k=2; P=95 %). Ovako niska vrijednost mjerne nesigurnosti pruža mogućnost uvrštavanja stvarno izmjerene vrijednosti

sile opterećivanja u izraz za izračun vrijednosti tvrdoće. Na taj način je za metodu HV10 izmjerena stvarna vrijednosti sile F_{HV10} = 98,107 N. Uvrštavanjem ove vrijednosti sile i izmjerene vrijednosti ubrzanja sile teže u izraz za izračunavanje tvrdoće došlo je do promjena vrijednosti tvrdoće i odstupanja etalonskog tvrdomjera koje su unutar ±0,5HV. Stoga i mala promjena sile opterećivanja, koja je unutar propisanih granica odstupanja sukladno zahtjevima trenutno važeće norme, može utjecati na vrijednost izmjerene tvrdoće.

5. LITERATURA

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[3] DIN EN ISO 6507-3: Metallic materials - Vickers hardness test - Part 3: Calibration of reference blocks (ISO 6507-3:2005)

[4] EA 10-16, Guidelines on the Estimation of Uncertainty in Hardness Measurements, 2001

ODREĐIVANJE KINETIČKIH PARAMETARA CEMENTNOG SUSTAVA KAO POKAZATELJA MOGUĆNOSTI ZBRINJAVANJA OTPADNOG MULJA IZ POGONA POCINČAVANJA

DETERMINATION OF KINETIC PARAMETERS OF CEMENT SYSTEM AS A INDICATOR OF FIXING ABILITY OF WASTE MUD FROM A ZINC-PLATING PLANT

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Izvorni znanstveni rad / Original scientific paper

Sažetak: Različitim gospodarskim djelatnostima i proizvodnim procesima nastaje veća količina po okoliš potencijalno štetnog materijala te se nastoje iznaći načini njihovog neškodljivog zbrinjavanja. U radu je ispitivana mogućnost dodavanja industrijskog mulja, opterećenog spojevima teških metala u cementni matriks s udjelima koji bitno ne narušavaju hidratacijske procese i strukturu nastalog cementnog kompozita, uz uvjet trajne solidifikacije i stabilizacije otpadne tvari. Praćena je toplina hidratacije i vršena su konduktometrijska mjerenja uz različite dodatke mulja i smjese mulja i otpadnog zeolita portland cementu. Određivanje topline hidratacije provedeno je do 48 sati hidratacije uporabom diferencijalnog mikrokalorimetra pri 20 °C i uz vodo-cementni omjer, V/C = 0,5 te uz voda-kruto omjer, V/K = 0,5 za cemente uz dodatke mulja ili smjese mulja i zeolita. Za određivanje specifične vodljivosti korišten je digitalni konduktometar i metalna elektroda. Mjerenja su vršena pri temperaturi od 20 °C i uz vodo-cementni omjer, V/C = 0,5 te uz različite dodatke zasićenog zeolita i mulja u iznosu od 0 – 50 %. Rezultati toplina hidratacije ukazuju na činjenicu da dodatak mulja bitno utječe na kinetiku hidratacijskih procesa i blokira vezivanje uzorka već pri udjelima mulja do 10 %. Bitno se smanjuje konačna toplina hidratacije i odgađa se vrijeme uspostave maksimuma. Dodavanjem zasićenog zeolita u reakcijski sustav smanjuje se negativni utjecaj otpadnog mulja te je moguće primijeniti povećani udio smjese zeolita i mulja i do 30 %, a da se bitnije ne utječe na vrijednosti topline hidratacije, brzine i stupnja reakcije. Međutim, primjenom matematičkih modela moguće je predvidjeti maksimalnu vrijednost topline hidratacije kao i vrijeme do uspostave maksimuma, brzinu reakcije i stupanj proreagiranosti reakcije za bilo koji udio mulja i smjese mulja i zeolita. Ovi modeli se temelje na eksperimentalnim podacima i predstavljaju temelj budućeg istraživanja u smislu programiranja i dobivanja kompozita unaprijed određenih svojstava kao i uvid u mogućnosti primjene takvog materijala u građevinske svrhe.

Ključne riječi: mulj iz pogona pocinčavanja, otpadni zeolit, solidifikacija/stabilizacija, hidratacija cementa, toplina hidratacije, specifična vodljivost

Abstract: Various economic functions and manufacturing processes result great quantity for environment potentially harmful material and its attempt to find out ways their harmlessly fixing. The study has examined possibility of addition of the industrial mud saturated with heavy metals in cement matrix in content which do not affect the cement hydration processes and structure of incurred cement composite, by terms of uninterrupted solidification and stabilisation of harmful substance. The development of hydration heat and conductometrical measurements ware traced in hydration of Portland cement, CEM I, with varying additions of mud and the waste zeolite + mud mixture. Hydration heats were determined by differencial microcalorimetry up to 48 hours of hydration. Measurements were carried out at a temperature of 20 ^{o}C with the constant water/cement (W/C) or water/solid ratio (W/S) of 0.5 for cement samples with additions of mud and the waste zeolite + mud mixture. The conductometrical measurements were made by a digital conductometer using metal electrodes. Measurements were carried out at a temperature of 20 ^{o}C with the constant water/cement (W/C) ratio of 0.5 with varying additions of the waste zeolite + mud mixture, in quantities from 0 – 50 mass %. The results obtained for hydration heat indicate that the additions used affect the cement hydration kinetics and delays binding and hardening already in the amount of industrial mud of 10 mass %. When the addition content increases, especially mud, the values of heat measured are lower and heat maximums are shifted to later times. Mixing the mud from a zinc-plating plant with saturated zeolite reduces the adverse effect of mud on reaction system. From the results obtained it may be concluded that the addition of the mixture of mud and saturated zeolite until w = 30 % is satisfactory with regard to the quantity of the addition and to its effect on hydration heat, hydration rate and hydration degree. However, maximum value of hydration heat, time to maximum, hydration rate and hydration degree can be predict by using matematical models for any addition of mud and mud + zeolite mixture. These models are based on experimental results and represent a base for future research within the meaning programming and composite production with well known properties and getting access in application ability of this material in civil engineering purpose.

Keywords*:* Mud from a zinc-plating plant, Waste zeolite, Solidification/Stabilization, Cement hydration, Hydration heat, Specific conductivity

UVOD

Procesi solidifikacije i stabilizacije štetnog otpadnog materijala moraju se voditi na način da otpadni materijal što manje utječe na hidratacijske procese i da se štetna tvar ne oslobađa iz nastalog cementnog kompozita. Ovi procesi se temelje na procesima hidratacije klinker minerala C_3S, C_2S, C_3A i C_4AF čime sustav s vremenom prelazi iz viskoznog, tecljivog stanja u kamenu sličnu tvorevinu. Uvođenjem otpadne tvari u ovakav složen sustav čini taj sustav još kompleksnijim jer se uz reakcije hidratacije odvija cijeli niz drugih reakcija. Nastali produkti utječu na kinetičke procese u cementnom kompozitu i time mijenjaju svojstva cementnog gela.

Procesi stabilizacije i solidifikacije predstavljaju fizikalno i kemijsko vezanje štetne tvari u strukturu cementnog kompozita. Uspješnost ovih procesa ovisi upravo o spomenutim procesima hidratacije kao i o mogućnostima prelaska cementnog gela u konačno čvrsto stanje. Praćenje procesa hidratacije moguće je mjerenjem toplina hidratacije, mjerenjem specifične vodljivosti cementnih pasta te određivanjem čvrstoća i drugim metodama.

Hidratacija se prati određivanjem krivulje topline iz koje je moguće analizom i matematičkom obradom odrediti brzinu i stupanj reakcije kao i oslobođenu toplinu u svakom trenutku procesa. Kontinuirano praćenje oslobođene topline vrši se pomoću mikrokalorimetra. Određivanje specifične vodljivosti daje podatke o početku vezivanja cementnog kompozita što predstavlja vrlo važan parametar koji ukazuje na utjecaj dodataka na procese u cementnom sustavu te na svojstva konačnog produkta[1-6].

EKSPERIMENTALNI DIO

Ispitivanja su provedena na uzorcima industrijskog portland cementa uz dodatak otpadnog mulja iz pogona pocinčavanja u iznosu od w = 10 – 40 % i smjese mulja i zeolita zasićenog cinkovim ionima u iznosu w = 10 – 40 % sa udjelom mulja u smjesi w = 20 – 50 %. Portland cement je komercijalni proizvod CEMEX-Dalmacijacement, Kaštel Sućurac, Hrvatska. Prema europskoj normi EN-197 ovaj portland cement ima oznaku CEM I. Nakon 28 dana hidratacije razvija tlačnu čvrstoću od 42.5 MPa.

U tablici 1. prikazana su fizikalna i mehanička svojstva portland cementa.

Tablica 1. Fizikalna i mehanička svojstva portland cementa

Fizikalno svojstvo	Vrijednost
Specifična površina po Blaine-u, (cm^2/g)	3300
Standardna konzistencija, (%)	26
Početak vezivanja, (min)	85
Kraj vezivanja, (min)	150
Prosječne čvrstoće na savijanje, (MPa)	
- poslije 3 dana	6,52
- poslije 28 dana	8,44
Prosječne čvrstoće na tlak, (MPa)	
- poslije 3 dana	33,5
- poslije 28 dana	50,7

Kemijski sastav cementa određen je EDXRF TWIN-X uređajem. Dobiveni sastav je: SiO_2 22.85, Al_2O_3 4.81, Fe_2O_3 2.79, CaO 65.23, SO_3 2.54, MgO 1.61, Na_2O 0.18.
Prirodni zeolitni tuf potječe iz nalazišta Donje Jesenje, Hrvatska. Sadrži mineral klinoptilolit čija je formula $(NaK)_2O \cdot Al_2O_3 \cdot 10SiO_2 \cdot 8H_2O$. Kemijski i mineralni sastav prirodnog zeolita prikazan je u tablici 2. Kao zamjenski dodatak korišten je prirodni zeolit zasićen s Zn^{2+}-ionima, koji je dobiven zasićivanjem otopinom koja sadrži 9,0 mmol/dm^3 $ZnSO_4$. Nakon zasićivanja zeolit je sušen pri temperaturi od 105 °C, zatim je usitnjen i prosijan kroz standardno sito od 4900 očica tako da veličina čestica odgovara veličini čestica portland cementa.

Tablica 2. Kemijski i meneralni sastav prirodnog zeolita

Kemijski sastav, (%)		Mineralni sastav-kvalitativni
SiO_2	64.93	Glavna komponenta-klinoptilolit
Al_2O_3	13.66	
Fe_2O_3	2.03	Smjese - muskovit
K_2O	1.88	- ilit
Na_2O	3.66	- feldspat
CaO	2.99	- sepiolit
MgO	1.10	- kvarc
Gubitak žarenjem	9.84	

Mulj, korišten kao zamjenski dodatak, dobiven je iz otpadnih voda pogona pocinčavanja nakon procesa oksidacije (propuhivanje zrakom) i taloženja u bazenima. Mulj je sivo-smeđe boje, sitnozrnate strukture i vlažan. Udio vlage određen sušenjem pri 105 °C do konstantne mase iznosi 56,17 mas. %., a gubitak žarenjem pri 800 °C iznosi 19,25 mas. %. Izmjerena pH vrijednost iznosi 4,88 (50 % suhog mulja i 50 % destilirane vode). Sastav mulja nije konstantan, a najvećim dijelom zastupljeni su cinkov hidroksid, željezov hidroksid, kalcijev hidroksid i nečistoća iz oborinskih voda (zemlja, pijesak, prašina i dr.)
Za određivanje topline hidratacije uzorci su pripremljeni mješanjem portland cementa s odgovarajućim dodatkom mulja (10 – 40 mas. %, M) ili smjese mulja i zeolita (10 – 40 mas. %, K) te je masa uzoraka bila konstantna i iznosila je 4,0000 g. Mjerenja su vršena pri 20 °C i konstantnom voda/kruto omjerom V/K = 0.5.
Za konduktometrijska mjerenja uzorci su pripremljeni mješanjem cementa i dodataka pri istim udjelima kao i kod određivanja topline hidratacije samo je razlika u tome što je masa uzoraka iznosila 100 g. Mjerenja su provedena pri 20 °C i konstantnom voda/kruto omjerom V/K = 0.5.

APARATURA I METODE

Mikrokalorimetrijska mjerenja, korištena za određivanje utjecaja dodataka na procese hidratacije i očvršćavanja, određena su uz pomoć difierencijalnog mikrokalorimetra[7]. Uz pomoć ALMEMO 2390-8 data loggera praćena je promjena napona dU = f(t), uslijed promjene temperature uzorka kao rezultata hidratacijskih reakcija. Snimljene vrijednosti su prebačene na računalo te su uz pomoć posebnog programa izračunate vrijednosti toplina hidratacije, relativnog stupnja reakcije kao i brzina oslobađanja topline za zadane uvjete hidratacije.
Za određivanje specifične vodljivosti korišten je konduktometar[8] ISKRA MA 5964 koji je spojen na računalo preko RS 232 C digitalnog priključka. Za konduktometrijska mjerenja

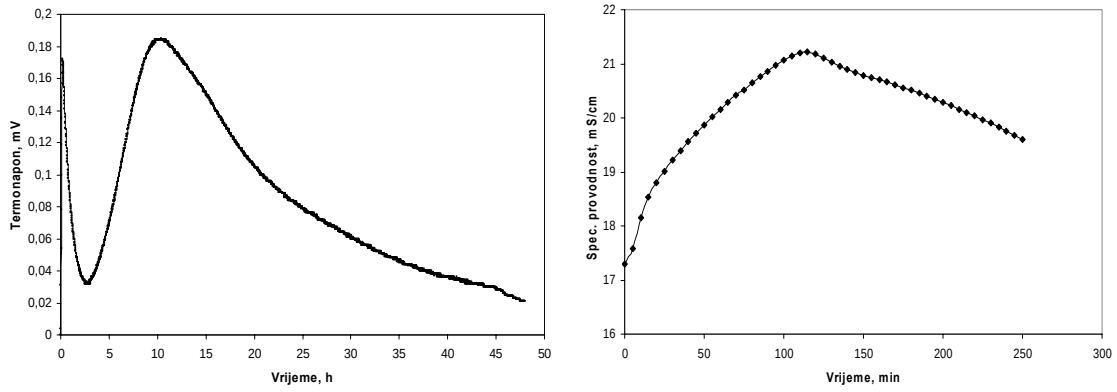
korištena je metalna elektroda, koja je napravljena od nehrđajućeg čelika s konstantom CC = 0.2950 cm^{-1}.

REZULTATI I RASPRAVA

Početni rezultati su pokazali da dodatak mulja iz pogona pocinčavanja utječe na hidrataciju cementa i odgađa vezivanje i očvršćavanje cementne paste.

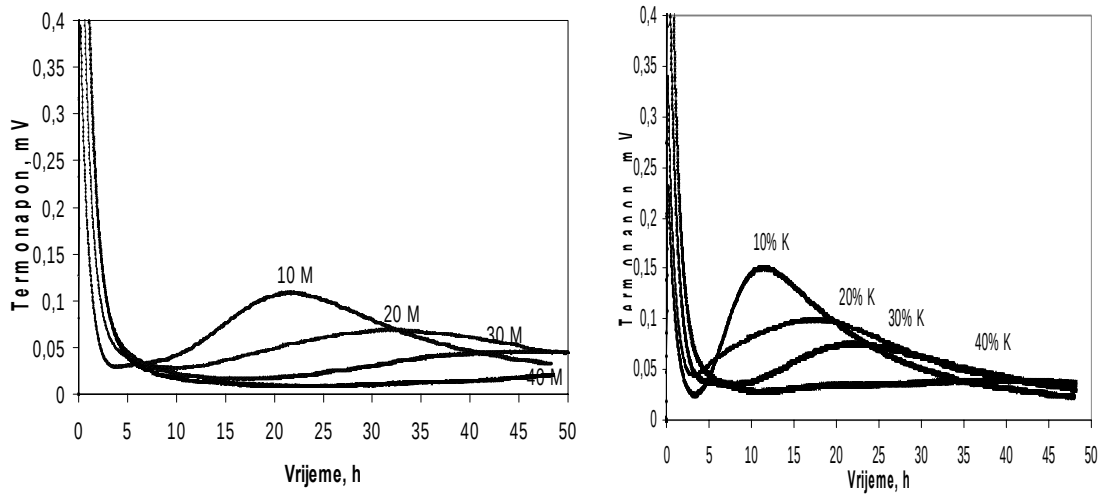
U ovom radu specifična vodljivost je kontinuirano praćena s ciljem određivanja maksimuma vodljivosti. Ti maksimumi pokazuju vrijeme vezivanja te ih je moguće uspoređivati s rezultatima mikrokalorimetrije.

Na slici 1. prikazane su tipične krivulje mikrokalorimetrije i specifične vodljivosti za portland cement CEM I bez dodataka.



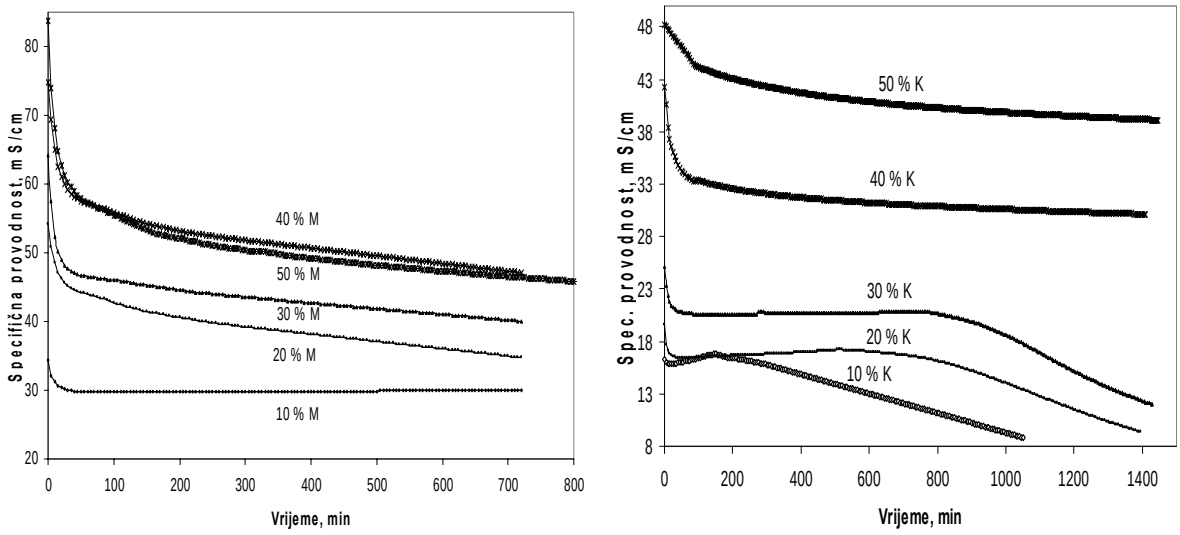
Slika 1. Mikrokalorimetrijska (a) i konduktometrijska (b) krivulja za cement CEM I uz V/C = 0,5 i t = 20 °C

Kod mikrokalorimetrijske krivulje za cement bez dodatka uočava se vrlo izražen drugi maksimum. Povećanjem udjela mulja i smjese mulja i zeolita maksimumi poprimaju niže vrijednosti, a pojava maksimuma registrira se u kasnijim vremenima hidratacije (slika 2a). Već kod dodatka mulja u iznosu od 10 % glavni hidratacijski maksimum je znatno pomaknut prema kasnijim vremenima hidratacije. Uz dodatak zasićenog zeolita (slika 2b) ovaj negativni utjecaj je nešto smanjen te je moguće koristiti smjesu mulja i zasićenog zeolita do iznosa od 30 %.



Slika 2. Krivulje dU = f(t) uz dodatak mulja (a) i smjese mulja i zeolita (b)

Vrijednosti toplina hidratacije, brzina oslobađanja toplina i stupanj reakcije znatno se smanjuju dodatkom mulja i nešto manje dodatkom smjese mulja i zeolita.
Kod konduktometrijskih mjerenja serije cementnih pasta uz dodatak w = 10 – 50 % mulja ne pokazuju tipičan izgled krivulja sa jasno istaknutim maksimumima, a vrijednosti specifične vodljivosti su znatno više (slika 3a). Ovo pokazuje da mulj, već pri iznosu od 10 mas. % znatno utječe na hidratacijske procese. Specifična vodljivost cementnih pasti uz dodatak smjese mulja i zeolita (slika 3b) zadržava izgled krivulje sve do dodatka od 30 % smjese. Maksimumi specifične vodljivosti su pomaknuti prema kasnijim vremenima.



Slika 3. Specifična vodljivost u ovisnosti o dodatku mulja (a) i smjese mulja i zeolita (b)

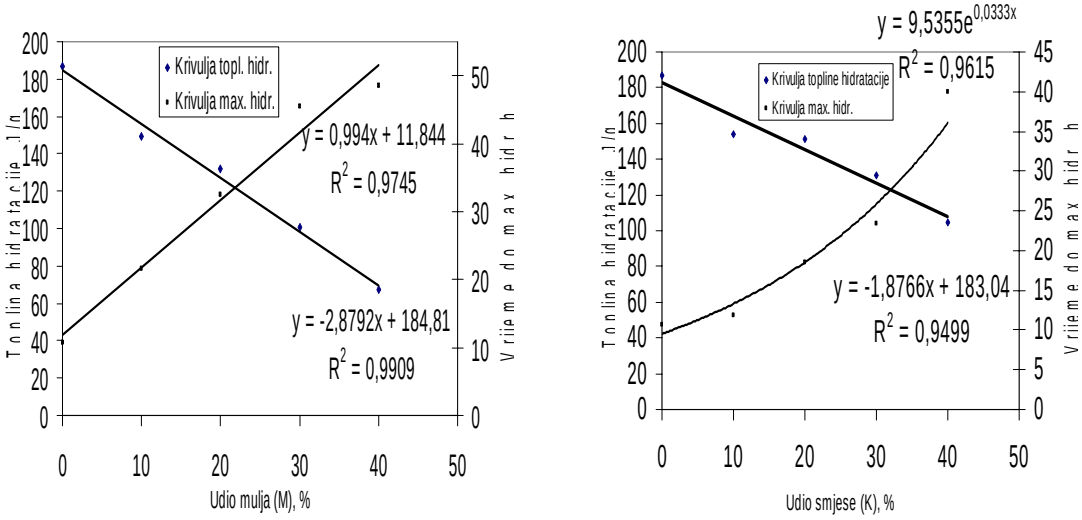
MATEMATIČKI MODELI

Tablica 3. Razvijena toplina hidratacije nakon 48 sati i vrijeme do uspostave maksimuma u ovisnosti o dodatku mulja (M) i smjese kompozita (K)

Uzorak CEM I uz dodatak 10 – 40 % smjese mulja i zeolita			
Uzorak	Dodatak, K, %	Toplina hidr., J/g	Vrijeme do max., h
CEM I	0	186,8909	10,633
CEM I + K	10	153,8794	11,916
CEM I + K	20	151,3313	18,466
CEM I + K	30	130,9090	23,433
CEM I + K	40	104,5441	39,983
Uzorak CEM I uz dodatak 10 – 40 % mulja			

Uzorak	Dodatak,M, %	Toplina hidr., J/g	Vrijeme do max., h
CEM I	0	186,8909	10,633
CEM I + M	10	149,5399	21,650
CEM I + M	20	131,6972	32,483
CEM I + M	30	100,5598	45,400
CEM I + M	40	67,4203	48,460

Toplina hidratacije kod cementa bez dodataka iznosi 186,89 J/g nakon 48 sati hidratacije i vrijeme do postizanja maksimuma je 10,63 sati. Topline hidratacije cementa uz dodatke su niže i treba više vremena do postizanja maksimuma.
Analizom rezultata iz tablice 3 mogu se dobiti matematičke ovisnosti toplina hidratacije o dodatku mulja i smjese kompozita.



Slika 3. Ovisnost topline hidratacije i vremena do postizanja maksimuma o dodatku mulja (a) i smjese mulja i zeolita (b)

Slijedeće jednadžbe mogu se koristiti za izračunavanje vrijednosti toplina hidratacije i predviđanje vremena maksimuma hidratacije za bilo koji dodatak mulja i smjese mulja i zasićenog zeolita,

$$y(\text{toplina}) = -2{,}88x + 184{,}81 \quad (J/g) \qquad (1)$$

gdje je y(toplina)-toplina hidratacije u J/g, a x je količina dodanog mulja u mas. %.
Isto tako moguće je napisati matematičke relacije za određivanje vremena do postizanja maksimuma:

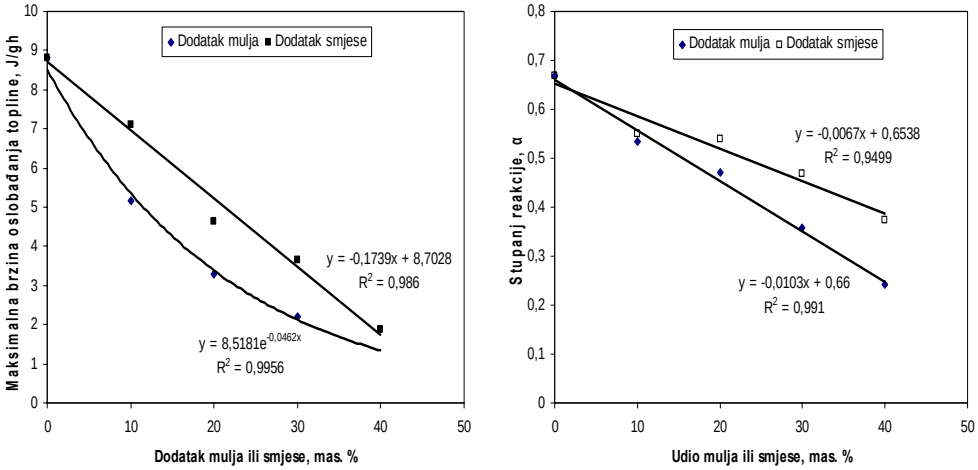
$$y(\max) = 0{,}99x + 11{,}84 \quad (h) \qquad (2)$$

gdje y(max) predstavlja vrijeme do postizanja maksimuma u satima, a x je udio dodanog mulja.
Na isti način se izvode jednadžbe uz dodatak smjese mulja i zasićenog zeolita.

$$y(\text{toplina}) = -1{,}88x + 183{,}04 \quad (J/g) \qquad (3)$$

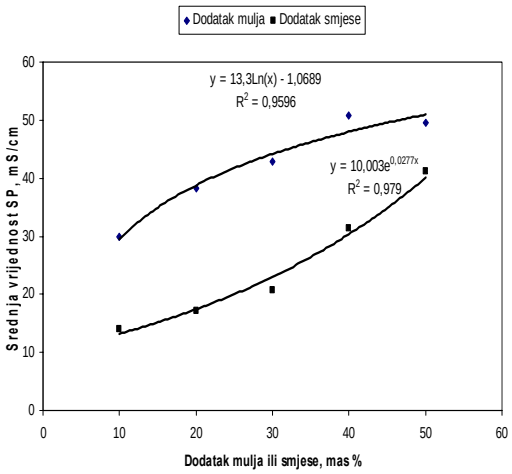
$$y(\max) = 9{,}5355e^{0{,}0333x} \quad (h) \qquad (4)$$

gdje je x količina dodane smjese mulja i zeolita
Korištenjem podataka za brzinu razvijanja topline i stupnja reakcije za svaki dodatak dobiju se slijedeće ovisnosti (slika 4).



Slika 4. Brzina razvijanja topline i stupanj reakcije u ovisnosti o udjelu mulja i smjese

Analizom konduktometrijskih mjerenja dobile su se matematičke relacije pomoću kojih je moguće predvidjeti srednju vrijednost specifične vodljivosti uz dodatak mulja i smjese mulja i zeolita (slika 5).



Slika 5. Ovisnost srednje vrijednosti specifične vodljivosti o dodatku mulja i smjese mulja i zeolita

ZAKLJUČAK

Mikrokalorimetrijska mjerenja omogućuju kontinuirano praćenje i određivanje utjecaja različitih iznosa mulja iz pogona pocinčavanja te smjese mulja i zeolita zasićenog cinkovim ionima na procese hidratacije. Povećanjem udjela mulja i smjese mulja i zeolita registriraju se niže vrijednosti toplina kao i pojava maksimuma krivulja u kasnijim vremenima hidratacije.

Određivanje specifične vodljivosti daje podatke o početku vezivanja cementnog kompozita što predstavlja vrlo važan parametar koji ukazuje na početak i kraj vezivanja u cementnom sustavu te na svojstva konačnog produkta. Povećanje dodatka odgađa vrijeme vezivanja kompozita, a vrijednosti specifične vodljivosti rastu. Dodaci mulja i smjese mulja i zeolita ne utječu na mehanizam procesa hidratacije, već utječu na kinetičke parametre i dinamiku odvijanja procesa hidratacije cementa.

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SYNTHESIS AND CHARACTERIZATION OF EPOXY RESIN/LAYERED DOUBLE HYDROXIDE NANOCOMPOSITES

SINTEZA I KARAKTERIZACIJA NANOKOMPOZITA NA OSNOVI EPOKSIDNE SMOLE I SLOJEVITOG HIDROKSIDA

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Izvorni znanstveni rad / Original scientific paper

Abstract: Ca-Al hydroxide with layered double hydroxide-like structure modified by the incorporation of benzoate anions ($Ca_4Al_2(OH)_{12}(C_6H_5COO)_2 \cdot x\ H_2O$, LDH-B) was prepared by a variant of the rehydration method, by adding benzoic acid and CaO into mixture of water and acetone used to convert tricalcium aluminate ($Ca_3Al_2O_6$) into final layered structure. Modification of layers with benzoate anions was confirmed by Fourier transform infrared spectroscopy (FTIR). Nanocomposites based on an epoxy resin and LDH-B were prepared by *in situ* polymerisation, with polyoxypropylene diamine as a curing agent. Nanocomposites prepared with different contents of the LDH-B (5, 10, and 15 %) were characterised by X-ray diffraction analysis (XRD), FTIR, differential scanning calorimetry (DSC), thermogravimetric analysis (TGA) and transmission electron microscopy (TEM). XRD results indicated that the characteristic layered structure of the LDH-B had disappeared, and TEM analysis confirmed that LDH-B was partially dispersed within the matrix forming an intercalated structure, which becomes partly exfoliated in the sample with 5 % filler. Results of thermal analysis showed somewhat improved thermal properties in comparison to the neat epoxy resin, while the glass transition temperature initially decreases but then increases to values over that of neat epoxy resin for the sample with 15 % filler.

Sažetak: Slojeviti Ca-Al hidroksid strukture nalik slojevitim dvostrukim hidroksidima (LDH) modificiran je benzoatnim anionima ($Ca_4Al_2(OH)_{12}(C_6H_5COO)_2 \cdot x\ H_2O$, LDH-B) modificiranom rehidracijskom metodom, dodavanjem benzojeve kiseline i CaO u otopinu vode i acetona kojom se trikalcijski aluminat ($Ca_3Al_2O_6$) transformira u konačnu slojevitu strukturu. Prisutnost benzoatnih aniona unutar slojeva potvrđena je spektroskopijom u infracrvenom području (FTIR). Nanokompoziti na osnovi epoksidne smole i LDH-B pripravljeni su *in situ* polimerizacijom, uz poli(oksipropilen)diamin kao umreživalo. Nanokompoziti s različitim udjelima LDH-B (5, 10, i 15 %) karakterizirani su rendgenskom difrakcijom, FTIR-om, razlikovnom pretražnom kalorimetrijom (DSC), termogravimetrijskom analizom (TGA) i transmisijskom elektronskom mikroskopijom (TEM). Rendgenska analiza ukazuje da je karakteristična slojevita struktura LDH-B nestala, a TEM analiza potvrdila je da je LDH-B djelomično raspršen unutar matice tvoreći interkaliranu strukturu, koja postaje djelomično raslojena u uzorku s 5 % punila. Toplinska analiza ukazala je na djelomično poboljšanje toplinskih svojstava u usporedbi s nemodificiranom epoksidnom smolom, dok se staklište isprva snižava da bi postalo više nego za čistu smolu kod uzorka s 15 % punila.

Keywords: epoxy, layered nanofiller, morphology, nanocomposites, thermal stability

Ključne riječi: epoksidna smola, slojevito nanopunilo, morfologija, nanokompoziti, toplinska postojanost

1. INTRODUCTION

Polymer/layered double hydroxide (LDH) nanocomposites have attracted a great interest in the field of material chemistry in recent years due to their novel mechanical, thermal and optical properties [1] which are mainly attributed to the high-degree dispersion of layered inorganic compounds in polymer matrix. LDHs are layered materials consisting of positively charged metal oxide/hydroxide sheets with intercalated anions and water molecules. The general formula of those materials is $\left(M^{2+}_{1-x}M^{3+}_{x}(OH)_2\right)^{x+}A^{n-}_{x/n}\cdot mH_2O$, where M^{2+} and M^{3+} are divalent and trivalent metal cations, and A^{n-} is an anion. In the original structure, the neighbouring sheets strongly attract each other through electrostatic interaction and hydrogen bonding. The gallery distance between LDH layers is generally under 1 nm, preventing monomer or polymer molecules from penetrating into the layers. Furthermore, the hydrophilic surface of the LDH layers is incompatible with hydrophobic polymer molecules, preventing homogeneous dispersion of LDH layers in polymer matrix. Therefore LDH is modified with suitable organic anions to increase the gallery distance and reduce hydrophilic character of the layer surface.

The anions are typically intercalated into LDH interlayers by one of three approaches. The first is the coprecipitation method, which requires the addition of an M^{2+}/M^{3+} metal salt solution to a base solution of the desired anions [2]. The second is the direct ion exchange method, in which LDHs are stirred in a concentrated solution of desired anions [3]. The third is the rehydration method, in which calcined LDH is added to a solution of desired anions [4]. The intercalated LDH/water-soluble polymer nanocomposites have been prepared successfully [5-7], either by the direct intercalation of polymeric anions into LDH, or by intercalation of monomeric anions into LDH followed by *in situ* polymerization. The intercalation of hydrophobic monomers or polymers is much more difficult [8-11]. In this study, preparation of epoxy/LDH nanocomposites by the *in situ* polymerization is presented.

2. EXPERIMENTAL

Materials used in the synthesis of benzoate-intercalated Ca-Al layered double hydroxide-like structure (LDH-B) were calcium carbonate, $CaCO_3$, p.a. (Kemika, Croatia), aluminum hydroxide, $Al(OH)_3$, reagent grade (Aldrich) and benzoic acid, C_6H_5COOH, p.a. (Kemika). The materials were used without further purification. To prepare nanocomposite materials, an epoxy resin, diglycidyl ether of bisphenol A (DGEBA, Epikote 828 EL, Shell Chemicals) with the epoxy equivalent weight of 190 g/mol was used, with poly(oxypropylene) diamine (Jeffamine D230, Huntsman Corporation) as a curing agent.

Initial substance for synthesis of LDH-B, tricalcium aluminate ($Ca_3Al_2O_6$), has been prepared by firing wet-homogenized stoichiometric mixture of $CaCO_3$ and $Al(OH)_3$ at 1350 °C for 3 h. LDH-B was synthesized by a variant of the rehydration method, by which tricalcium aluminate is converted to layered tetracalcium aluminate. The reaction between finely milled tricalcium aluminate, additional stoichiometric amount of calcium oxide (freshly prepared by firing $CaCO_3$) and benzoic acid was performed in mixture of deionized water and acetone. The reaction mixture was poured into a tightly screwed polyethylene flask, vigorously shaken for 24 h at room temperature, then filtered and rinsed with acetone in order to prevent agglomeration and cementing of the freshly prepared filler.

To prepare the neat epoxy resin system, DGEBA and a stoichiometric amount of Jeffamine D230 were mixed and stirred at room temperature in a closed vessel for 1 h. To prepare the composite systems with 5, 10 and 15 % of filler, epoxy resin was mixed with desired amount of LDH-B at 75 °C for 24 h and sonicated for 15 min. After cooling the mixture to room

temperature, a stoichiometric amount of the curing agent Jeffamine D230 was added and mixture stirred for 1 h. The mixture was then poured into mould and cured at 80 °C for 3 h, and then postcured at 120 °C for 1 h.

Fourier transform infrared (FTIR) spectra of the materials were recorded on a Bruker Vertex 70 FTIR spectrometer in ATR mode. Spectra were obtained using resolution of 4 cm^{-1}, averaged over 16 scans between 400 and 4000 cm^{-1}. X-ray diffraction (XRD) patterns were determined using a Philips PW1730 generator and PW1860 goniometer using CuK_{α} radiation. Differential scanning calorimetry (DSC) measurements were carried out on a Netzsch DSC 200 operating in a nitrogen atmosphere, at the heating rate of 10 K min^{-1}, with sample size ~20 mg. Each sample was scanned twice, first from room temperature to 180 °C, then cooled back to room temperature and heated to 500 °C. The thermogravimetric analysis (TGA) was performed on a Perkin Elmer thermobalance TGS-2, under a nitrogen gas flow of 150 cm^3 min^{-1}, at the heating rate of 20 K min^{-1}. The transmission electron microscopy (TEM) images were obtained on a transmission electron microscope JEOL JEM-200CX with accelerating voltage of 200 kV. The samples were cut to thickness of 80-110 nm on an ultratome Leica Ultracut R with a glass knife.

3. DISCUSSION OF RESULTS

Characteristic maxima of LDH-B (2ϑ = 31° and 36°) are present in XRD spectra of all epoxy/LDH-B systems indicating successful incorporation of LDH-B into polymer matrix (Figure 1). On the other hand, the disappearance of maxima at 6°, 12°, 18° and 24°, which originate from the layered structure of the filler, indicate intercalation and possibly exfoliation of LDH-B to form the nanocomposite.

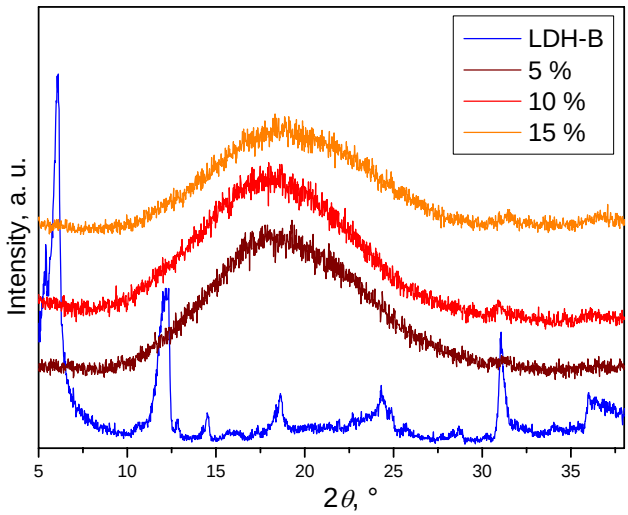

Figure 1. XRD spectra of investigated samples

Figure 2 shows FTIR spectra of benzoic acid, LDH-B, neat epoxy and an epoxy/LDH-B nanocomposite. Benzoic acid shows C=O stretching vibration at 1700 cm^{-1}, and CH-out-of-plane bending of the phenyl ring at 900-600 cm^{-1}. In the spectrum of LDH-B characteristic bands of COO^- asymmetrical and symmetrical stretching vibrations are observed at 1650-1550 and 1450 cm^{-1}, respectively, indicating the presence of benzoate anions within the LDH-like layers. Phenyl ring bands at 900-600 cm^{-1} are observed in the spectra of both LDH-B and the composite. Neat epoxy has several characteristic absorption bands: C-aryl bond stretching at 1505 and 1205 cm^{-1} and CH-in-plane-deformation of aryl group at 825 cm^{-1}, which are all present in spectrum of the nanocomposite.

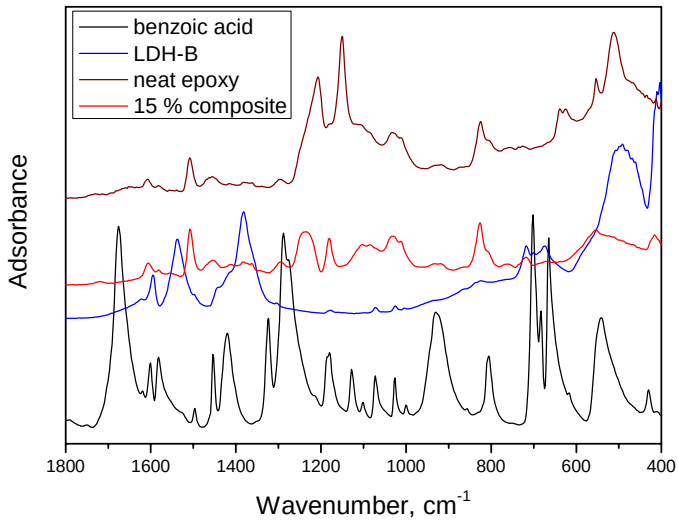

Figure 2. FTIR spectra of listed samples

Morphology of epoxy/LDH-B nanocomposites was further studied by the TEM analysis (Figure 3). With smaller magnification (Figure 3a) it can be seen that LDH-B is homogeneously dispersed within the epoxy matrix. Larger magnification confirms intercalation of polymer matrix within layered structure of LDH-B, but no complete exfoliation in any of the nanocomposites. Only nanocomposite with 5 % of filler shows partial exfoliation.

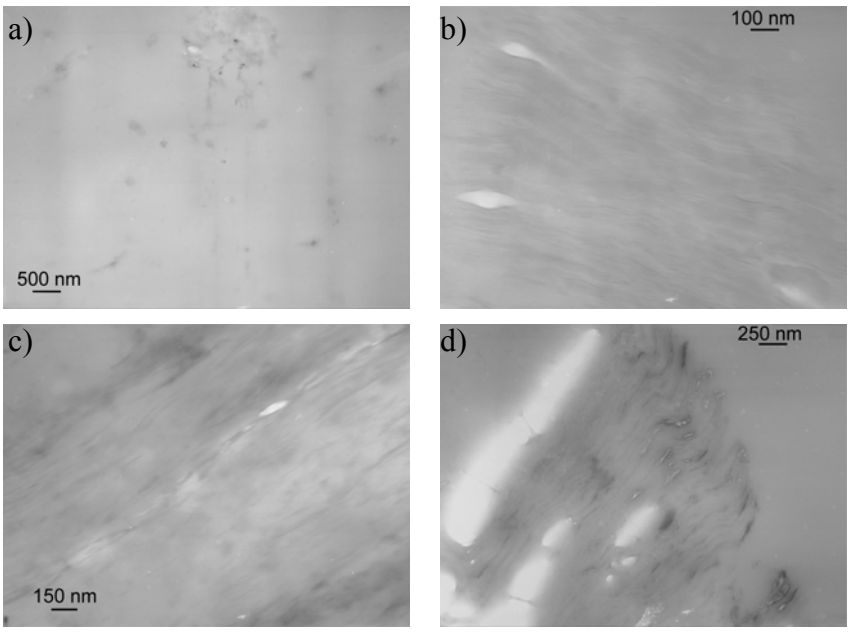

Figure 3. TEM photographs of epoxy/LDH-B nanocomposites with a, b) 5 %, c) 10 % and d) 15 % filler.

Glass transition temperatures (Table 1) of 5 % and 10 % epoxy/LDH-B nanocomposites are lower than that for neat epoxy, but they increase by 5-10 °C in the second measurement, indicating further curing at temperatures above 120 °C used in preparation of samples.

Table 1. Glass transition temperature, T_g, initial degradation temperature, T_i, temperature of maximum rate of degradation, T_{max}, and weight content of residue at 1000 °C, *w*(residue), for investigated samples.

Material	T_g / °C		T_i / °C	T_{max} / °C	*w*(residue)
	1st run	2nd run			
Neat epoxy	71	72	388	421	1,96 %
5 %	62	67	361	402	11,39 %
10 %	60	70	350	400	13,07 %
15 %	78	86	339	393	15,10 %

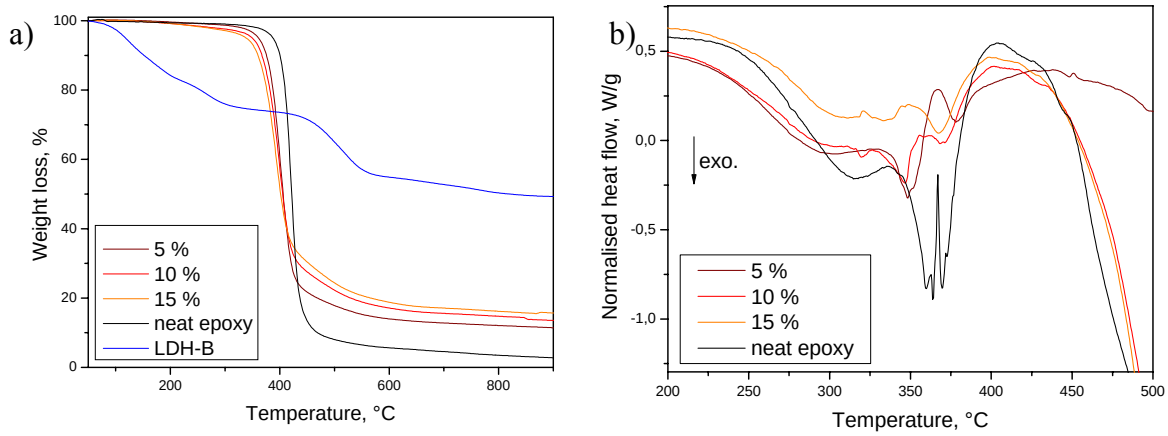

Figure 4. a) TGA curves and b) DSC curves for investigated samples.

Thermal stability of epoxy/LDH-B nanocomposites was studied by TGA and DSC (Figure 4). All nanocomposites degrade in a single step similar to neat epoxy, but maximal rate of degradation, T_{max}, as determined from derived TGA curve, is ~20 °C lower than for neat epoxy and decreases slightly with increased content of filler (Table 1). Intercalated filler does not present a significant barrier for diffusion of volatile degradation products, and presumably even acts as a catalyst for dehydration or chain scission, the two main mechanisms of degradation of crosslinked epoxy. Initial weight-loss (T_i, determined from TGA curves as 5 % weight loss) is also shifted to lower temperatures, but more marked decrease with increasing filler content shows influence of initial degradation of LDH-B that proceeds in two steps at 80-200 °C and 230-300 °C. Presence of filler somewhat inhibits initial degradation of epoxy resin by homolytic bond scission which is not accompanied by weight-loss but is marked by exothermic reaction on DSC curves (Figure 4b). Presence of inorganic filler expectedly increases weight content of residue after full degradation at 1000 °C, *w*(residue), and the effect is most marked for nanocomposite with 5 % filler content, probably due to its partially exfoliated structure.

4. CONCLUSIONS

Benzoate anions intercalated into the LDH-like layers have increased the organophilicity of the filler, enabling the preparation of epoxy-matrix nanocomposites. Successful intercalation has been confirmed by XRD and TEM measurements, and sample with 5 % filler shows partial exfoliation. Thermal properties of the nanocomposites were somewhat improved in comparison to the unmodified resin: glass transition temperature of sample with 15 % filler is higher than for unmodified epoxy resin, and weight residue at 1000 °C is significantly increased, particularly for partially exfoliated nanocomposite with 5 % filler.

ACKNOWLEDGMENTS

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DJELOVANJE RAZLIČITIH POVRŠINSKI AKTIVNIH TVARI NA SVOJSTVA OTOPINE ZA VLAŽENJE

DEFINING THE PROPERTIES OF FOUNTAIN SOLUTION DEPENDING ON TYPE OF SURFACE ACTIVE SUBSTANCE

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Prethodno priopćenje / Preliminary note

Sažetak: Osnovna uloga otopine za vlaženje je u kratkom vremenu potpuno se adsorbirati na slobodnim površinama tiskovne forme u tankom sloju, te na taj način onemogućiti prihvaćanje bojila na iste. U otopinu za vlaženje se dodaju površinski aktivne tvari, koje smanjuju napetost površine otopine i time poboljšavaju adsorpciju na tiskovnoj formi. Cilj ovog istraživanja je odrediti djelovanje dvije vrste površinski aktivnih tvari na fizikalno-kemijska svojstva otopine za vlaženje. Za istraživanje su pripremljena dva seta otopina od demineralizirane vode u koju su dodani dodaci za korigiranje pH vrijednosti te korekciju električne provodljivosti. U pripremljene otopine dodane su površinske aktivne tvari u različitim volumnim koncentracijama od 0 do 10 %. Ispitivanje fizikalno kemijski svojstava sastajalo se od određivanja pH vrijednosti, određivanja električne provodljivosti te mjerenja kontaktnog kuta između pojedine otopine i uzorka konvencionalne tiskovne forme. Izvršena mjerenja su pokazala da dodatkom površinski aktivnih tvari otopina za vlaženje zanemarivo povisuje pH vrijednost i također zanemarivo smanjuje električnu provodljivost otopine. Povećanjem koncentracije površinski aktivnih tvari znatno se smanjuje napetost površine i kontaktni kut s time da je smanjenje različito ovisno o vrsti korištenih površinski aktivnih tvari. Na temelju dobivenih rezultata predložen je optimalan odnos sastojaka otopine za vlaženje u procesu reprodukcije.

ključne riječi: plošni tisak, otopina za vlaženje, površinski aktivne tvari, površinska napetost

Abstract: The most important role of the fountain solution is to quickly cover nonprinting areas of the printing plate in a thin layer. To enable this function, in fountain solutions must be added surface active substances, which will decrease the value of surface tension of solution in which it is added. The goal of this research was to determine how the type of surface active substance changes physical and chemical properties of fountain solution in which they are added. Two types of fountain solutions were prepared for the research. Both were prepared from deionised water in which addition that give solution pH stability and defined conductivity were added. Afterwards, two types of samples were made with addition of defined surface active substance in volume fraction from 0 to 10 percent. To define physical and chemical properties of prepared fountain solutions, pH value, conductivity and surface tension were measured. Finally, to determine interaction between samples of solution and printing plate, contact angle was measured. Conventional printing plate was used in this research. Obtained results showed that both solution types have similar behaviour of the pH value and conductivity for all volume fractions of surface active substances. As expected, both surface active substances cause significant decrease of surface tension and contact angle with increase of their volume friction in a solution. According to the results, the optimal ratio between fountain solution's ingredients in printing process is proposed.

Key words: offset printing, fountain solution, surface active substance, surface tension

1. Introduction

In lithography difference between the printing areas and nonprinting areas is achieved through their opposite physical-chemical properties. The printing areas attract substances with oil solvent – printing ink. The nonprinting areas are built from aluminium-oxide and in the printing process they attract water based solutions – fountain solution. The main role of the fountain solution is to quickly and completely cover all nonprinting areas of the printing plate in a thin layer. To achieve that task in water, which is the basis for fountain solution, are added some substances to improve its physical-chemical properties. One of the most important addition is surface active substances. The role of those substances is to reduce solution's surface tension and consequently, improve wetting of the nonprinting areas on the printing plate.

The aim of this paper is to determine physical-chemical properties of fountain solutions made with different type of surface active substances and see which solution gives better results in wetting of the nonprinting areas on the printing plate.

2. Experimental

In this research two sets of the fountain solutions were made. Both sets of samples were made of deionised water in which additions for pH stability (Combi plus) and defined conductivity (Adisal) were added. Afterward, in these prepared samples, surface active substances were added. The two types of surface active substances were compared, sample set A made with IPA and sample set B with IPA100. All additions used were from same supplier. Each set was made by increasing volume fraction of surface active substances from 0 to 10 percent.

For defining the physical-chemical properties of prepared samples, pH value, conductivity and surface tension were measured. The measurement of pH value was performed with pH meter "WTW" GmbH pH 340/SET – 1, and conductivity was measured with used "WTW" GmbH LF 330/SET. The surface tension was measured with stalagmometer.

Finally, to determine behaviour of prepared samples on the nonprinting areas, measurement of contact angle of prepared solutions on conventional offset printing plate was performed. The measurement of contact angle was made on Dataphyisics OCA 30 measuring unit with "Sessile drop method". All measurements were made in series of 5 measurement.

3. Results and discussion

One can see in figure 1 that adding both types of surface active substances cause decrease of conductivity values. The dependence of conductivity on volume fraction is linear, Type A causes slightly larger decrease of conductivity.

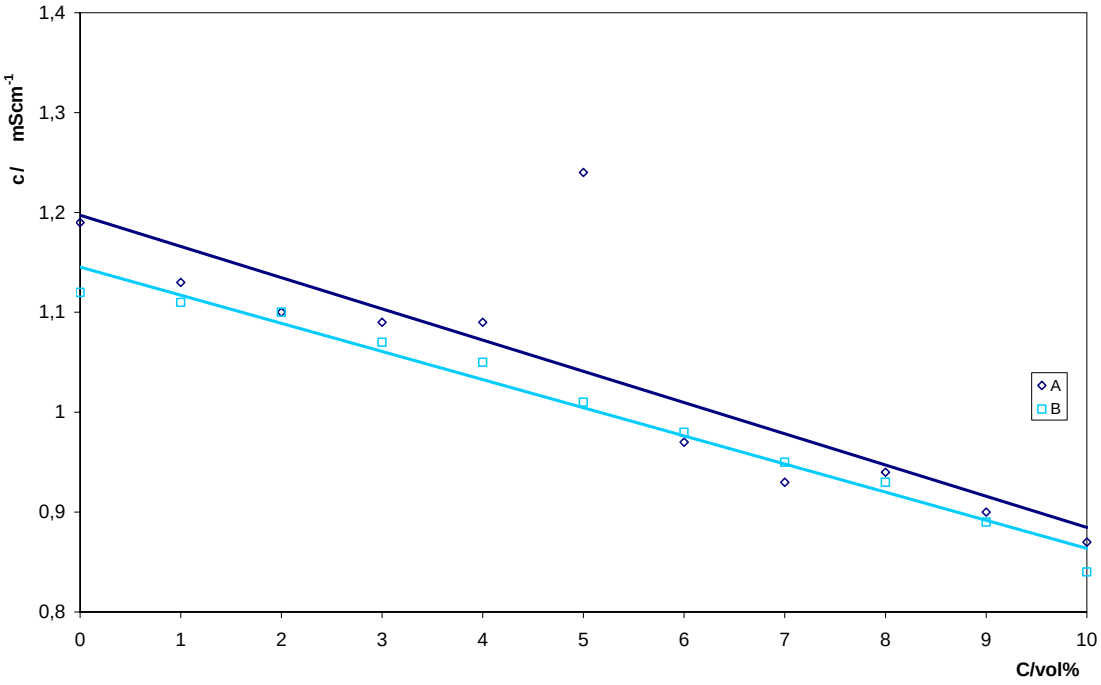

Figure 1. Electrical conductivity of samples A and B

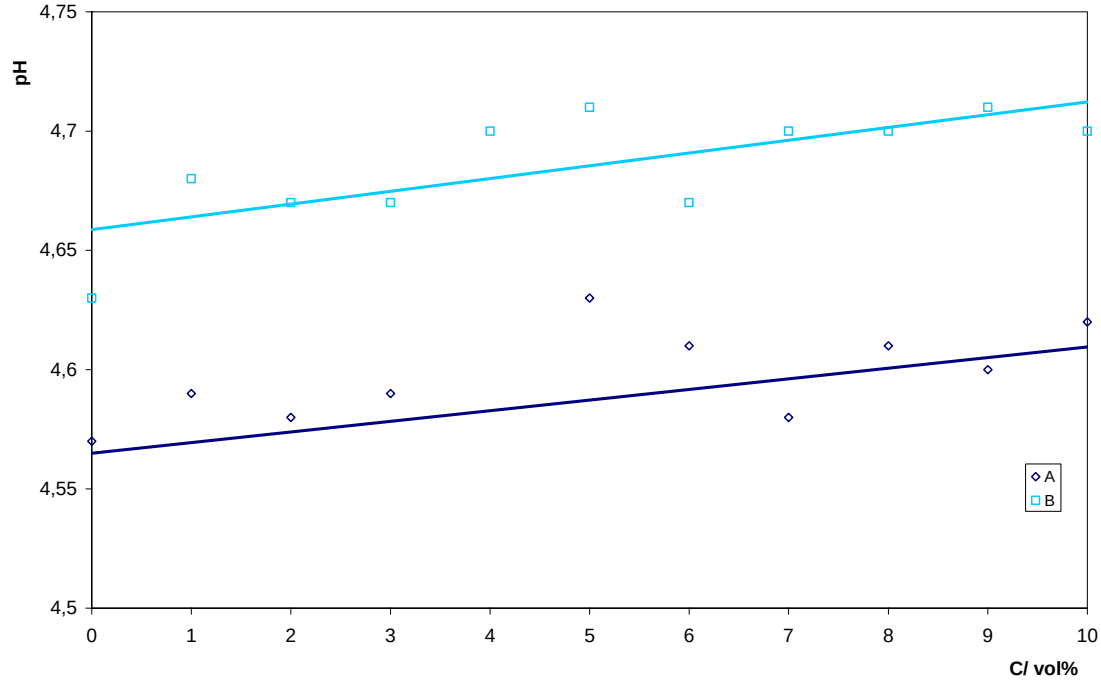

Figure 2. pH values of samples A and B

It can be seen in figure 2 that pH values of prepared fountain solution samples rises with increase of volume friction of added surface active substances. One can also see that type B causes higher pH value, but the difference is not significant (less than 0,2 pH).

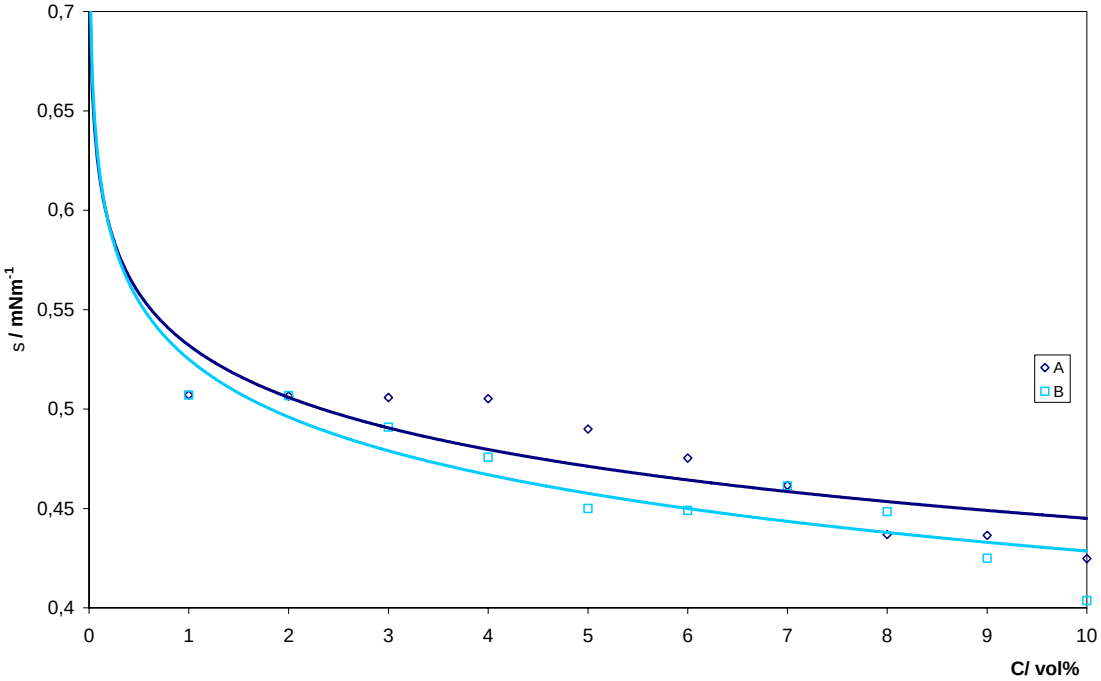

Figure 3. Surface tension of samples A and B

The value of surface tension significantly decreases with increase of added surface active substances. One can see in figure 3 that decrease of surface tension of samples B is greater than of samples A.

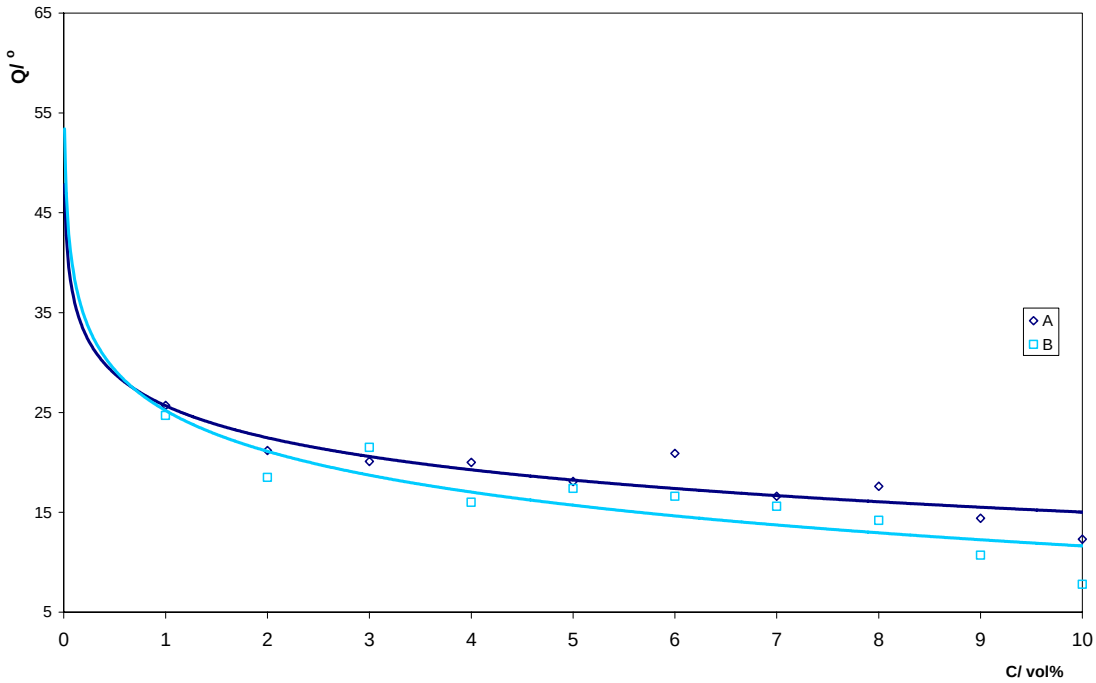

Figure 4. Contact angle for samples A and B

Results of contact angle measurement show that contact angle between the nonprinting areas on the printing plate and samples A and B decreases as the volume fraction of surface active substance increase. Observing Figures 3 and 4 one can see that curves are similar for both dependence of surface tension and contact angle on volume friction of added surface active substances.

4. Conclusion

The results have shown that type of surface active substances have impact on physical-chemical properties of fountain solution. In both samples (A and B) electrical conductivity of solutions is linearly decreasing while adding more surface active substances, that is because surface active substances increase concentration of uncondactive compound.

pH value is not significantly influenced by presence of surface active substances in prepared solutions, but slightly larger changes are when type B is added into the solution.

As expected, surface active substances cause changes in the surface tension of the fountain solution as well as in contact angle values on the nonprinting areas of the printing plate. It can be seen that type B surface active substance causes greater decrease of surface tension, and consequently decrease of contact angle values.

From results obtained in this research one can concluded that for getting better wetting on the nonprinting areas of the printing plate one should use type B surface active substance. It can be also concluded that volume fraction of surface active substance would not be larger than 8% because afterwards the decrease of surface tension is not significant.

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OŠTEĆENJA ČELIČNE UŽADI U EKSPLOATACIJSKIM UVJETIMA

DAMAGES OF STEEL WIRE ROPES IN EXPLOATATION CONDITION

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Stručni članak / Professional paper

Sažetak:
Radni vijek čeličnih užadi je ograničen zbog promjene njihovih svojstava tijekom eksploatacije pod svojstvima radnih uvjeta i opterećenja. Redovni nadzor tokom eksploatacije omogućava kontrolu razvoja oštećenja i normalni proces starenja užadi. Na taj način se ustvrđuje pravo vremena zamjena užadi i njihova dobra eksploatacija. U članku su prikazani i analizirani osnovni oblici oštećenja čeličnih užadi: mehaničko trošenje, umor, korozija, otkaz izazvan preopterećenjem i smicajni lom. Prikupljeni podaci mogu doprinijeti boljoj konstrukciji dizalice i užeta i poboljšanju postupaka održavanja.

Ključne riječi: čelična užad, trošenje, umor, lom

Abstract:
Service life of steel wire ropes is limited due to change of properties during exploitation under working condition and loads. Regular inspection during operation enables damage development inspection and provides a regular rope ageing process. In this way timely replacement of ropes and safe service is assured. Basic types of steel rope damages (mechanical wear, fatigue, corossion, failure due to over-load and shearing collapse) are presented in the article and analysed. Collecting data can be contribute to better design of lifting equipment and ropes and improved maintenance procedures.

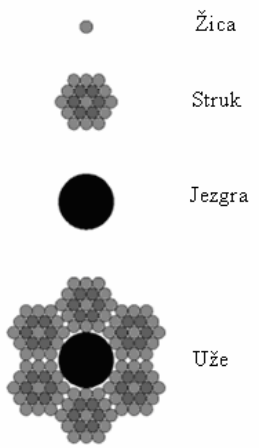
Key words: steel ropes, wear, fatigue, fracture

UVOD

Čelična užad su potrošni elementi na dizalicama, jer tijekom eksploatacije dolazi do promjene svojstava užadi, čime je njihov radni vijek ograničen. Redovni nadzor uz pravilno izveden pregled i ispitivanje tijekom eksploatacije i praćenje normalnog procesa starenja užadi omogućavaju procijenu preostalog vijeka i pravovremenu zamjenu užeta. Analiza stanja užadi i oštećenja zbog kojih su povučena iz eksploatacije pruža informacije o dizalici, načinu na koji je operator koristio dizalicu i o integritetu korištenog užeta. Prikupljeni podaci su značajni za usavršavanje konstrukcije dizalice i sistema užadi, kao i za poboljšanje postupaka održavanja u cilju povećanja sigurnosti u eksploataciji. Predmet ovog članka su osnovni tipovi oštećenja, koji se susreću pri kontroli, ispitivanju i analizi stanja čeličnih užadi u eksploataciji. Radi lakšeg praćenja teksta prikazana je konstrukcija žičanog užeta, preuzeta iz „Wikipedije“, [1].

Žičano uže se sastoji od više strukova, spiralno namotanih (‘upredenih’). Na sličan način je svaki struk spiralno namotan od metalne žice, po pravilu od čelične žice.

Čelično uže je specificirano oznakom, koja daje broj žica i broj strukova, kao i podatke o konstrukciji užeta. U danom primjeru (slika 1) oznaka „6×19 FC RH OL FSWR“ pokazuje broj snopova u užetu (6), broj žica u struku (19), vlaknastu jezgru (FC), namotavanje udesno (RH), uobičajeni tip namotavanja (OL) i savitljivo čelično žičano uže (FSWR).



Slika 1. Čelično uže 6×19 FC RH OL FSWR i sastavni dijelovi

2. MEHANIČKO TROŠENJE

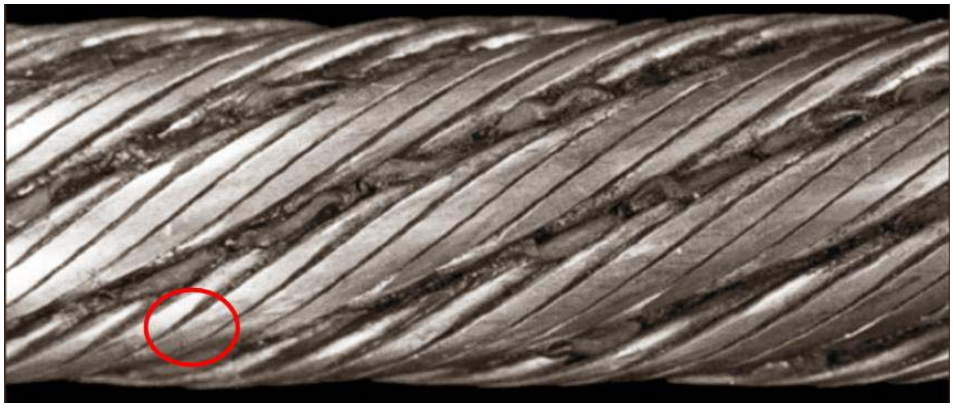
Mehaničko trošenje čeličnih užadi nastaje zbog skidanja površinskog sloja materijala pri abraziji. Trošenje može biti smanjeno odgovarajućim podmazivanjem. Trošenje na velikim bubnjevima za namotavanje u više slojeva može biti smanjeno izborom užeta pogodne konstrukcije. Zbog trošenja užeta na koturaljkama, bubnjevima i susjednim užadima, početni poprečni presjek i početna nosivost će se vrlo brzo smanjivati.

Sve dok je brzina smanjivanja početnog poprečnog presjeka uslijed trošenja veća od brzine rasta umorne pukotine, u žicama užeta neće doći do umornog loma (slika 2).

Mehaničko trošenje ne treba miješati s plastičnom deformacijom. Plastična deformacija je intenzivna površinska deformacija materijala, bez ili sa malo gubitka materijala. Slike 3 i 4 pokazuju primjere plastičnog trošenja.

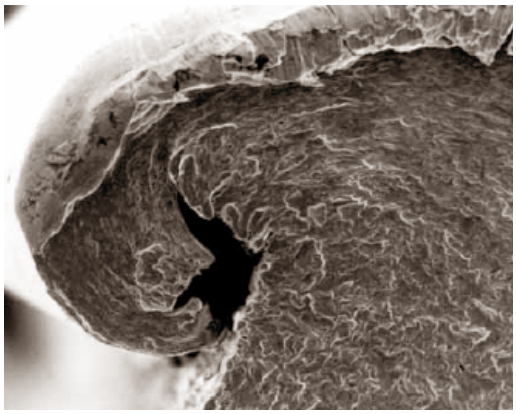
3. POJAVA UMORA ZBOG SAVIJANJA UŽETA

Umorne pukotine se javljaju zbog savijanja užeta oko vodećih točki, na mjestu kontakta spojenih strukova užeta i bubnjeva, odnosno koturaljki, ili na mjestima kontakta između žica unutar pojedinačnog struka. Umorna pukotina, koja je poprečna na uzdužnu os žice, nastaje tokom rada zbog višestrukog savijanja (slike 5 do 8).
Umorne pukotine nastaju mnogo češće na mjestima kontakta užeta i koturaljki nego na spojnim strukovima koji u trenutku savijanja nisu u kontaktu sa koturljkama.

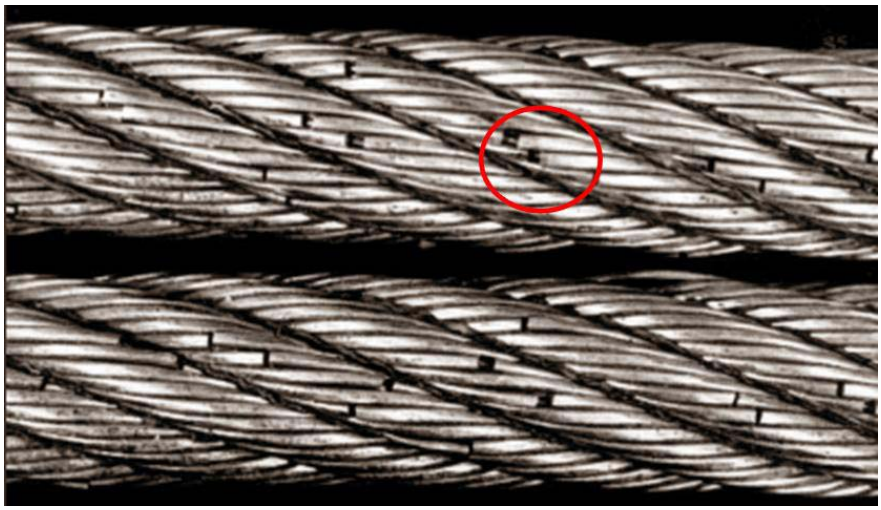


Slika 2. Ravnomjerno jako mehaničko trošenje spojnih strukova užeta bez pojave umornih pukotina na žicama

Slika 3. Plastično trošenje na površini žica spoljnjih strukova



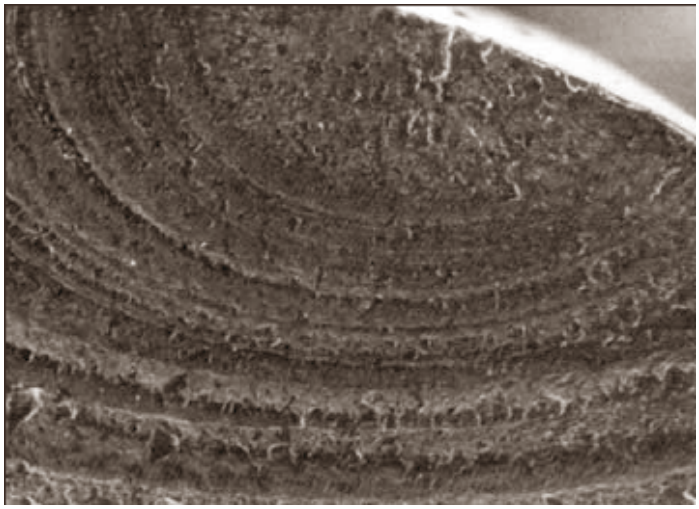
Slika 4. Smicanje materijala pri intenzivnom plastičnom trošenju spoljnjih strukova



Slika 5. Savojni umorni lom užeta u spojnim strukovima

Slika 6. Umorne pukotine na mjestu kontakta dodira pojedinačnih žica. Inicirane pukotine se vide nakon kidanja struka zatezanjem.

Slika 7. Umorna pukotina nastala na mjestu žice sa koturaljkom

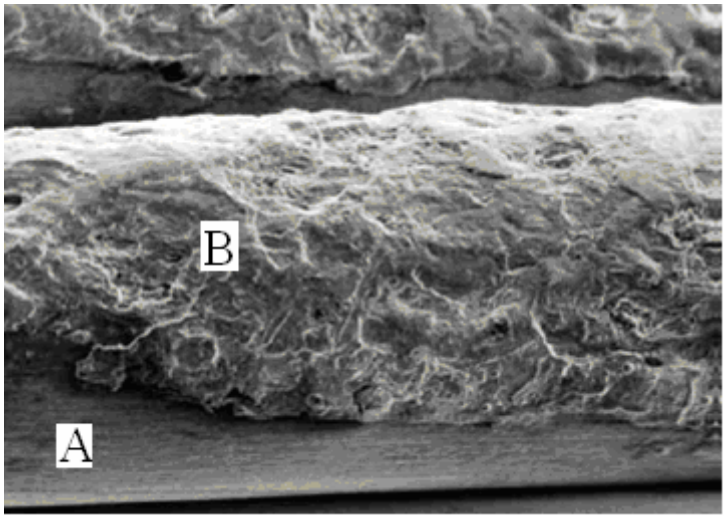


Slika 8. Linije umora i odmora oko mjesta iniciranja pukotine, uvećani detalj sa slike 7

Otpornost na umor čeličnih žičanih užadi se povećava povećanjem broja žica i smanjenjem njihovog poprečnog presjeka na spojnim strukovima. Ovo povećanje otpornosti na umor istovremeno utječe i na smanjenje opornosti užeta na trošenje.
Otpornost užeta se istovremeno može povećati nosačem koturaljke ili bubnja. Dodatno trošenje ili korozija će povećati brzinu nastanka i rasta pukotina. Odgovarajuće podmazivanje užeta i kontrola podmazivanja u eksploataciji će smanjiti trenje između užeta i vodećih točki u kontaktu i na taj način povećati otpornost užeta na umor.

4. KOROZIJSKA OŠTEĆENJA

Kod čeličnih užadi se razlikuje atmosferska korozija, koja proizvodi ravnomjerni sloj korozije, slika 9, od lokaliziranih oblika korozije, kao što je pitting, koji stvara duboke jamice na mjestima gdje je zaštitni sloj oštećen ili nedostaje.
Korodirana čelična užad tokom rada gube čvrstoću i savitljivost. Na korodiranoj površini žice dolazi do lakšeg stvaranja umornih pukotina u odnosu na zaštićenu površinu. Pri visokim lokalnim naprezanjimaa nastaju pukotine od napetosne korozije. Obujam korozije je u direktnoj vezi sa veličinom površine izložene koroziji, odnosno, njezinog direktog doticaja s atmosferskim utjecajem. Usporedbe radi, čelično uže ima oko 16 puta veću razvijenu površinu u odnosu na čeličnu šipku istog poprečnog presjeka, i njihova sklonost koroziji je znatno veća.
Sklonost koroziji se može umanjiti smanjenjem izložene površine, što se može postići galvanskom zaštitom. Plastične prevlake se koriste za zaštitu jezgri užeta. Istovremeno, i unutrašnje i svakodnevno podmazivanje čeličnog užeta mogu smanjiti ili spriječiti koroziju.
Problem kod užadi je što dolazi do njihovog širenja zbog korozije. Detektirano povećanje poprečnog presjeka užeta pri pregledu može biti znak da je došlo do početka unutrašnje korozije. Statički opterećena užad su podložnija koroziji u odnosu na užad koja su dinamički opterećena, koja su pokretna na dizalici.

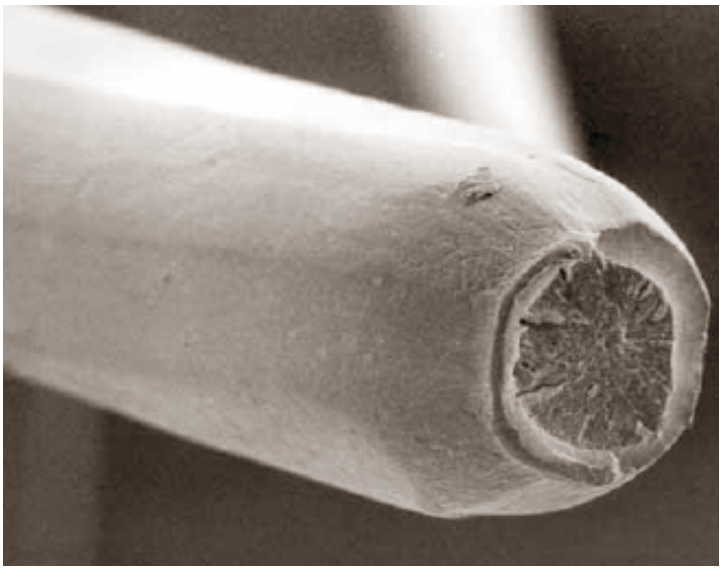


Slika 9. Atmosferska površinska korozija „B“ na jednoj žici i dio žice neoštećen korozijom „A“, ×100

5. LOM ZBOG VLAČNOG PREOPTEREĆENJA

Do loma užeta dolazi i kada pri zatezanju zbog preopterećenja dođe do prekoračenja vlačne čvrstoće materijala žice. Lom je tada duktilan, s izraženim suženjem i karakterističnim konusom klizanja završnog loma (slika 10).
Do loma zbog preopterećenja će doći samo ako je zbirni poprečni presek materijala, izložen kombiniranom vlačenju i smicanju, veći od 50% ukupnog poprečnog presjeka materijala užeta. Slike 10 i 11 prikazuju tipične slučajeve loma žice zbog vlačnog preopterećenja.

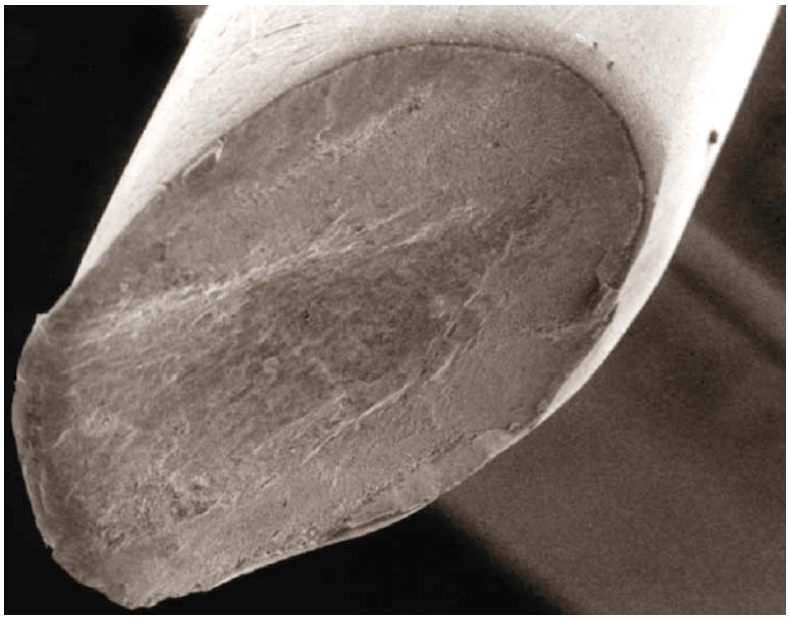
Slika 10. Tipičan duktilni lom završen konusom smicanja



Slika 11. Vidljivo suženje na mjestu prijeloma vlsčnim opterećenjem

6. SMICAJNI LOM

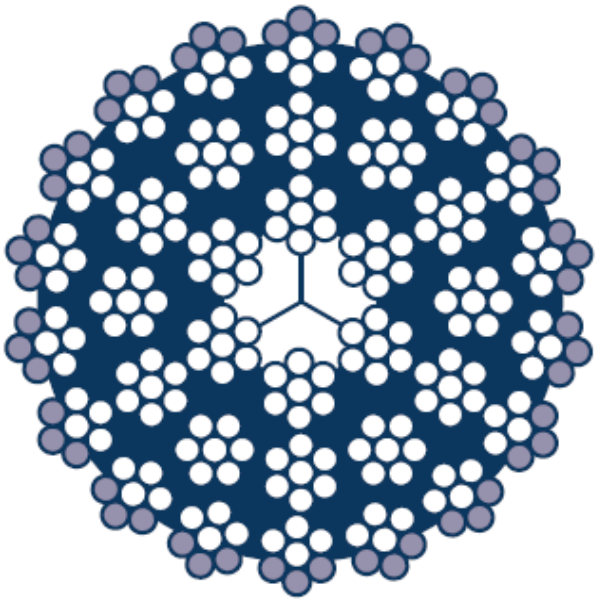
Smicajni lom se najčešće javlja kao kombinacija visokih vlačnih naprezanja i istovremenog djelovanja vertikalne sile na strukove. Prijelomna površina je pod kutem bliskim kutu od 45° u odnosu na uzdužnu os žice, u pravcu maksimalnog tangencijalnog naprezanja, slika 12.



Slika 12. Tipičan lom žice smicanjem pod kutom od oko 45°, u pravcu maksimalnih tangencijalnih naprezanja

7. STRUČNI OSVRT

Tijekom vizualnog pregleda moguće je ustvrditi samo stanje vidljivih dijelova spojenih žica. Međutim, površina poprečnog presjeka spojenih žica predstavlja samo oko 40% ukupnog poprečnog presjeka užeta. Zbog sapletosti žica samo je polovina dužine spojenih žica vidljiva pri pregledu, slika 13. Na osnovu toga se može zaključiti da je za vizualni pregled dostupno samo oko 20% ukupnog poprečnog preseka žica užeta. Za preostalih 80% poprečnog preseka moguća je samo procijena stanja, pri čemu se mogu očekivati manja oštećenja jer je njegov položaj zaštićen.
Ipak, vrlo često vidljivih 20% poprečnog preseka izgleda dobro, dok je veliki broj prekinutih žica u užetu skriven u unutrašnjosti. Čelična užad sa unutrašnjim prekidima žica bez ikakvog znaka oštećenja na površinskim strukovima predstavljaju vrlo opasan slučaj.



Slika 13. Samo 20% spojenih žica užeta se može ispitati vizualno (svijetlo sivo), dok 80% ostaje neispitano

8. ZAKLJUČAK

Čelična užad dizalica su izložena nepovoljnim uvjetima eksploatacije i velikom opterećenju tokom rada, zbog čega dolazi do prikazanih vidova oštećenja. Važno je da se spriječi pojava katastrofalnih otkaza, pa se stanje užadi mora neprekidno kontrolirati.
To je osnovni razlog zbog kojeg kontrola užadi mora biti stalna, od trenutka prijema materijala, tokom ugradnje i naročito tokom rada dizalice.

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DETERMINATION OF VICKERS HARDNESS APPLYING DIFFERENT LOADS

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Prethodno priopćenje / Preliminary note

Abstract:

In paper procedure of Vickers hardness measurements applying different loads is described. Measurements were made on referent hardness block with nominal value of hardness 199 HV 10 in the field of macrohardness, semi-microhardness and microhardness with the purpose of different load analysis on measured hardness values. Applied loads (forces) vary in the range from 0,196 N (measuring method HV 0,02) to 294,20 N (measuring method HV 30) while measurements were carried out on two different hardness testers from which one is referent hardness tester.

On the basis of carried measurements comparison of measured Vickers hardness on different measuring spots and comparison of measured hardness values and nominal hardness of referent hardness block is carried out. Certain conclusions are brought.

Keywords: Vickers hardness, load, macrohardness, semi-microhardness, microhardness

1. INTRODUCTION

Vickers method is standard method for material hardness determination especially for metals with hard surface and the most common use is for the scientific purposes. It consists of indenter indentation in material with prescribed force F (N). Depending on applied load (force) Vickers hardness can be defined as macrohardness, semi-microhardness and microhardness as presented in table 1.1

Table 1.1 – Values of applied load for different measuring method [1]

Macrohardness test - Conventional hardness		**Semi-microhardness test**		**Microhardness test**	
Measuring method	***Applied load F, N***	***Measuring method***	***Applied load F, N***	***Measuring method***	***Applied load F, N***
HV 5	49,03	HV 0,2	1,961	HV 0,01	0,09807
HV 10	98,07	HV 0,3	2,942	HV 0,015	0,1471
HV 20	196,1	HV 0,5	4,903	HV 0,02	0,1961
HV 30	294,2	HV 1	9,807	HV 0,025	0,2452
HV 50	490,3	HV 2	19,61	HV 0,05	0,4903
HV 100	980,7	HV 3	29,42	HV 0,1	0,9807

It is well known that there are many influential factors on hardness measurements and one of them is the value of applied force. One of the advantages of Vickers method comparing with other hardness methods is independence of measured hardness value about applied load because of indenter geometry in the field of macrohardness [2]. Is that the case in the field of semi-microhardness and microhardness will be examined in this paper?

2. VICKERS HARDNESS MEASUREMENTS

Vickers hardness measurements were carried out applying different loads which cover field of macrohardness, semi-microhardness and microhardness with the purpose of different load analysis on the measured hardness values.

Vickers hardness measurements provided in this paper consist of:

- Vickers hardness measurements using measuring methods HV 0,02; HV 0,03; HV 0,05; HV 0,1; HV 0,2; HV 0,5; HV 1; HV 2; HV5; HV 10 on hardness tester 1
- Vickers hardness measurements using measuring methods HV 10; HV 20; HV 30 on hardness tester 2

During measurements different loads were used and they vary from 0,196 N (measuring method HV 0,02) to 294,20 N (measuring method HV 30). Vickers hardness measurements are carried out on two different hardness testers, as mentioned above, according to HRN EN ISO 6507-1. The sample on which measurements are carried out is referent hardness block with the nominal value of hardness 199 HV 10 and is showed in figure 2.1.

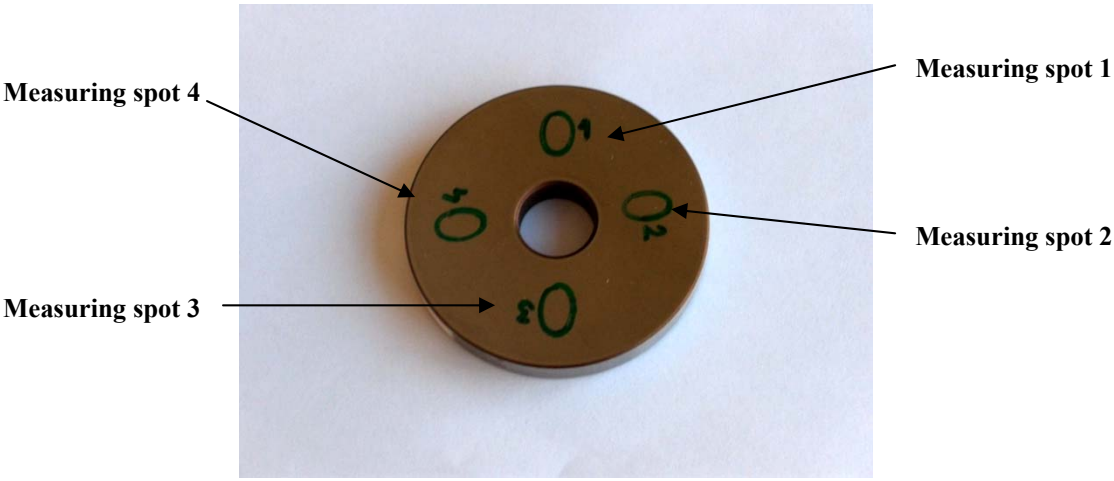

Figure 2.1 – Referent hardness block for hardness measurements

It can be seen from the figure 2.1 that hardness measurements are carried out on four different measuring spots.

Hardness testers on which the measurements were made are located in the Laboratory for Testing Mechanical Properties of Materials at Faculty of Mechanical Engineering and Naval Architecture and have following characteristics:

Hardness tester 1

- Manufacturer: Zwick, Germany;
- Type: 3212001;
- Serial number: 115696;
- Measuring method: analogue

Figure 2.2 – Hardness tester 1

Hardness tester 2 – Referent hardness tester

- Manufacturer: Indentec, UK;
- Type: 5030 TKV
- Serial number: 05281
- Measuring method: digital

Figure 2.3 – Hardness tester 2

3. VICKERS HARDNESS MEASUREMENTS RESULTS

Vickers hardness measurements besides indentation of diamond indenter in material surface with prescribed force F (N) consists of indentation analysis. Analysis of square-shaped indentation is carried out on high precise optic microscopes where the length of diagonals of square are measured. Optic microscope is integral part of hardness testers 1 and hardness tester 2.

Results of hardness measurements on different measuring spots are presented in tables 3.1 and 3.2.

Table 3.1 – Results of hardness measurements carried out on hardness tester 1

Meas. spot	No. of meas.	HV10	HV5	HV2	HV1	HV0,5	HV0,2	HV0,1	HV0,05	HV0,03	HV0,02
1	1	206	206	206	208	223	223	228	268	265	296
	2	201	201	210	210	224	224	249	232	247	266
	3	199	203	205	208	216	241	232	232	252	258
	4	203	203	209	208	228	222	222	249	251	276
	5	201	204	207	213	221	233	242	257	276	262
	$\bar{x}$	**202,0**	**203,4**	**207,4**	**209,4**	**222,4**	**228,6**	**234,6**	**247,6**	**258,2**	**271,6**
2	6	205	199	204	205	223	226	224	234	251	253
	7	199	203	210	208	222	233	228	249	265	241
	8	202	204	209	206	222	238	247	246	247	271
	9	203	204	210	213	220	215	245	268	244	307
	10	203	206	203	216	227	223	232	254	284	258
	$\bar{x}$	**202,4**	**203,2**	**207,2**	**209,6**	**222,8**	**227,0**	**235,2**	**250,2**	**258,2**	**266,0**
3	11	203	203	203	213	221	228	224	262	257	307
	12	203	203	211	206	226	224	243	249	265	266
	13	201	201	209	211	221	234	245	249	280	271
	14	201	204	207	205	223	237	235	262	257	266
	15	201	203	207	213	214	228	242	257	247	245
	$\bar{x}$	**201,8**	**202,8**	**207,4**	**209,6**	**221,0**	**230,2**	**237,8**	**255,8**	**261,2**	**271,0**
4	16	201	201	210	213	222	228	245	246	265	290
	17	199	206	204	205	220	232	233	241	272	266
	18	203	206	207	210	220	227	245	268	238	280
	19	199	203	206	210	223	232	228	268	272	266
	20	201	206	207	209	226	228	236	249	257	258
	$\bar{x}$	**200,6**	**204,4**	**206,8**	**209,4**	**222,2**	**229,4**	**237,4**	**254,4**	**260,8**	**272,0**

From the table 3.1 can be seen that there are no significant changes in average values of measured hardness on different measuring spots for all measuring methods. For measuring methods HV 10; HV 5; HV 2; HV 1; HV 0,5; HV 0,2; HV 0,1 the difference of average values on different measuring spots are maximum 3,2 HV. First bigger difference in average measured hardness on different measuring spots can be seen for measuring methods HV 0,05 and is 8,2 HV. Mentioned is not increasing for methods HV 0,03 and HV 0,02.

Variations of measured hardness results on the same and different measurement spots are increasing as the applied load is smaller.

Important thing to notice is that measured average hardness values differ from nominal value of referent hardness block which is 199 HV. Mentioned difference is increasing as applied load is smaller and gains 36% for measuring method HV 0,02.

Table 3.2 – Results of hardness measurements carried out on hardness tester 2

Measuring spot	Number of measurement	HV10	HV20	HV30
1	1	202,7	201,9	203,3
	2	202,5	201,9	200,2
	3	205,3	200,1	200,0
	4	203,0	203,2	200,6
	5	201,9	201,6	200,0
	$\bar{x}$	**203,1**	**201,7**	**200,8**
2	6	201,5	202,5	200,9
	7	200,7	202,2	202,8
	8	201,9	201,1	200,2
	9	204,5	202,7	200,6
	10	200,3	203,0	201,6
	$\bar{x}$	**201,8**	**202,3**	**201,2**
3	11	201,4	199,9	199,7
	12	202,3	201,3	200,9
	13	203,0	203,2	201,3
	14	201,4	203,2	201,3
	15	205,0	201,7	202,2
	$\bar{x}$	**202,6**	**201,9**	**201,1**
4	16	204,4	202,6	200,6
	17	200,6	202,1	198,8
	18	201,8	202,1	202,7
	19	202,1	200,4	201,8
	20	201,9	201,9	200,5
	$\bar{x}$	**202,2**	**201,8**	**200,9**

From the table 3.2 can be seen that there are no changes in average values of measured hardness on different measuring spots for measuring methods HV 10, HV 20 and HV 30. The average values of measured hardness differ for less than 2 HV on different measuring spots what is approximately 1% of measured hardness and differ for less than 2% from nominal value of referent hardness block (1.7% for HV10, 1.5% for HV20) and 1,0% for HV30).

4. STATISTICAL ANALYSIS OF MEASUREMENT RESULTS

Statistical analysis of measurement results in the field of macrohardness, semi-microhardness and microhardness are presented on figures 4.1, 4.2, 4.3 and 4.4.

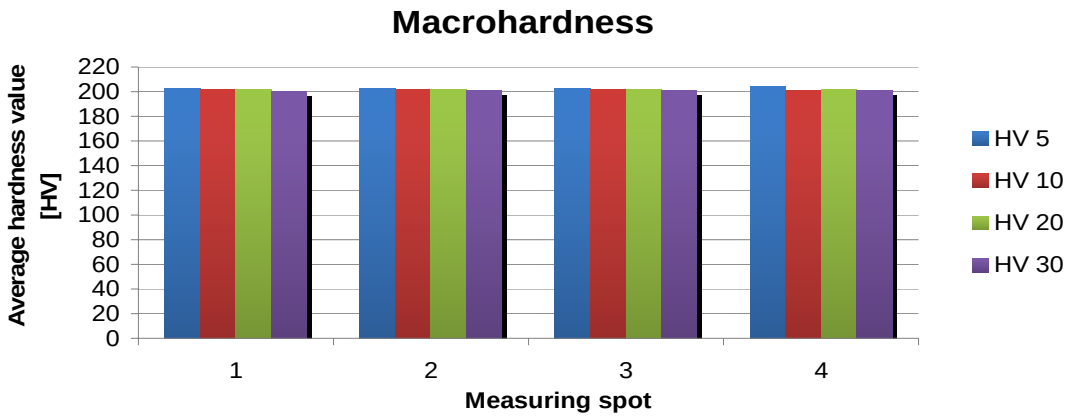

Figure 4.1 – Measured values of macrohardness on different measuring spots

As presented on figure 4.1 values of macrohardness (convectional hardness) measured with measuring methods: HV 5, HV 10, HV 20 and HV 30 are more or less constant while average hardness values measured on different measuring spots are in the range from 201 (for measuring method HV 30) to 203 Vickers (for measuring method HV5).

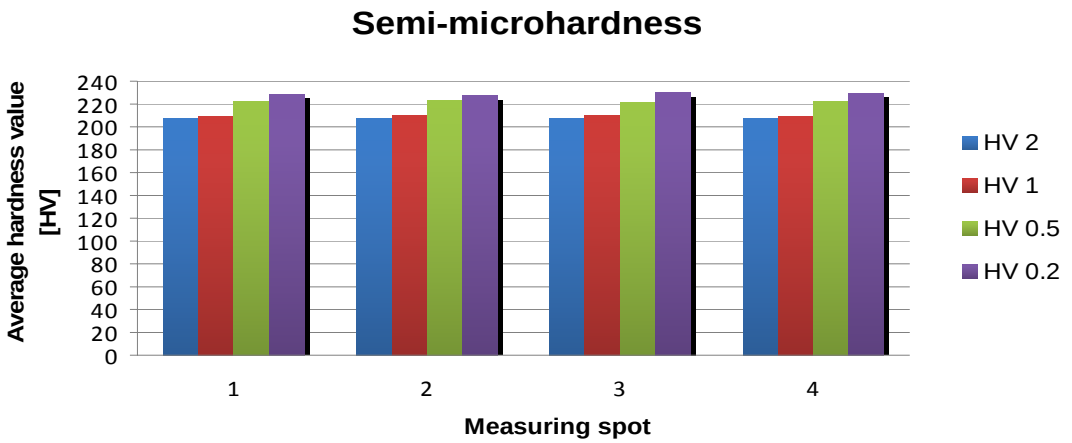

Figure 4.2 – Measured values of semi-microhardness on different measuring spots

As presented on figure 4.2 values of semi-microhardness measured with different measuring methods: HV 0,2; HV 0,5; HV 1 and HV 2 are significantly different and they vary from 207 (for measuring method HV 2) to 230 Vickers (for measuring method HV 0,2) what is more than 10%. Average hardness values on different measuring spots are more or less the same but variations of measuring results are registered for measuring methods HV 0,5 and HV 0,2.

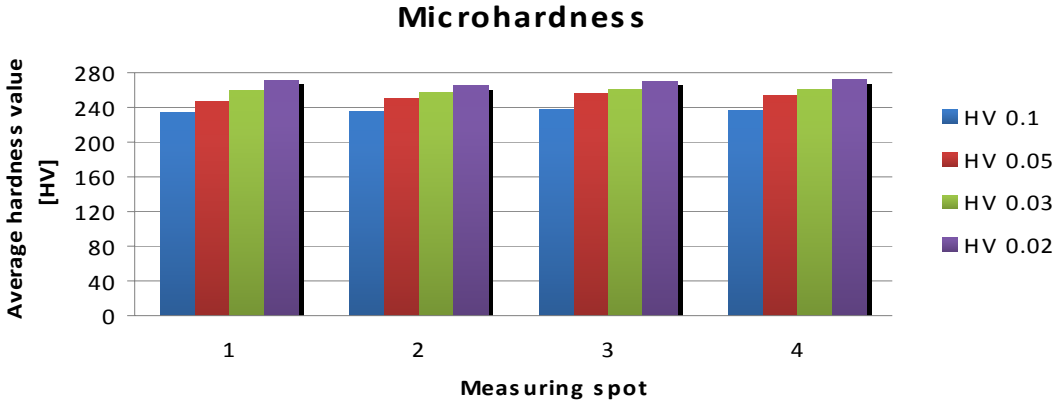

Figure 4.3 – Measured values of microhardness on different measuring spots

As presented on figure 4.3 values of microhardness measured with different measuring methods: HV 0,1, HV 0,05, HV 0,03 and HV 0,02 are significantly different and they vary from 234,6 (the smallest average value for measuring method HV 0,1) to 272 Vickers (the biggest average value for measuring method HV 0,02) what is more than 15%. This behaviour is similar like in case of semi-microhardness but variations are bigger and increase as the applied load is smaller. Exponential growth of measured hardness can be noticeable. It is important to emphasize that the measured average values of Vickers hardness differ from nominal value of referent hardness block significantly, even for 73 Vickers what is 36% for the smallest applied load (the biggest average value for measuring method HV 0,02). Deviations of measured average hardness values from nominal value of referent hardness block in correlation with applied load are presented on figure 4.4

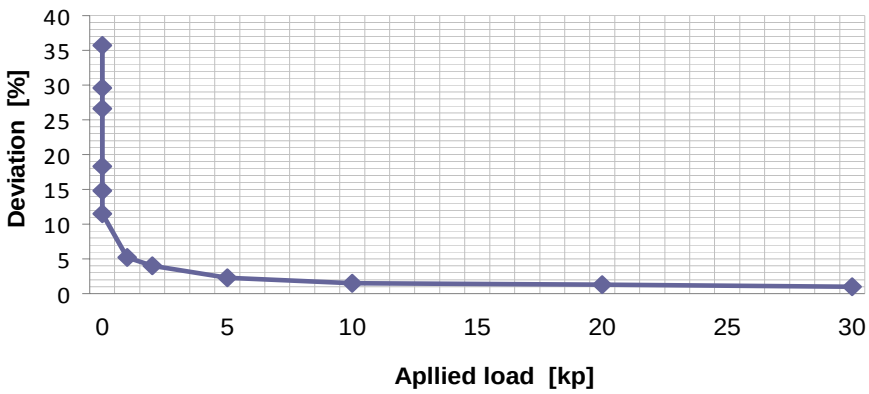

Figure 4.4 – Deviations from nominal hardness in correlation with applied load

From the figure 4.4 can be concluded that deviations of measured Vickers hardness from nominal hardness value are decreasing with growth of applied force. Deviations in the field of macrohardness are approximately 2% while in the field of microhardness gain up to 36% for measuring method HV 0,02.

5. CONCLUSION

Based on obtained results can be concluded that the applied load (force) has significant influence on the measured values of Vickers hardness in the field of semi-microhardness and microhardness while in the field of macrohardness hardness (conventional hardness) values are independent on applied load what is one of the advantages of Vickers hardness method.

Hardness values measured with smaller loads (forces) show considerably big deviations from nominal value of reference hardness block as well as variations of measured results. One of the reasons for mentioned can be the size of indentation. Indentations are much smaller and if they are analysed under the same magnification as bigger indentations than is logical that the values of hardness would deviate more.

Also there are many influential factors such as temperature, vibrations, sample surface preparation etc. which can leave trace on hardness measurements especially in case of very small loads.

Subjectivity of measurement, which is one of disadvantages of Vickers method, and bad evaluation, can also be the reason for bigger deviations in case of small indentations.

Variations of measured results which are noted during analysis of results, especially in case of small loads, can be a consequence of relatively small number of carried measurements.

Average hardness values on different measuring spots are more or less very similar and there are no significant changes on different measuring spots what is a consequence of material homogeneity of reference hardness block.

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5. LITERATURE

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INFLUENCE OF MULTIPLE PRELOAD ON RESULTS OF TESTING MACHINE CALIBRATION

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Pregledni članak / Subject review

Abstract:
Preload plays an important role in the calibration procedure of a testing machine and represents an inevitable part of the calibration process. Preload affects the calibration results in the form of relative errors of the measuring system of force which is indirectly reflected also on the class of the measuring range. By performing one or several preloading there is a significant change in the values of characteristic relative errors: accuracy, repeatability and reversibility which represent the classification criteria in determining the class. A greater number of preloads makes worse the error of accuracy whereas the error of repeatability and in particular the error of reversibility are reduced in the absolute amount. Furthermore, preload affects also the residual force which remains on the standard measurement instrument after removing load. Already one preload minimizes this residue and thus allows valid testing. Therefore, the preload in checking the testing machine represents an important precondition of calibration with the aim of obtaining a right information about the accuracy of the tested measurement instrument.

Key words: preload, calibration, testing machine, force

1. INTRODUCTION

One of the most frequent tests of mechanical properties is certainly the tensile test which is carried out on the instruments that are called testing machines on which the test specimen is loaded by tensile force until fracture and the elastic and plastic behaviour of the material is monitored. The fracture of specimens determines the basic mechanical properties that characterise the mechanical resistance of materials, and that are the yield strength and tensile strength [1]. The basis for their determination is the measurement of force that has to be valid for the values of mechanical properties to be correct.

Over years the accuracy of the testing machines deteriorates due to various forms of damaging, failures and wear of the vital parts and there is need for systemic periodic calibration of the force-measuring system within certain time periods. The calibration of the testing machine according to DIN EN ISO 7500-1 standard is carried out by standard equipment of the same or better class that also has to be calibrated in order to realize continuous chain of comparisons and thus the traceability of measuring instrument all the way to the national standard [2].

For the needs of this paper, a testing machine of nominal force 400kN manufactured by WPM, Germany, type: EU 40mod was calibrated, Figure 1.

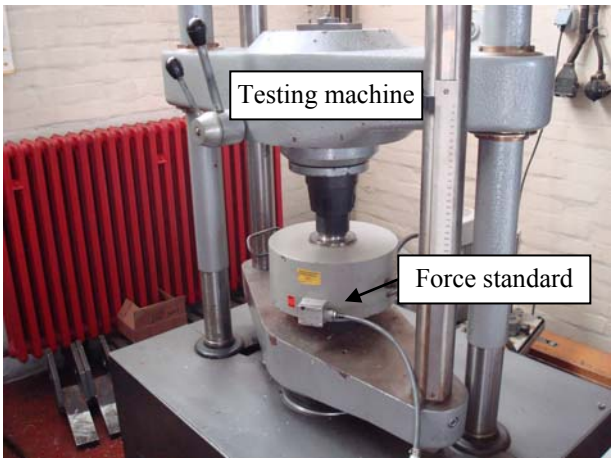

Fig. 1 – Compression calibration of a testing machine

Calibration was carried out by standard measuring system made of the portable standard of force of nominal value 500kN (manufacturer: Hottinger Baldwin Messtechnik GmbH, Germany; type: Z4/500 kN; serial number: 88923; class: 00; calibration code: M 0359 DKD-K-15501 07-05) and digital measuring amplifier DMP 40 (serial number: 122020096; calibration mark: 21759 DKD-K-00101 2008-08) of carrier frequency 225 Hz manufactured by Hottinger Baldwin Messtechnik GmbH, Germany [3].

2. PROBLEM ANALYSIS

The portable standard of force should be mounted on the testing machine in such a way that in the unloaded condition any, even the least load remaining from the previous calibrations has been eliminated. Therefore, the calibration should contain preload as one of the essential factors of valid testing. The testing machine with the mounted standard of force should be loaded until the maximum force, for the direction of force at which the calibration is carried out and then unloaded in order to minimize the effect of residual load.

Since the available literature does not provide data on the influence of multiple preload on the calibration results, in order to analyze the resulting effects, calibrations with a

single or several preloads, up to a maximum of 4, have been carried out in order to quantify the law of change of the characteristic values of the force-measuring system which is indirectly reflected also on the classification of the measuring range of the testing machine. With the aim of best possible analysis of the resulting effects, a comparison has been made with the starting condition and calibration without preload.

Determining of the optimal number of preloads would contribute to the quality of the testing process which is very important in the implementation of everyday calibrations.

3. CALIBRATION PROCEDURE

Calibration generally means a set of operations which are used to determine under certain conditions the connection between the values read on a certain measuring instrument or measuring system, or values represented by a material measure or a reference material, and the corresponding values realized by standards [4].

In case of testing machines the calibration is carried out by comparison of the force values read on the force indicator of the testing machine (F_i) and the values of true forces (F) measured by means of standard measuring instrument. Since electric force standard on the principle of strain gauges connected to Wheatstone bridge is used for calibration, under the action of the load the strain gauges are deformed and their resistance i.e. values of output voltage from the Wheatstone bridge are changed [5]. The result of calibration in the form of change of output voltage per 1V of excitation voltage is expressed by mV/V. Induced small voltage changes are additionally amplified by means of an amplifier and then at the A/D converter analogue signal is converted into a digital one and sent to the computer where acquisition is done and the results of calibration are graphically processed, Figure 2.

Fig. 2 – Standard measuring system [6]

Thus, calibration in fact establishes a relationship between the reference values of voltage changes ($X_{ref.}$) which correspond to certain forces induced on the testing machine (F_i) and the measured voltage changes (X) that correspond to true forces (F) [7].

4. RESULTS OF CALIBRATION

Figure 3 shows diagrams representing the results of calibration per measuring points (80kN, 160kN, 240kN, 320kN, 400kN) for different number of preloads. All the values have been measured at the ambient temperature of 22.3°C at the loading rate of 1kN/s, frequency of Butterworth filter 8.7Hz and the resolution of the force indicator r=0.1kN.

The following reference values of voltage change ($X_{ref.}$) correspond to the values of discrete forces respectively: 0.32029 mV/V; 0.64054 mV/V; 0.96076 mV/V; 1.28093 mV/V; 1.60105 mV/V.

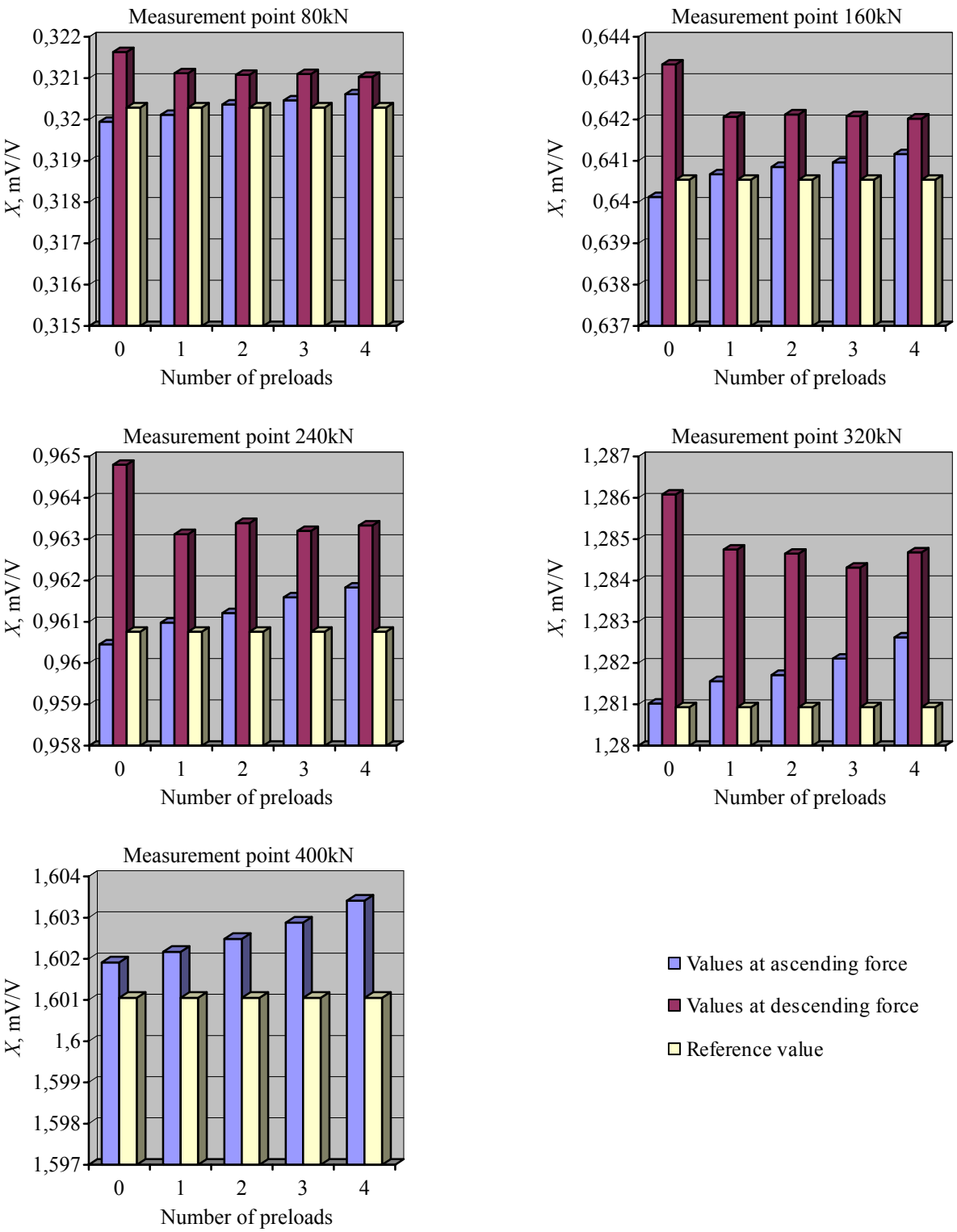

Fig. 3 – Results of measurement per measurement points for different number of preloads

Preload causes change in the value of the measurement signal, including the true force. The measurement results show that with a larger number of preloads the value of the output signal measured in ascending series at increasing testing force increases. A somewhat different situation is in descending series with decreasing test force where for each measurement point

the value of signal is highest without preload, and then it falls and becomes stable already after only one preload (Figure 3).

The values of relative resolution (a) per measurement points are listed in Table 1.

Table 1 Values of relative resolution of the force indicator of the testing machine

F_i, kN	80.0	160.0	240.0	320.0	400.0
a, %	0.13	0.06	0.04	0.03	0.03

Table 2 contains systematized results of calibration in the form of relative errors of the measurement system of the testing machine and the respective class.

Table 2 Relative errors and class of the testing machine

Number of preloads	F_i kN	Relative error of accuracy q %	repeatability b %	reversibility υ %	zero series 1 f_{01}	series 2 f_{02} %	series 3 f_{03}	Class
0	80.0	0.11	0.09	-0.42	0	0	0	0.5
	160.0	0.07	0.05	-0.44				
	240.0	0.03	0.04	-0.42				
	320.0	-0.01	0.03	-0.40				
	400.0	-0.05	0.03	-				
1	80.0	0.06	0.10	-0.26	0	0	0	0.5
	160.0	-0.02	0.07	-0.24				
	240.0	-0.02	0.05	-0.24				
	320.0	-0.05	0.04	-0.30				
	400.0	-0.07	0.04	-				
2	80.0	-0.02	0.06	-0.25	0	0	0	0.5
	160.0	-0.05	0.06	-0.25				
	240.0	-0.05	0.04	-0.27				
	320.0	-0.06	0.04	-0.29				
	400.0	-0.09	0.04	-				
3	80.0	-0.06	0.08	-0.25	0	0	0	0.5
	160.0	-0.07	0.06	-0.24				
	240.0	-0.09	0.05	-0.25				
	320.0	-0.09	0.05	-0.26				
	400.0	-0.11	0.04	-				
4	80.0	-0.10	0.07	-0.23	0	0	0	0.5
	160.0	-0.10	0.01	-0.23				
	240.0	-0.11	0.02	-0.27				
	320.0	-0.13	0.01	-0.29				
	400.0	-0.15	0.01	-				

5. CONCLUSION

The carried out tests clearly show that the number of preloads has an important role in the calibration procedure of the testing machine. One or several preloads change the values of the measured true force which influences also the final calibration results in the form of measured errors of the force-measuring system.

Based on the test results it is found that the measurement range of the tested testing machine is of class 0.5 for all the carried out calibrations with or without preload. However, preload causes change in the value of relative error of reversibility and to a lesser extent also relative errors of accuracy and repeatability, and it is possible that in some other testing machines that have marginal values of characteristic errors such calibrations that include a different number of preloads result in different classes of the measuring range. In case of the tested testing machine, continuous deterioration of the error of accuracy with a greater number of preloads is evident. However, this trend could have also been different if the reference value was higher than the measured one. Regarding the error of repeatability, as a rule it decreases by multiple loading due to lower dispersion of results. What is especially significant is the error of reversibility. With calibration without preload the values of this error are significantly higher and a very frequent case in testing machines of older years is that precisely because of the error of reversibility the testing machine has to be assigned a worse class. Therefore, in order to have valid calibration results, and to be able to accurately classify the measurement range, the calibration procedure has to contain preload as an inevitable factor of valid testing.

Furthermore, the influence of the residual force, remaining on the standard device after unloading, should not be neglected. This residue is always the highest in first loading regardless of whether it is preload or the measurement series and so from this aspect also at least one preload has to be carried out in order to minimize the influence of the residue and for the measurement results in the first measurement series to be truly credible and accurate.

From all this it follows that by performing preloading in the calibration procedure of the testing machine the error of measurement is reduced and thus valid calibration is made possible which gives a right information about the accuracy of the tested machine.

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Thermal Spray Coatings – Effect of Selected Coating Parameters on Corrosion Resistance

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Abstract

Thermal Spray coatings have long been adopted as a surface modification technique. Unique in their ability to mechanically bond to the surface of most substrate materials, the Thermal Spray coatings offer a generic solution to improving mechanical, corrosion or tribo-corrosion properties of the affected substrate material. Of the available systems, Flame Spray techniques offer the simplest and most cost-effective method of applying these coatings. In the current study, an investigation was conducted into the comparative performance of a selection of these coating systems – a polymer coating, with various coating thicknesses, and a metallic coating - in a number of Corrosion Test environments, when applied to a Mild Steel Alloy. The effect of chlorides on the life-to-failure of these systems is predicted and reviewed. Electrochemical Impedance Spectroscopy and Immersion Testing were carried out, in conjunction with microscopic and metallographic studies. Using these combined methodologies, it has been shown that the efficacy of the Thermal Spray coatings reviewed is dependent on both the inherent nature of the coating material and the coating thickness.

Introduction

Development in surface engineering processes has resulted in the growth of new technologies for increase of wear resistance, corrosion resistance and for aesthetic function. Besides the traditional processes – surface hardening, carburising, nitriding etc, a number of advanced physical technologies have been developed and are being increasingly used, like the laser and plasma assisted processes. For engineers – especially in design and in definition of production processes - the right choice of appropriate surface treatment is a very important task. Indeed, the development of new coatings and application processes is generally accompanied, or even preceded by, the introduction of newer environments which are more aggressive and provide more stringent tests. Nowadays in this field, a lack of adequately prepared guidance and expert proposals is evident.

The two most aggressive forms of material loss are Corrosion and Wear but, in applications where these two elements work in tandem, the results can be catastrophic. It is impossible to deduce the environmentally influenced mechanical behaviour of a system from its behaviour in separate corrosion and erosion experiments[i] as corrosion, which can be either "synergistic" or "additive"[ii]., may have only minimal impact on certain systems, such as aerospace coatings, but, when incorporated into a mechanical abrasive test, can lead catastrophic failure. Likewise, the wear characteristics of an engineered surface may have exemplary resistance to deterioration but the introduction of a corrosive element may ultimately lead to the untimely and premature failure of the system. The dynamic nature of these aggressive systems has compelled both industry and academia to address the short-comings of the traditional surface modification techniques.

Engineering Coating Development can be loosely categorised under the following headings:

- Organic Coatings, including systems embedded into an organic matrix
- Thermal Spray Coatings
- Vapour Deposition Coatings
- Chemical/Electrodeposition Coatings

One of the most aggressive forms of mechanical and chemical attack on a surface, leading to extensive material loss, is termed Tribocorrosion. This is a complex degradation process, affecting surface and near-surface material, which results from the combined effects of mechanical loading and environmental influences and many aspects of the phenomenon remain to be elucidated. In terms of the magnitude of the material loss, the effect of corrosion on erosion (often referred to as synergy) is a much more prominent feature for both materials.[iii] The areas of tribocorrosion under consideration are erosion-corrosion, abrasion-corrosion, cavitation-corrosion and flow-induced corrosion[iv]. Although its cost to the industrialised world has not yet been fully quantified, the cost of corrosion to national GNPs runs between 3% and 5%[v].

Experimental

Test Panels

- Mild Steel was chosen as the substrate material, due to its widespread use in industry.
- The Test Panels were machined from flat plate, to a size of 100mm x 130mm.

- A total of 30 test panels were produced.

Pre-Treatment

Cleaning and de-greasing

Prior to the coating treatment, the panels were Grit Blast, using a 60/40 Fe_2O_3/Al_2O_3 Grit Blend.

Coating Application

Two distinct coating types were applied to different test panels. A polymer coating, in the EverTuff range, and an Inconel 625 coating; both supplied by Castolin Eutectic. Coating application is described below:

Figure 1 TeroDyn System 3500

EverTuff ET 11:

- Was applied using a TeroDyn System 3500(Figure 1), produced and supplied by Castolin Eutectic
- Coatings were applied at two thicknesses - ~100µm and ~350µm

Inconel 625

- Was applied with the CDS 8000 system(Figure 2), produced and supplied by Castolin Eutectic
- Coating thickness were to be 90-110µm

Figure 2 CDS 8000 Flame Spray gun

Sample Preparation – Cross Sections

- Cross Sections(CS), taken from an untested panel of each coating, were mounted in an epoxy resin (Sampl-Kwick fast cure acrylic resin, produced by Buehler).
- The CS samples were then ground to a 1200 SiC grit finish, followed by polishing in successively finer grades of diamond paste (Buehler Sample Preparation system) to a 0.05 micron finish.
- Samples were then etched for 5 minutes in a 2% Nital solution.

Hardness Testing

CS Samples for each coating system were Hardness Tested, using the Buehler Micromet II Microhardness Indentor, as outlined in ASTM E384-99e1 : Standard Test Method for Microindentation Hardness of Materials.

Coating Thickness Measurements

Coating Thicknesses were measured on CS samples of each coating system using optical microscopy and PC-based image capturing software.

Corrosion Testing

EIS Testing

Short-Term Corrosion Testing was carried out using EIS (Electrochemical Impedance Spectroscopy) and was performed for 4 wks. The solution was chosen on the basis of the Long Term Test regimes:

- 0.5M NaCl

Immersion Testing

A single panel , per coating, was tested in each environment. The Immersion Testing was performed for 6 weeks in three separate environments:

Test	**Enviromnent**
pH 3	Acetic Acid [CH_3 OOH]
pH 7	NH_4CL
pH 12	Na OH

Table 1 : The Immersion (Corrosion) Test Environments

Results and Discussion

Micrographic examination results are displayed in Figure 3. It can be noted from these images that while the polymer coating (i and ii) has good interfacial integrity and no apparent porosity, the Inconel 625 coating has extensive porosity and does not adhere well to the surface of the substrate. This is typical of this process and has been found by numerous other authors[vivii].The implication of this is that these coatings tend to have poor corrosion resistance[viii]. A number of methods are used to overcome this issue. With metallic coatings

it is possible to fuse the coating, post application. This involves re-heating the coating to plastic region of the material, thus allowing flow in the coating, causing voids and pores to close and providing a better interfacial bond with the substrate. An alternative method is to

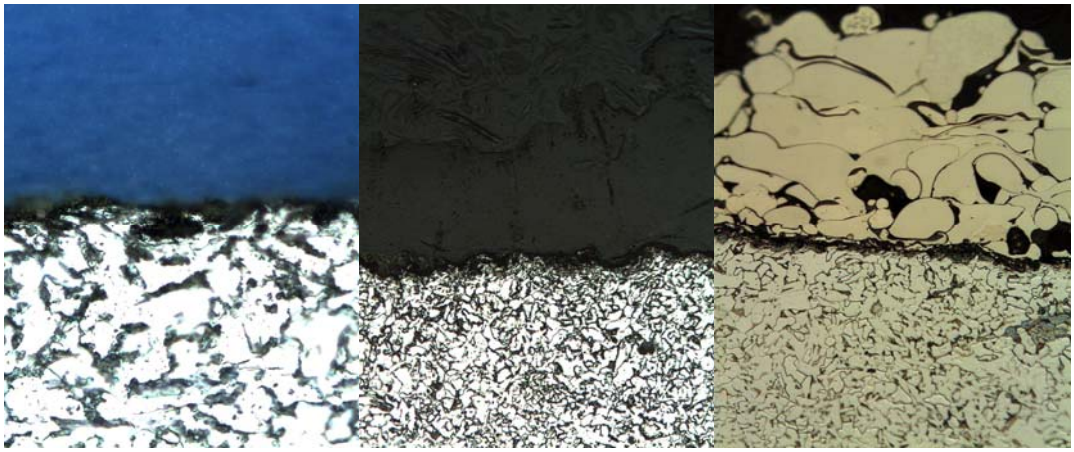

Figure 3 Micrographs showing Polymer Coating (i) 350m[500x] (ii) 100m[200x] and (iii) Inconel 625[200x]

use self-fluxing powders, which are a type of thermal spraying material, having functions of self-deoxidization and self-slag formation when melting.

The EIS testing was carried out in a typically marine environment (0.5M NaCl). Whilst this is a very aggressive environment, it can be seen (Figure 4) that the thick(>300µm) polymer

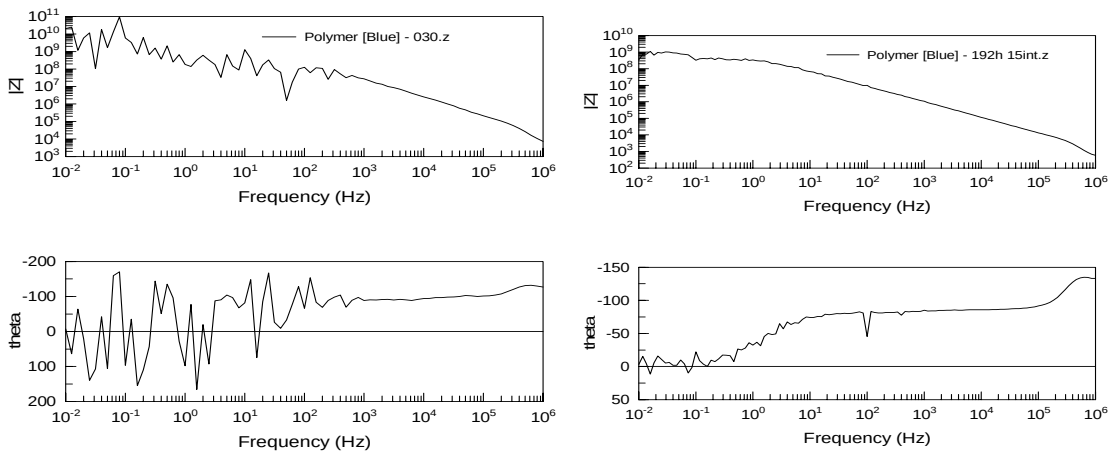

Figure 4 EIS Results for Polymer Coating (>300m) (i) 30 hr (ii) 192 hr

coating maintained elevated resistance to the corrosive environments ($10^{-9}\Omega cm^{-2}$) over the duration of the test). The noise at the lower frequencies is typical of coatings with very high impedance readings. The reason for this high level of resistance is associated with the high level of integrity in the coating, along with the greater thickness. For the thinner coating (100µm), initial resistance to degradation was high but this began to drop after 96 hrs in solution. It is suggested that the thinner coatings suffer from a greater occurrence of through-

defects, resulting in a greater propensity to attack in aggressive environments. This can also be seen with the Inconel 625 samples (Figure 5), where coating thickness was also in the

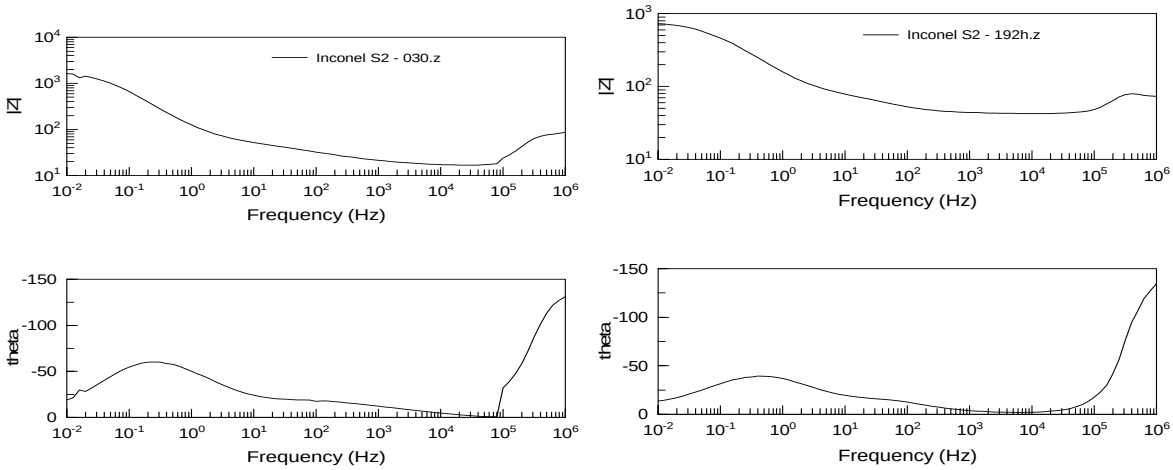

Figure 5 EIS Results for Inconel 625 Coating after (i) 30 hours (ii) 192 hours

region of 100µm, with obvious inhomogeneities occurring in the coatings, such as porosity through the coating and interfacial anomalies suggesting poor adhesion, resulting in through-coating defects and limited or no resistance to chemical attack, with an initial impedance value of $10^{-3}\Omega cm^{-2}$. It was initially assumed that the organic (polymer) coatings would have superior corrosion resistance, though it can be seen from these results that the integrity of the coating is very dependent on the thickness.

Reading	Inconel 625	EverTuff ET 11
1	87.2	1.85
2	81.4	2.06
3	120.6	2.13
4	93.5	1.95
5	59.1	1.68
Average	88.36	1.54

Table 2 Table showing microhardness results for the coatings.

Microhardness results are shown in Table 2. This is an important property and has been related back to coating integrity by some authors[ix]. The disparity between the metallic and polymer coatings is as expected and needs no further analysis. Attempts to quantify the adhesion properties of the coatings, using the Dolly Pull Test (ASTM D4541) produced unquantifiable results, as all of the failure occurred at the adhesive/dolly interface between, and are therefore not reported here.

Conclusions

The work detailed in this paper looked at the effect of coating type and coating thickness on the corrosion behaviour of selected Flame Spray coating materials. An organic and a metallic coating were chosen for the analysis.

It was found that the coating thickness for polymer had a dramatic effect, resulting in the initialisation of corrosion failure in the thinner coating after 96 hrs. It was also found that the use on non-self-fluxing metallic coatings (Inconel 625) resulted in a coating with a large degree of porosity and interfacial inhomogeneties.

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Modeliranje mazivoga sloja kod dresiranja trake

Izvorni znanstveni rad / Original scientific paper

Sažetak

Analizira se utjecaj poprečne hrapavosti trake na procese dresiranja sa mazivima.Analiza polazi od Reynoldsove diferencijalne jednadžbe za podmazivanje u koju je inkorporirana poprečna hrapavost trake.U proračunu se uzima u obzir i visina maziva na traci te njezin utjecaj na visinu maziva na ulaznom presijeku zone deformacije.Istraživanja su pokazala da poprečna hrapavost ima dvojak utjecaj na visinu maziva na ulaznome presijeku zone deformacije.Za malu hrapavost trake visina mazivog sloja ima tendencija laganoga opadanja u odnosu na nominalnu visinu (kada se proces opisuje glatkoćom površina) da bi dalje s porastom hrapavosti, debljina mazivog sloja rasla.Izvršeno je i modeliranje mazivog sloja za slučaj trenja nedovoljno okvašenih površina.Okosnicu analize nosila je numerička metoda Monte-Carlo , a izvedeno je i približno analitičko rješenje koje je u usporedbi s numeričkom metodom dalo dobru podudarnost.

Ključne riječi:hrapavost površine,emulzije,Reynoldsova diferencijalna jednadžba, Monte-Carlo metoda,točke motrišta Auto-CAD-a.

1.Uvod

Matematičko modeliranje[1-3] danas je potreba u metalurgiji.Ono je specifično u području plastične deformacije metala.Ako analiza teče u području glatkih površina metala[4-5] njezin matematički zapis glasi :

$$\frac{dp}{dx} = \frac{6\mu(v_0 + v_R)}{\varepsilon^2(x)} - \frac{12\mu Q}{\varepsilon^3(x)} \tag{1}$$

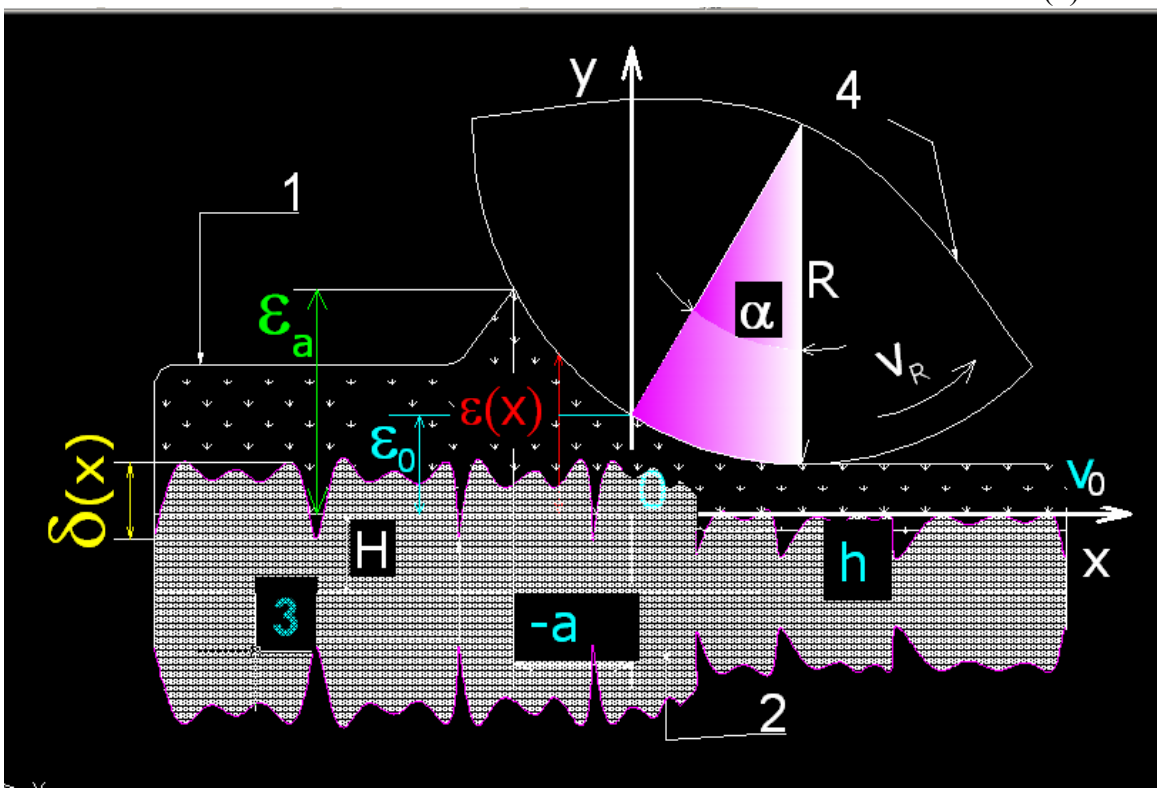
$$Q(x) = \int_0^{\varepsilon(x)} u dy = -\frac{1}{12\mu}\frac{dp}{dx}\varepsilon^3(x) + \left(\frac{v_0 + v_R}{2}\right)\varepsilon(x) \tag{2}$$

Geometriju kontakta maziva[8,9,10] opisuje izraz (4),dužinu mazivoga klina izraz (5).

$$\varepsilon(x) = \varepsilon_0 + R\left[\cos\alpha - \sqrt{1-\left(\sin\alpha - \frac{x}{R}\right)^2}\right] \tag{3}$$

$$a = R\left[\sqrt{1-\left(\cos\alpha - \frac{\varepsilon_a}{R} + \frac{\varepsilon_0}{R}\right)^2} - \sin\alpha\right] \tag{4}$$

$$\varepsilon(x) = \varepsilon_0 - \alpha\, x + \frac{x^2}{2R} - \frac{\alpha\, x^3}{2R^2} + \frac{x^4}{8R^3} \tag{5}$$

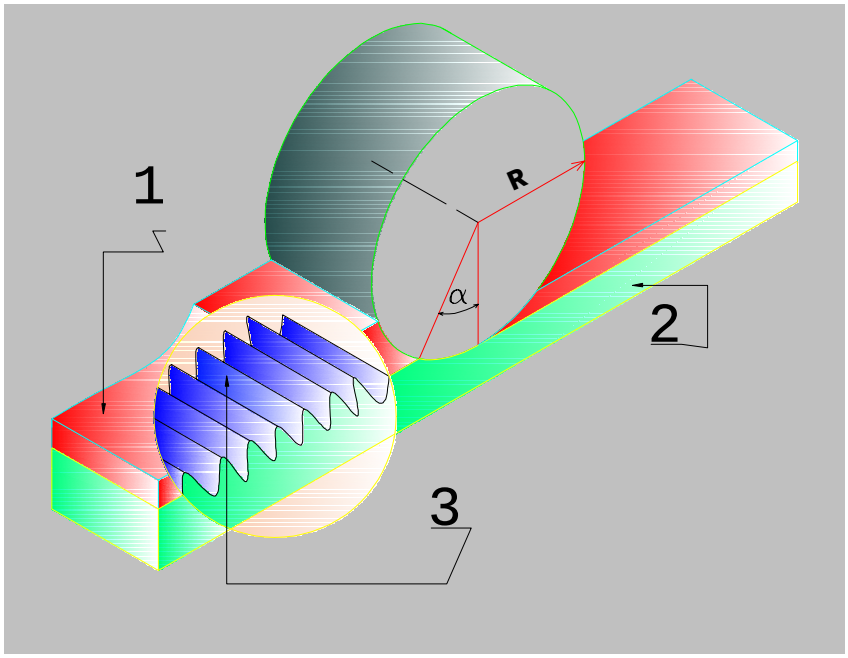


Slika 1.Opis modela (top pogled), tribomehaničkoga sistema.
1-mazivi sloj - **ε(x)** - nominalna visina kada se proces opisuje glatkoćom površina
2-traka – u procesima dresiranja ima mali zahvatni kut **α**
3-poprečna hrapavost trake- **δ(x)** - slučajna visina uslovljena hrapavosti trake
4-valjak- opisuje se glatkoćom površina : u **tablici 5**. daje mu se hrapavost R_Z = 8 μm

Za slučaj poprečne hrapavosti trake[6] matematički opis glasi prema **slici 1**.

$$\left\langle \frac{dp}{dx_0} \right\rangle = 6\mu(v_0 + v_R)\left[\left\langle \frac{1}{\varepsilon^2(x_0)} \right\rangle - \frac{\left\langle \frac{1}{\varepsilon^2{}_0} \right\rangle}{\left\langle \frac{1}{\varepsilon^3{}_0} \right\rangle}\left\langle \frac{1}{\varepsilon^3(x_0)} \right\rangle\right] \tag{6}$$

$$\langle \varepsilon(x_0) \rangle = \varepsilon(x) + \delta(x) \tag{7}$$



Slika 2.Homogena izotropna hrapavost-**3** (izometrijski pogled) gdje je **R** radijus valjaka dok **α** označava kut zahvata.

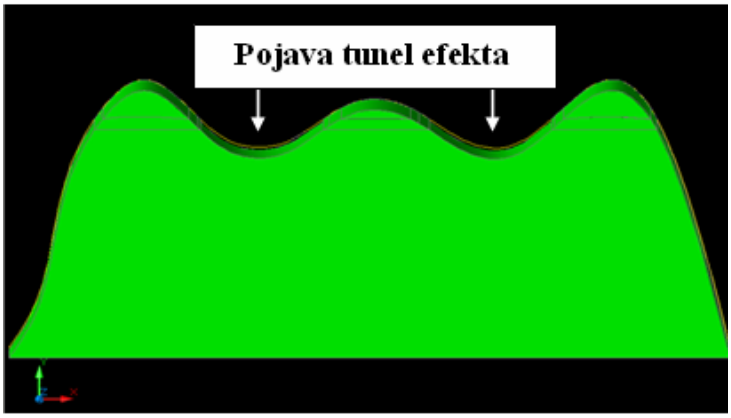
U prvim prilazima ovoj problematici kretalo se od homogene izotropne hrapavosti datoj na **slici 2**.Računala skromnih mogućnosti nisu mogli tretirati složenije profile hrapavosti.

Na mazivi klin (4) dodaje se refleksija hrapavosti trake, kao i na ε_0.Ovaj proračun moguće je ostvariti samo numeričkim metodama u matematičkim aplikacijama.U programu MATHEMATICA korištena je numerička metoda Monte-Carlo.

U teorijskim istraživanjima za model poprečne hrapavosti trake uzeta je sljedeća funkcija:

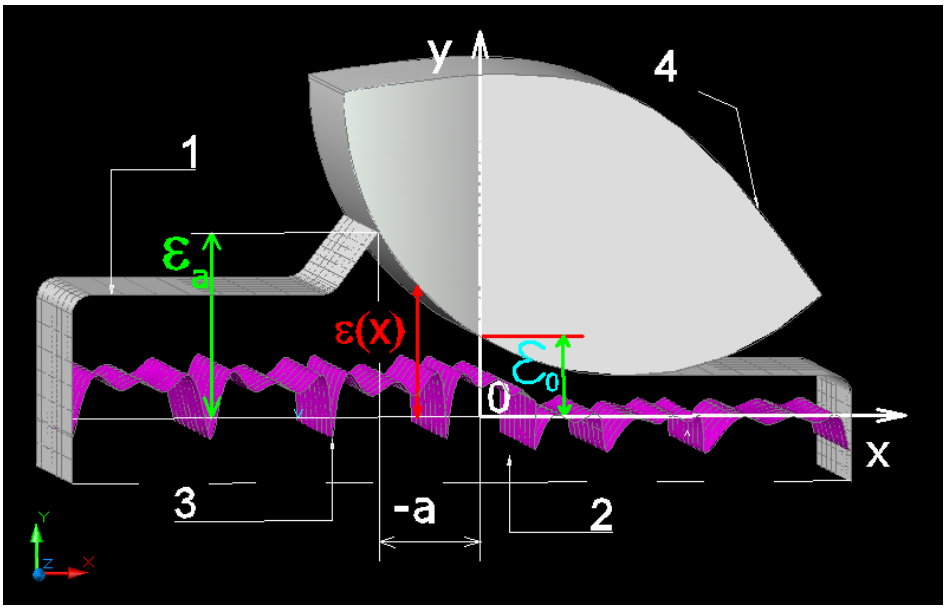
$$\delta(x) = \tfrac{4}{\pi}\left(\sin x + \tfrac{1}{3}\sin 3x + \tfrac{1}{5}\sin 5x\right)R_z \tag{8}$$

Njezin graf modeliran[1] je u AutoCAD-u i daje se na **slici 3**. ukupne dužine 32 **μm.**



Slika 3.Odabrani teorijski model poprečne hrapavosti trake

[1] Teorijska istraživanja i drugih autora daju prednost približno ovakvoj konfiguraciji hrapavosti trake



Slika 4.Profil hrapavosti pročavan u ovome radu (3D pogled)

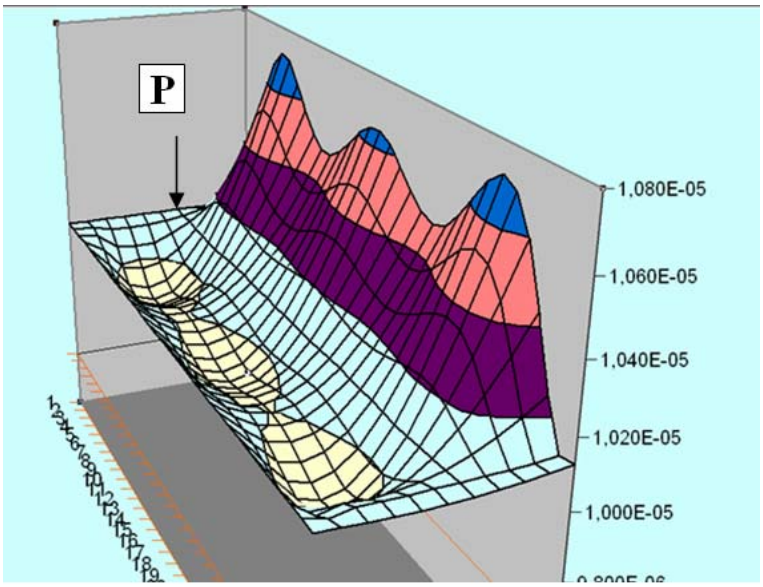
ε_0 - visina maziva na ulaznom presijeku zone deformacije

ε_a- visina maziva na traci ispred valjaka

a - dužina mazivoga klina

2.DISKUSIJA REZULTATA

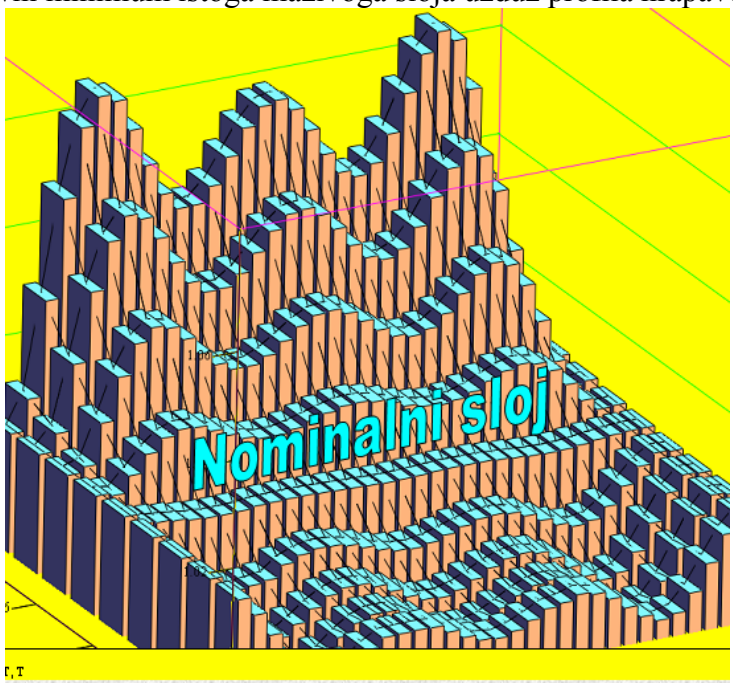
Proračun mazivoga sloja dijagramski je urađen u Excelu i dan je na **slici 5** u 10 klasa hrapavosti uzduž profila hrapavosti na **slici 3**. podijeljen u 32 klase.



Slika 5.3D-prikaz mazivoga sloja modeliran preko diferencijalne jednadžbe(6) na aplikati; apscisa sadrži 10 razreda hrapavosti [0-10**μm**] uzimajući u obzir i hrapavost kada $\mathbf{R_z}\rightarrow 0$.Ordinata sadrži 32 klase razreda dužine 32 **μm.**

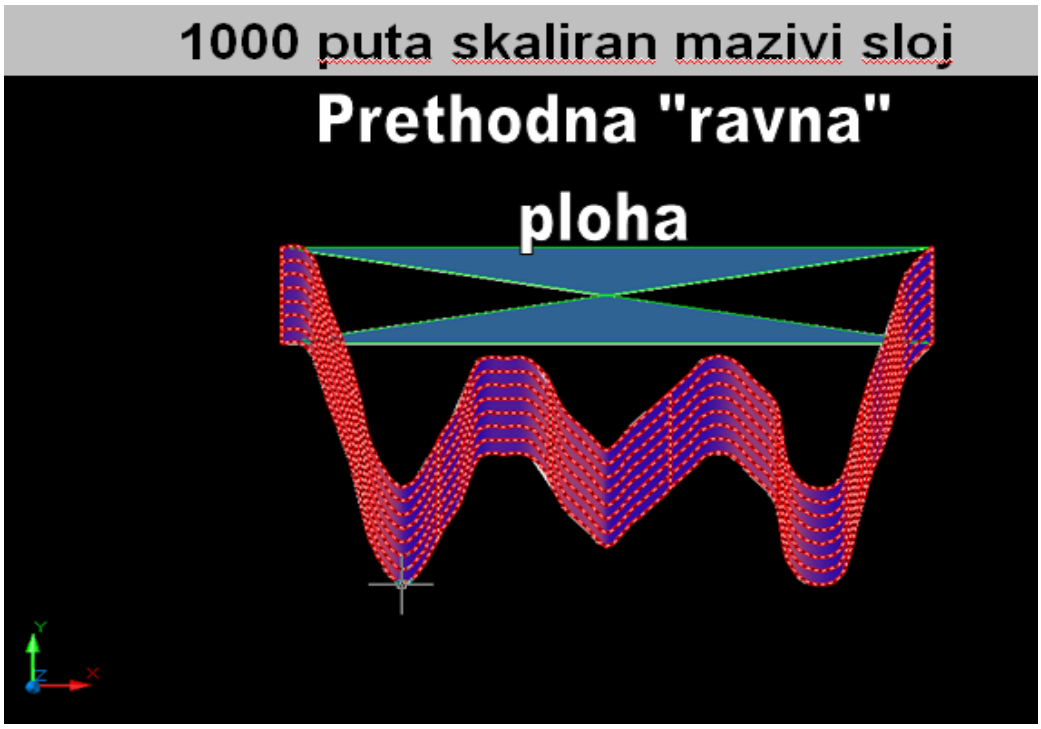
Isti prikaz predstavlja se i histogramski u MathCADProfessional-u na **slici 6** .Prva klasa Rz→0 nije ucrtana radi bolje preglednosti.Na istoj slici primjećujemo inverziju grafa.Tamo gdje mazivi sloj za veće razrede hrapavosti od nominalnoga sloja, koji nosi približno 6. razred hrapavosti(na prelazu sa 6 na 7 razred hrapavosti primjećujemo ravnu crtu **slike 5**. odnosno

ravnu stepenicu u histogramu **slike 6**) , ima relativni maksimum, ispod nominalne visine javlja se relativni minimum istoga mazivoga sloja uzduž profila hrapavosti trake.



Slika 6.Zakrenuti histogramski prikaz matematičkih izračunavanja istih podataka mazivoga sloja kao i na **slici 5**.Nominalni sloj predstavlja 6 klasu hrapavosti i prividno djeluje kao ″ravna″ ploha.

Prethodna ″ravna″ ploha (pravac strelice **P** na **slici 5**.) nominalnoga sloja sa **slike 6**. zumirana u incrementu promjenljivih dekada[2] 1000 puta u AutoCAD-u daje se na **slici 7** .



Slika 7.Nano mazivi sloj u incrementu prati profil teorijski postavljene poprečne hrapavosti trake(8) , odnosno mazivi sloj je determiniran sa profilom hrapavosti.

[2] Točnost numeričke integracije je na 8 znamenki.

Slika 7. prikazuje kongruenciju nomimalnoga mazivoga sloja sa profilom hrapavosti,gdje su i drugi autori dobili slične rezultate također obrađujući sinusnu hrapavost trake nešto jednostavnijega oblika od **slike 3** [7-10] i funkcije (8).

U **tablici 1**.daju se uobičajene karakteristike geometrijskih , reoloških i kinematičkih karakteristika procesa u teorijskim istraživanjima prema rusko-ukrajinskim autorima.
Tablica 1.Uobičajene karakteristike maziva za teorijska izračunavanja

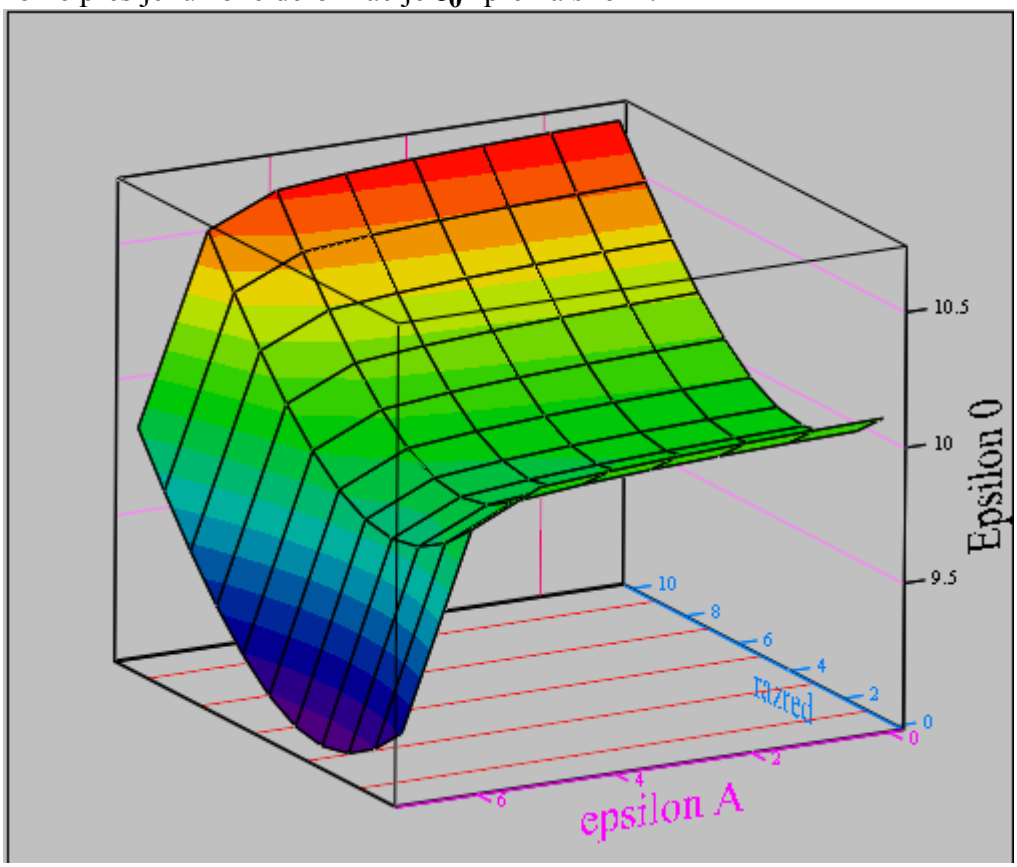
Parametar	Vrijednost	Jedinica
γ-piezokoeficijent viskoznosti	**2,18E-7**	**Pa^{-1}**
p_0-pritisak valjanja	**20E6**	**Pa**
v_R-obodna brzina gibanja valjaka	**10**	**m/s**
V_0-brzina trake	**6**	**m/s**
R-radijus valjaka	**0,35 (0,25)**	**m**
μ_0-dinamička viskoznost maziva $\mu=\mu_0 \exp(\gamma * p_0)$ **Formula Barussa**	**0,024-0.048**	**Pas**
α-kut zahvata	**0-0,02**	**rad**
ε_a-visina maziva na traci	**0,001-0,00001**	**m**
A-tehnološki parametar	**1965512 (3934525)**	**m^{-1}**
$A=(1-\exp(-\gamma * p_0)/6\mu_0\gamma(v_0+v_R))$		
$R_z \approx 6\delta$	**$R_z = (1 – 10)\ \mu m$**	**μm**

U **tablici 2**.predstavljene su karakteristike emulzije[11] koja se koristi kod hladnoga valjanja.
Tablica 2. Kakvoća emulzije

Pokazatelji kakvoće emulsije EFIROL (TU 0258-114-05015182-2002)	
Bazno naprezanje trenja MPA	26-29
Kinematička viskoznost pri 50 ^{0}C , mm^2/s	< 150
Kiselinski broj, mg KOH/g	< 20
Broj sapunske koncentracije , mg KOH/ g	>12
Težinski udio vode u koncentratu , %	< 5
Gustoća pri 20^0 C , kg/ m^3	860-990
Stabilnost 3-% emulsije	Treba izdržati ispitivanja
pH 3-% emulsije	7,5-9,5
Sklonost stvaranju pjene 3-% emulsija ,cm^3	< 120
Stabilnost pjene 3-% emulsije , cm^3	
Ne više od 2 minute	**40**
Ne više od 5 minuta	**30**
Korozijska agresivnost 3-% emulsije	U granicama ispitivanja

Efekti maziva su dobro poznati u praktičnim primjenama [12-13], od dobivanja čistije i sjajnije površine metala do ekonomskih ušteda u energiji.Maziva danas podržavaju masovnu produkciju u valjarstvu.

Na **slici 8**.daje se grafički prikaz analize utjecaja visine maziva na traci ε_a na visinu maziva na ulaznome presijeku zone deformacije ε_0 prema **slici 4**.



Slika 8.Utjecaj ε_a na ε_0 crtano u MathCADProfessionalu.

Epsilon A (ε_a) u granicama [0.001-0.0001 m]
Razred hrapavosti u granicama [(0.0 – 10) incrementa 2] **Rz** = 0.000010 m
Epsilon 0 (ε_0) u granicama [9 – 10.8] μm
Kut α = 0,02 rad

Rješenja diferencijalne jednadžbe (6) za slučaj **slike 8**. djelomično se prikazuju u **tablici 3**.
Tablica 3.Izlazni rezultati u programu MATHEMATICA mazivoga sloja u **μm.**

T :=

	0	1	2	3	4	5	6	7
0	10.102	10.095	10.087	10.075	10.059	10.039	9.92	9.207
1	10.003	9.996	9.988	9.976	9.959	9.934	9.819	9.099
2	9.941	9.935	9.926	9.914	9.898	9.872	9.757	9.031
3	9.92	9.914	9.905	9.893	9.876	9.851	9.735	9.008
4	9.94	9.933	9.925	9.913	9.896	9.87	9.755	9.03
5	9.998	9.991	9.983	9.971	9.954	9.929	9.814	9.093
6	10.09	10.083	10.075	10.063	10.046	10.021	9.907	9.193
7	10.21	10.204	10.195	10.184	10.167	10.143	10.03	9.322
8	10.354	10.348	10.339	10.328	10.312	10.287	10.175	9.475
9	10.517	10.51	10.502	10.491	10.474	10.45	10.339	9.645
10	10.693	10.686	10.678	10.667	10.651	10.627	10.517	9.828

Promatrana hrapavost je u 10 razreda dok je hrapavost profila trake podijeljena u 32 razreda. Primjećujemo da sa opadanjem visine maziva na traci principijelno opada i visina maziva na ulaznome presijeku zone deformacije metala.Kako je pokazano u radu [14] mazivi klin u tome slučaju posjeduje optimalnu geometriju koja može dovesti do ekonomskih ušteda maziva u tehnologiji plastične preradbe metala.

Numerička integracija diferencijalne jednadžbe (6), kontrolirana je preko približnih analitičkih riješenja do kojih se moglo doći da bi imala praktični interes.Ona su sadržana u formulama (9) i (11).Formula (9) predstavlja najjednostavniji oblik analitičkoga riješenja koja ne uzima u obzir visinu mazivoga sloja na traci, $\varepsilon_a >> \varepsilon_0$. Formula (11) otklanja taj nedostatak uz vidnu kompliciranost koju posjeduje.

$$315AR^3\alpha^7 - 168R^2\alpha^4 - 1824\delta^2 = 0$$

$$\varepsilon_0 = 0.5R\alpha^2 \ldots A = \frac{1-\exp(-\gamma p_0)}{6\mu\gamma(v_0+v_R)} \qquad (9)$$

$$\mathbf{W1} = A - \left[\frac{4}{3\cdot\alpha^3\cdot R} - 4\cdot\frac{R^2}{3\left[R\sqrt{1-\left(\cos(\alpha)-\frac{\varepsilon_a}{R}+\frac{\varepsilon_0}{R}\right)^2} - R\cdot(\sin(\alpha)-\alpha)\right]^3}\right] \qquad (10a)$$

$$\mathbf{-W2} = 3\cdot\delta^2\cdot\left[\frac{16}{7\cdot\alpha^7\cdot R^3} - 16\cdot\frac{R^4}{7\left[R\sqrt{1-\left(\cos(\alpha)-\frac{\varepsilon_a}{R}+\frac{\varepsilon_0}{R}\right)^2} - R\cdot(\sin(\alpha)-\alpha)\right]^7}\right] \qquad (10b)$$

$$\mathbf{W3} = \frac{(\varepsilon_0)^3 + 3\cdot\varepsilon_0\cdot\delta^2}{(\varepsilon_0)^2 + 6\cdot\delta^2} \qquad (10c)$$

$$\mathbf{W4} = \frac{8}{5\cdot\alpha^5\cdot R^2} - 8\cdot\frac{R^3}{5\left[R\sqrt{1-\left(\cos(\alpha)-\frac{\varepsilon_a}{R}+\frac{\varepsilon_0}{R}\right)^2} - R\cdot(\sin(\alpha)-\alpha)\right]^5} \qquad (10d)$$

$$\mathbf{-W5} = 32\cdot\frac{R^5}{9\left[R\sqrt{1-\left(\cos(\alpha)-\frac{\varepsilon_a}{R}+\frac{\varepsilon_0}{R}\right)^2} - R\cdot(\sin(\alpha)-\alpha)\right]^9} \qquad (10e)$$

$$\mathbf{W1+W2+W3*(\ W4 + W5) = 0} \qquad (11)$$

Tablica 4. donosi usporedbu numeričke metode i približnih analitičkih riješenja.

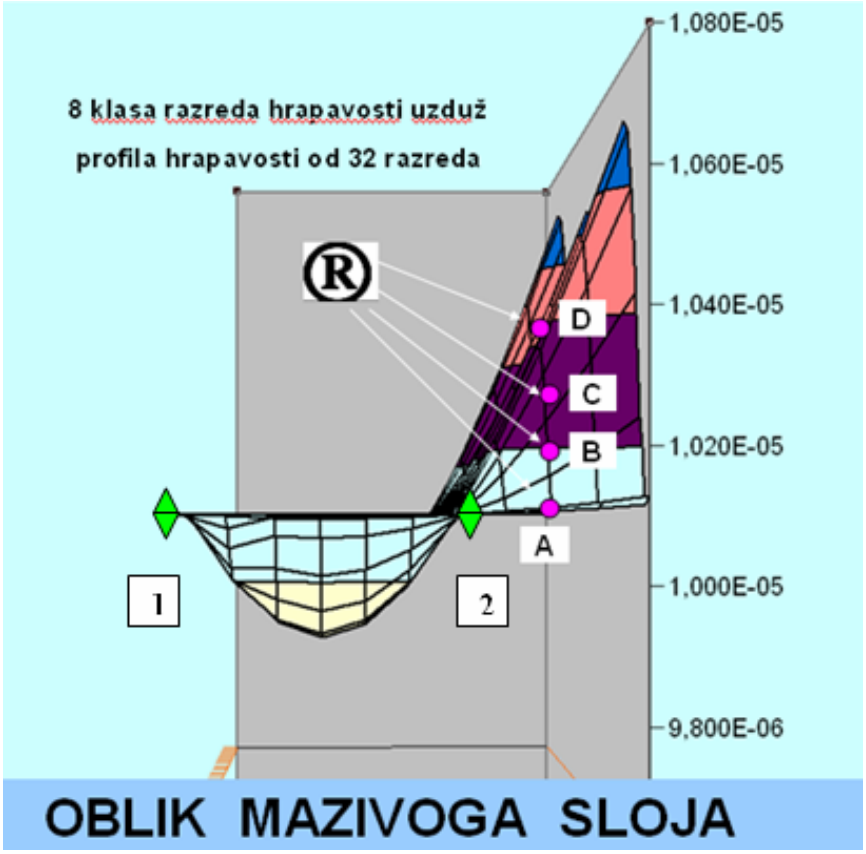
Tablica 4.Usporedba približnoga analitičkoga rješenja i numeričke metode Monte-Carlo u jednoj točki prolaza kroz graf.

Uvjeti primjera	Približna analitička rješenja (11) i (9)	Metoda Monte-Carlo dif.jed. (6)
x = 0 (ishodišni profil hrapavosti) $R_Z = 1$ μm $R_Z \approx 6\ \delta$ $\alpha = 0.00918759$ rad $A = 1965512\ m^{-1}$ R = 0.35 m	**$\varepsilon_a = 0{,}001$ m** **$\varepsilon_0 = 14{,}721$ μm (11)**	**$\varepsilon_a = 0{,}001$ m** **$\varepsilon_0 = 14{,}772$ μm**
	$\varepsilon_0 = 14{,}771$ μm (9)	
	$\varepsilon_a = 0{,}0001$ m **$\varepsilon_0 = 13{,}834$ μm (11)**	**$\varepsilon_a = 0{,}0001$ m** **$\varepsilon_0 = 13{,}761$ μm**
x = 0 (ishodišni profil hrapavosti) $R_Z = 10$ μm $R_Z \approx 6\ \delta$ $\alpha = 0.0092867$ rad $A = 1965512\ m^{-1}$ R = 0.35 m	**$\varepsilon_a = 0{,}001$ m** **$\varepsilon_0 = 15{,}024$ μm (11)**	**$\varepsilon_a = 0{,}001$ m** **$\varepsilon_0 = 15{,}077$ μm**
	$\varepsilon_0 = 15{,}092$ μm (9)	
	$\varepsilon_a = 0{,}0001$ m **$\varepsilon_0 = 13{,}511$ μm (11)**	**$\varepsilon_a = 0{,}0001$ m** **$\varepsilon_0 = 13{,}429$ μm**
x = 0 (ishodišni profil hrapavosti) $R_Z = 10$ μm $R_Z \approx 6\ \delta$ $\alpha = 0.00840867$ rad $A = 3934525\ m^{-1}$ R = 0.25 m	**$\varepsilon_a = 0{,}001$ m** **$\varepsilon_0 = 8{,}776$ μm (11)**	**$\varepsilon_a = 0{,}001$ m** **$\varepsilon_0 = 8{,}755$ μm**
	$\varepsilon_0 = 8{,}838$ μm (9)	
	$\varepsilon_a = 0{,}0001$ m **$\varepsilon_0 = 8{,}464$ μm (11)**	**$\varepsilon_a = 0{,}0001$ m** **$\varepsilon_0 = 8{,}429$ μm**

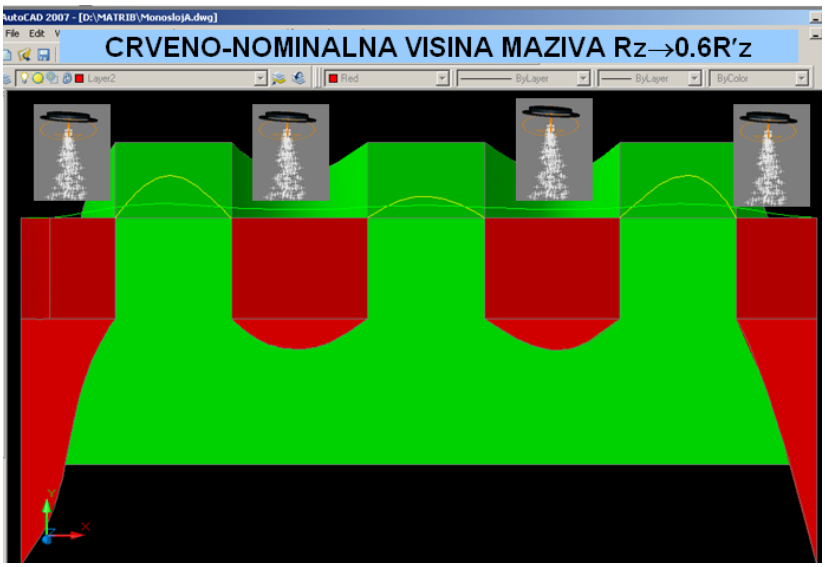
Vidljivo je u **tablici 4**. da jednostavniji analitički zapis formule (9) koji je iznuđen brojnim aproksimacijama dobro opisuje mazivi sloj za slučaj suviška maziva na traci ispred valjaka.

3.Modeliranje mazivoga sloja u području trenja nedovoljno okvašenih površina

U nizu slikovitih prikaza predstavlja se oblik mazivoga sloja u području trenja nedovoljno okavašenih površina gdje je inače i manji utjecaj hrapavosti površina na mazivi film.Krenimo od **slike 9**.Proračuni su uzeti iz 8 klase razreda hrapavosti.Sa ® je označen polažaj kamere koja će snimati sa frontalne strane mazivi sloj i slati snimke od **slike 10** do **slike 14**.



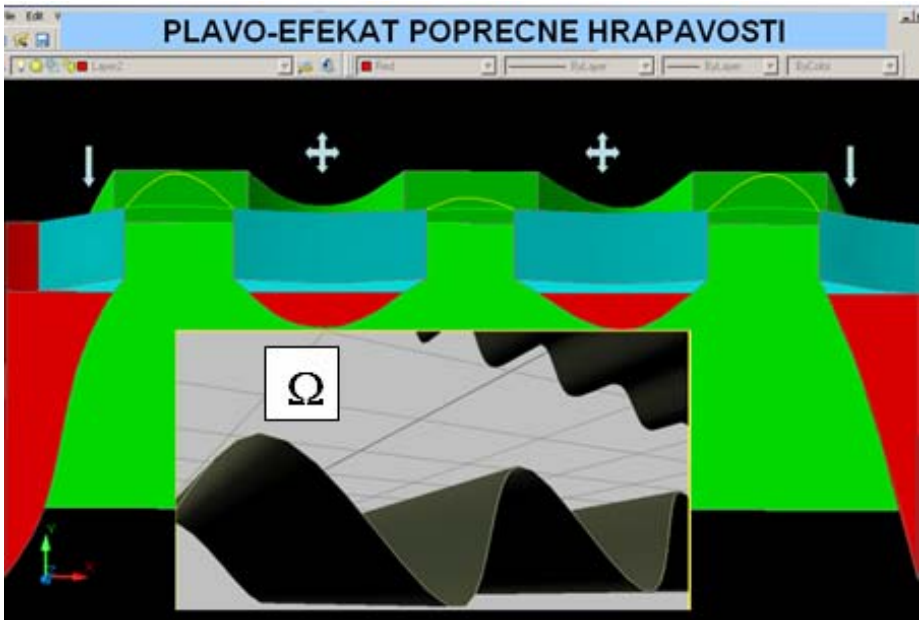
Slika 9.prikaz sa boka **slike 5**. gdje žuti dio koša proizlazi kao rezultat modeliranja mazivoga klina u području [-a ; 0] **,** gdje mala hrapavost trake osigurava stabilno podmazivanje, dok hrapavost površine forsira[3] takvi oblik(″pamti″) mazivoga sloja što je već pokazano na **slici 7**.



Slika 10. Pogled ®-**A.** (**slika 9**.)

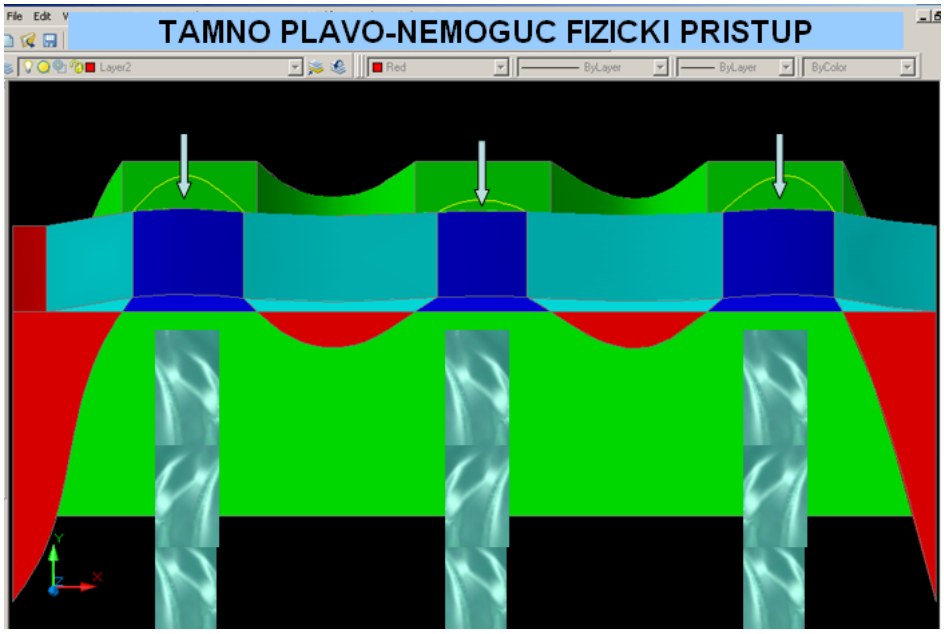
Visina mazivoga sloja (točka **2** na **slici 9**. teži obliku mazivoga sloja za $R_z \rightarrow 0$, točka **1** na istoj slici) može sa crvenim slojem da popuni teorijski promatranu hrapavost.To je prividna ″ravna″ površina u mikro području (visine ε_0 **= 1,014 E-5 m)** na **slici 10**. slična nominalnoj visini jer $R_z \rightarrow 0$.

[3] Površinski sloj hrapavosti trake determinira mazivi sloj sličnoga oblika.



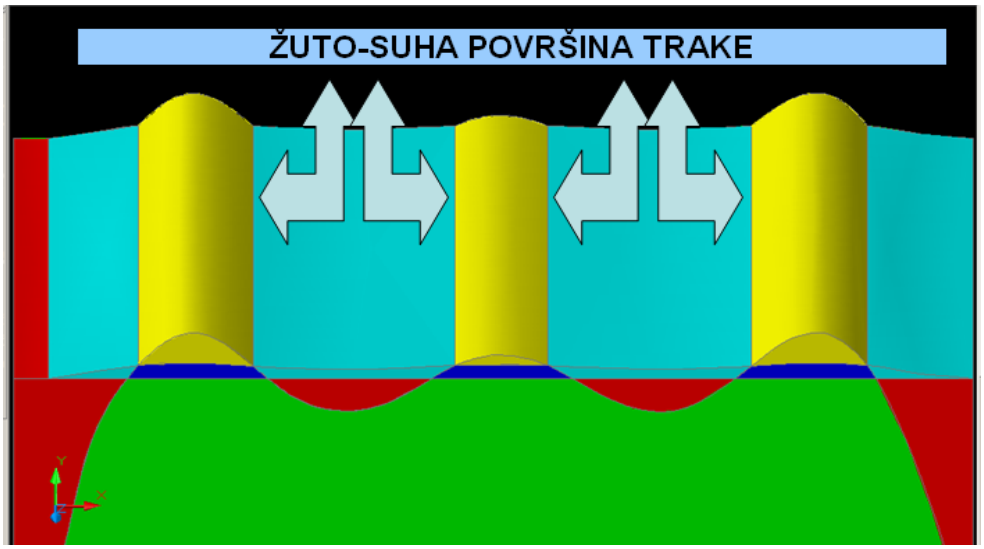
Slika 11. Pogled ®-**B.** (**slika 9**.)

S plavom bojom označen je pozitivni utjecaj poprečne hrapavosti površine trake koja uvlači u zonu deformacije više maziva nego za slučaj glatkih površina trake i valjaka **slika 11** što se može pripisati i "tunel efektu" na slici 3..Ovaj sloj reprezentativno nije veliki jer su izostala razmatranja istoga efekta kojega bi nadopunili valjci sa svojom hrapavosti i sa većom kinematikom od kinematike trake što ilustrira dopunska slika unutar **slike 11** a predstavljeno je u **tablici 5**.



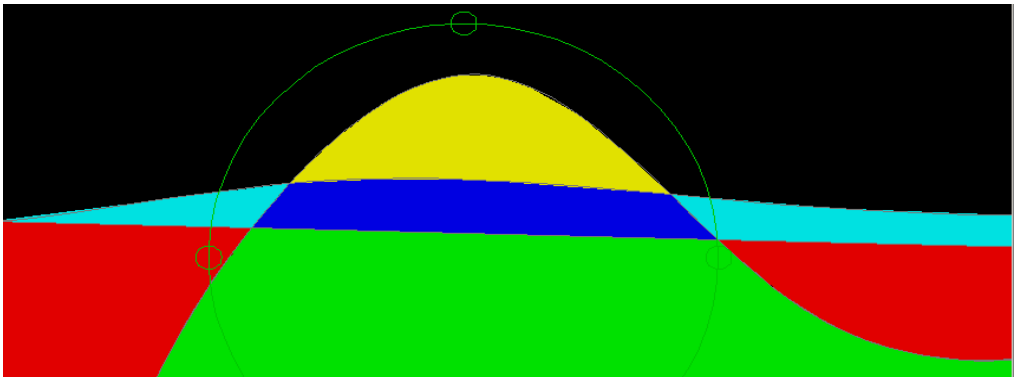
Slika 12. Pogled ®-**C** (**slika 9**.) ..R_Z= 8 μm

S tamno plavom bojom označen je čvrsti (solid) dio hrapavosti trake koje mazivo nije u mogućnosti da fizički popuni **slika 12**..U toj interakciji maziva i trake , mazivo ima tendenciju povećanja visine što je bliži dodir sa čvrstim tijelom trake.Zelena boja označava hrapavost trake.



Slika 13. Pogled **®-D.** (slika 9.)

Na **slici 13**. predstavljena je žuta[4] površina trake koja izranja kao ″neokvašena″ na ulaznome presjeku zone deformacije , odnosno mazivi sloj nema mogućnosti da je prekrije , jer su tako diktirani ; geometrijski , reološki i kinematički faktori proračuna.



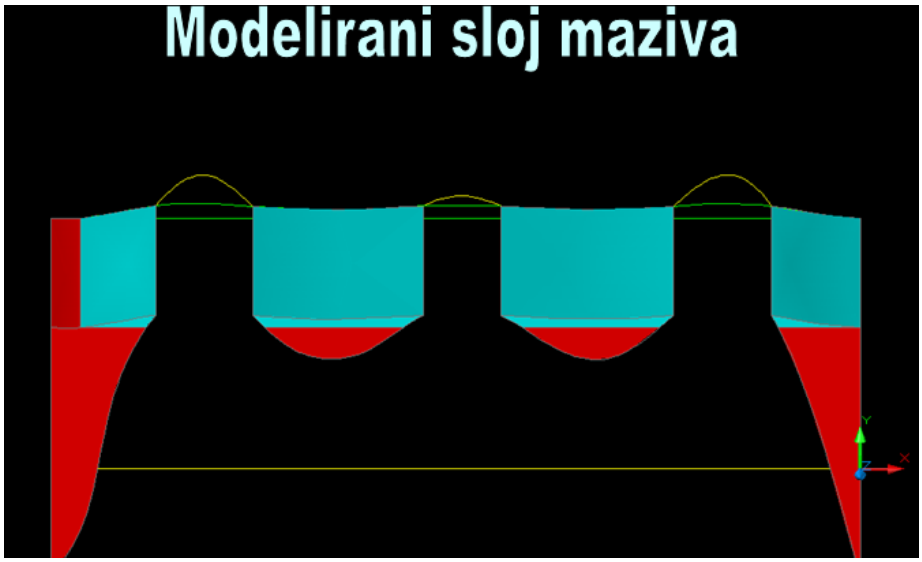
Slika 14.Zumirani prikaz lijevoga pika hrapavosti trake,uzduž nosećega profila hrapavosti podijeljenoga u 32 razreda pri numaričkim izračunavanjima duljine 32 μm.

Slika 14. jasno pokazuje kongruentnost mazivoga sloja sa konfiguracijom hrapavosti trake što je već ilustrirano na **slici 7**. i pojašnjava ″dubinu koša″na **slici 9**.U **tablici 5**. donosi se utjecaj hrapavosti valjaka ukazan na **slici 11**.područja **Ω.** u prolaznoj točki **tablice 4**.

Tablica 5. Utjecaj obostrane hrapavosti trake i valjka, kongruentno, na ε_0

	Metoda Monte-Carlo	
x = 0 (ishodišni profil hrapavosti) R_Z = 10 μm , hrapavost trake popr. R_Z = 8 μm,uzdužna hrapavost valjka $R_Z \approx 6\,\delta$ (GOST 2789-73) α = 0.00840867 rad A = 3934525 m^{-1} R = 0.25 m	**Jednostrana hrapavost trake** **ε_a = 0,0001 m** **ε_0 = 8,429 μm**	**Obostrana hrapavost trake i valjka** **ε_a = 0,0001 m** **ε_0 = 8,919 μm**
	$R_Z \rightarrow 0$ **ε_0 = 7,877 μm** **ε_a = 0,0001 m**	

[4] Po matematičkom proračunu ne mogu tri žuta pika da se prekriju mazivim slojem, visine ε_0.



Slika 15.Modelirani mazivi sloj izvučen Boolovom algebrom sa **slike 13**.

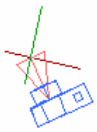
4.ZAKLJUČAK

Teorijska istraživanja utjecaja porečne hrapavosti trake na procese dresiranja s mazivima donese sledeće napomene;

- Poprečna hrapavost trake ima neku kritičnu veličinu kada počinje pozitivno da djeluje na mazivi sloj , povećavajući ga , u odnosu na glatke površine.Teorijsko objašnjenje je u činjenici da hrapavost površine determinira formu mazivoga sloja za bilo koji R_Z .
- Ako se poprečnoj hrapavosti trake doda kongruentna hrapavost valjka ,to jest uzdužna hrapavost valjka , visina mazivoga sloja na ulaznom presijeku zone deformacije trake će porasti.
- Izvedena približna analitička rješenja pokazuju sukladnost sa numeričkim integracijama diferencijalne jednadžbe (6) i osiguravaju sigurniju pristup analizi.
- Snažnim alatima Auto-CAD-a izvršena su modeliranja rješenja dobivenih u matematičkim programima gdje je pokazano da modelirani mazivi sloj prati teorijski model hrapavosti površine , što je u skladu i sa sličnim istraživanjima drugih autora u svijetu.
- Kada bi tehnološki proces vodili sa nominalnom visinom mazivoga sloja imali bi najbolju ritmičnost valjaka.To podrazumjeva i određenu hrapavost trake i valjaka.

5.Popis simbola i pojašnjenja slika

Simbol	Jedinica	Napomena
ε_0	m,(**μm**)	Visina maziva na ulaznom presjeku zone deformacije (slika 1)
$\varepsilon(x)$	m	Visina mazivoga sloja u području [-a : 0] , slike 1., formula (4).
ε_a	m	Visina maziva na trnu ispred ulaznoga presjeka zone deformacije
a	m	Dužina mazivoga klina (slika 1.) , formula (5).
α	rad	Kut dresiranja trake
v_R	m/s	Obodna brzina valjaka
v_T	m/s	Brzina gibanja trna
R	m	Radijus valjaka
R_Z	m	Oznaka hrapavosti površine trake
δ^2		Disperzija hrapavosti trake (i valjaka za **tablicu 5**.)
δ_X		Slučajna visina maziva uvjetovana hrapavosti trake (i valjaka)

< >		Operator matematičke nade
x , y		Koordinate Decartesovog sustava
Q(x)	-	Volumna potrošnja maziva (po perimetru trake)
μ_0	Pa s	Dinamička viskoznost maziva pri pritisku valjanja
μ	Pa s	Dinamička viskoznost maziva pri atmosferskom tlaku
u	m/s	Brzina gibanja maziva uzduž apscise
γ	m^2/N	Piezokoeficijent viskoznosti maziva
p	Pa	Tlak valjanja
Q	m^2/s	Potrošnja maziva po perimetru trna –jednodimenzijski model
dp/dx	Pa/m	Gradijent tlaka u mazivome sloju , formula (2)
sinα...	rad...	Oznaka trigonometrijske funkcije za zahvatni kut alfa
®		Oznake za točke motrišta kamera AutoCAD-a na slici 9.
H	M	Visina ulazne trake
h	m	Visina izlazne trake
>>, ≈ ^{0}C i % →, ^ mg i g	-	mnogo veće , približno oznaka stupnja temperature i oznaka za postosak (**tablica 2**.) teži , znak za potenciju oznaka za masu(miligrami i grami) u **tablici 2**.
A	m^{-1}	Tehnološki parametar: $A= [1- \exp(-\gamma p)] / [6\mu_0\gamma(v_C + v_T)]$
exp,π [14] **µm**	2.718... 1-14 10^ -6	Baza prirodnoga logaritma , (3.141...) Oznaka za reference Oznaka za mikrometar

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WEIBULL ANALYSIS OF FLEXURAL STRENGTH OF COLD ISOSTATICALLY PRESSED ALUMINA CERAMICS

WEIBULLOVA ANALIZA SAVOJNE ČVRSTOĆE HLADNO IZOSTATIČKI OBLIKOVANE ALUMINIJ OKSIDNE KERAMIKE

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Izvorni znanstveni rad / Original scientific paper

Abstract:
Flexural strength, σ_{fs}, of cold isostatically pressed alumina ceramics, (CIP)-Al_2O_3, with a purity of 99.8 % was determined by the three - point bend test. The flexural strength was found to range from 266.7 to 372.2 MPa. It is well known that the measured fracture of brittle ceramics shows large variability. Therefore, the probabilistic characteristics of the flexural strength were analysed by a two-parameter Weibull distribution function, with a scale parameter, σ_0, and the Weibull modulus, m. These parameters were determined by the linear regression method for σ_{fs} data measured. It was found that the measured flexural strength, σ_{fs}, of alumina ceramics follows the Weibull distribution.

Keywords: flexural strength, alumina ceramics, Weibull distribution

Sažetak:

Savojna čvrstoća, σ_{fs}, hladno izostatički prešane aluminij oksidne keramike, (CIP)-Al_2O_3, čistoće 99,8% određena je metodom u tri točke i iznosi 220,1 do 308,6 MPa. Poznato je da podaci prilikom mjerenja loma krhke keramike pokazuju veliko rasipanje, stoga su karakteristike vjerojatnosti savojne čvrstoće određene uz pomoć dvoparametarske Weibullove razdiobe, i to parametar skaliranja, σ_0, i parametar oblika, m. Ovi parametri savojne čvrstoće određeni su linearnom regresijom iz izmjerenih podataka. Izračunati podaci pokazuju da izmjerena savojna čvrstoća, σ_{fs}, slijedi Weibullovu razdiobu.

Ključne riječi: savojna čvrstoća, aluminij oksidna keramika, Weibullova razdioba

1. Introduction

Brittle materials, like ceramics have many useful properties like high hardness, stiffness (modulus of elasticity), wear resistance, high strength retention at elevated temperatures, corrosion resistance associated with chemical inertness etc. Moreover, their density is about half the one of steel so that the use in all technical applications is favourable, where the reduction of weight considerably diminishes the consumption of energy [1-3]. The major limitation of ceramics for structural and specific non-structural applications are the poor toughness and low strength reliability which leads to expensive test procedures for the characterization of the material and a more difficult design in construction. Therefore statistical analysis is indispensable for the mechanical characterization of ceramics materials. The Weibull distribution has been commonly used to describe the statistical variation in the flexural strength of brittle materials [4-6].

In the present work, the flexural strength data of cold isostatically pressed alumina ceramics, (CIP)-Al_2O_3, with a purity of 99.8 % was analyzed by a two-parameter Weibull distribution.

2. Experimental procedure

The experiments were performed on a cold isostatically pressed (CIP)-Al_2O_3 with a purity of 99.8 %, supplied by Applied Ceramics, Inc., Fremont, California, U.S.A.. The samples of alumina ceramics disk were sintered in gas furnace at 1650 °C. The Archimedes density of the CIP-Al_2O_3 was 3.91 g/cm^3. The chemical composition of investigated alumina ceramics, according to the manufacturer's declaration is shown in Table 1. Al_2O_3 ceramics contains MgO as a sintering aid and the usual impurities, i.e. SiO_2, CaO, Na_2O and Fe_2O_3.

Table 1. Chemical composition of the Al_2O_3 ceramics.

sample	wt. %					
	MgO	Fe_2O_3	SiO_2	Na_2O	CaO	Al_2O_3
alumina ceramics	0.066	0.015	0.02	0.05	0.013	rest

After sintering, alumina ceramics disk was cut into 33 rods. The test specimens (rods) were machined out of the alumina ceramics disks by a diamond core drill. Each rod has a radius of 5 mm and a length of 50 mm. After machining cylinders were thoroughly cleaned with alcohol in an ultrasound bath and dried in a sterilizer at 150 ± 5 ºC for 4 hours [7]. The specimens were than annealed at 1200 °C for 360 min in order to eliminate the residual stresses that may have appeared during machining. The roughness of samples was measured

by means of Perthometer S&P (Feinprut Perthen GmbH, Goettingen, Germany). The average roughness (R_a) of alumina ceramics is 1.2 μm. The flexural strength of alumina ceramics at room temperature was measured using a three-point bending test configuration (Figure 1) [8]. The three-point bending tests were done using a MESSPHYSIK testing machine (BETA 50-5) for loading and videoextensometer (NG version 5.15.3) for deflection measurement. The load applied and deflection of the sample were recorded simultaneously.

3. Results and discussion

3.1. Three -point bending test

Extremely low ductility of ceramic materials does not allow measuring their mechanical properties by conventional tensile test, which is widely used for metals. Brittle Materials, including ceramics, are tested by flexure test (transverse beam test, bending test). There are two standard Flexure Test methods: three-point test and four-point test. In three-point flexure test (Figure 1) a specimen with a round, rectangular or flat cross-section is placed on two parallel supporting pins. The loading force is applied in the middle by means of a loading pin. The supporting and loading pins are mounted in a way, allowing their free rotation about: axis parallel to the pin axis, axis parallel to the specimen axis. This configuration provides uniform loading of the specimen and prevents friction between the specimen and the supporting pins.

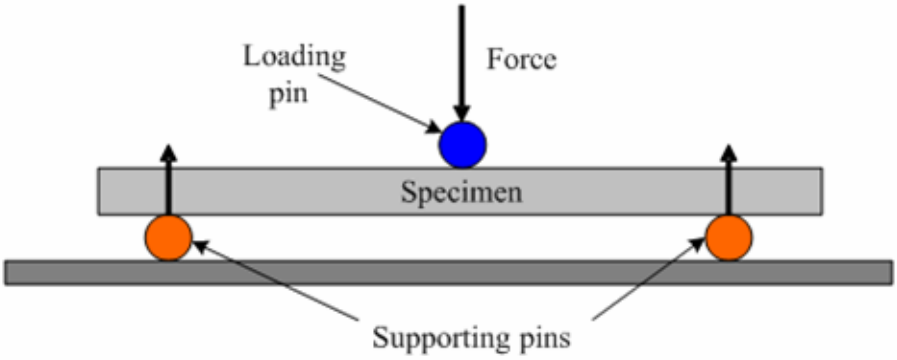

Figure 1. Three-point bending test [8]

The stress by the fracture, σ_{fs} using this test is called flexural strength (σ_{fs}), modulus of rupture (MOR), fracture strength or bend strength. For samples with round cross sections fracture strength is given by:

$$\sigma_{fs} = \text{MOR} = FL / \pi R^3 \quad (1)$$

Where

- F_f is the load at fracture in N,
- L is the distance between supporting pins in mm,
- R is the specimen radius in mm.

3.2. The Weibull distribution

The Weibull distribution has been used successfully to describe a wide range of problems including the mechanical properties of brittle materials and life time testing [4-6]. The two-parameter continuous probability density function for a strength variable s is given by:

$$P = \left(\frac{m}{\sigma_0}\right)\left(\frac{\sigma}{\sigma}\right)^{m-1} \left[\left(\frac{\sigma}{\sigma_0}\right)^{m}\right] \tag{2}$$

The density function is asymmetrical and will assume only positive values. The symbol m is the Weibull modulus and σ_0 is the scale parameter. The density function for m with values of 1, 4 and 10 is illustrated in Figure 2A.

The cumulative distribution function that gives the probability of failure P at a stress σ is expressed as:

$$P = \left[\left(\frac{\sigma}{\sigma_0}\right)^{m}\right] \tag{3}$$

where P is the probability of failure at stress σ, m and σ_0 are the Weibull modulus and scale parameter, respectively.

This function corresponds to the exponential function for m=1 and has a sigmoidal shape for m>1 (Figure 2B). The scale parameter σ_0 describing the stress level that causes failure in 63.2% of the specimens (P(σ_0)=1-1/e=0.632), m is the Weibull modulus which characterizes the fracture distribution width. The Weibull modulus or slope, m, is a measure of the materials homogeneity (scatter of flexural strength). A high value of m indicates a high degree of the homogeneity and a smaller scatter of the flexural strength (Figure 2).

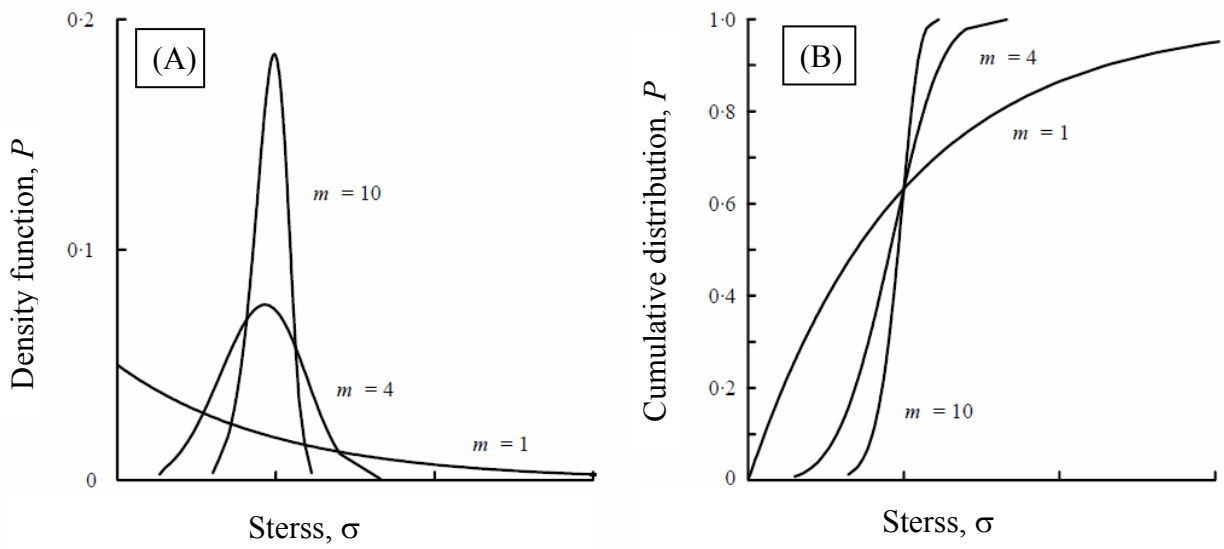

Figure 2. (A) The Weibull probability density function (equation 1) and (B) the cumulative distribution function (equation 2), for three values of the Weibull modulus m (1, 4, 10) at a constant scale parameter σ_0 [2].

3.3. Estimation of Weibull parameters

Several procedures have been proposed for the determination of Weibull parameters, such as: linear regression (the Weibull plot), weighted linear regression and maximum likelihood [9-12]. The Weibull plot (linear-regression method) is the most common and easiest way to obtain the Weibull parameters. The Weibull parameters are estimated by rearrange equation (2), taking the natural logarithms and expressing the cumulative distribution as a straight line and using linear regression to estimate the parameters. Rearrange equation (3) yields:

$$\ln \ln \left(\frac{1}{1 - P} \right) = m \ln \sigma - m \ln \sigma_0 \tag{4}$$

It can be seen that a straight line can be obtained by plotting $\ln \ln \left(\frac{1}{1 - P} \right)$ vs. ln σ. The slope is m and the intercept is m ln σ_0. Figure 3 shows the Weibull plot for the flexural strength of cold isostatically pressed alumina ceramics (CIP)-Al_2O_3 with values for parameters m of 16.6±1.06 and scale parameter σ_0 of 317 (R^2 = 0.8856). The scale parameter σ_0 is estimated from the intercept (m ln σ_0):

$$\sigma_0 = \exp\left(-\left(m \ln \sigma_0 \right) / m \right) \tag{5}$$

This is the stress when $P = 0.632$.

The data are fitted to equation (3) the Weibull cumulative distribution:

$$P = 1 - \exp\left[-\left(\frac{\sigma}{317}\right)^{16.6}\right] \quad (6)$$

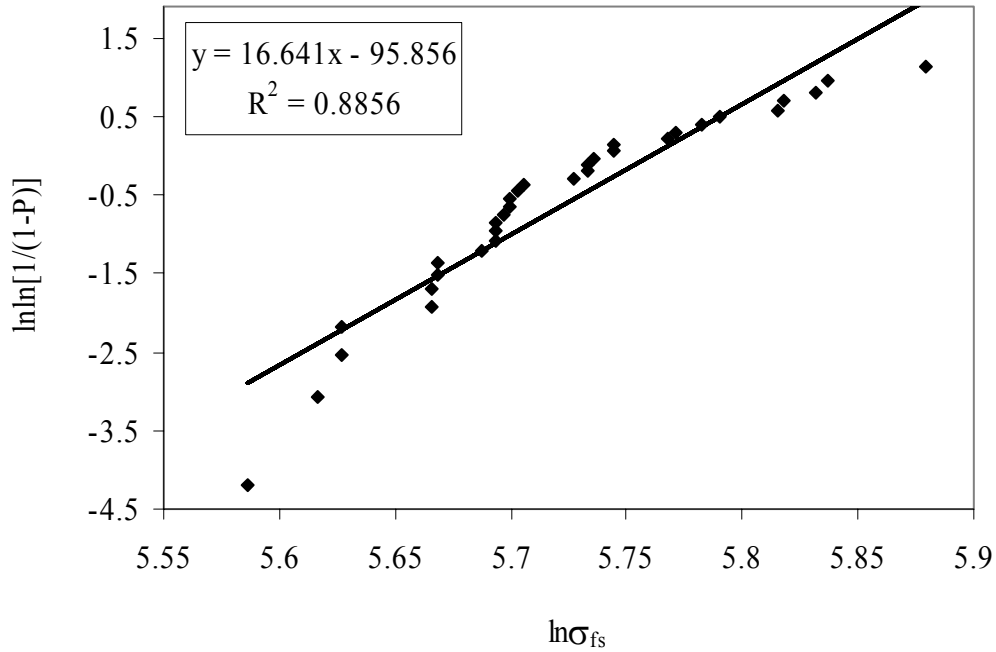

Figure 3. Weibull plots for the flexural strength of cold isostatically pressed alumina ceramics (CIP)-Al_2O_3). The Weibull modulus is equal to the slope of the regression line (*m*, 16.6±1.06) and the scale parameter σ_0 is estimated in equation (5), [exp (-(-95.856.5)/16.641)] = 317; R^2, coefficient of determination is 0.8856.

The cumulative probability of failure (*P*) is calculated using the following equation [9-12]:

$$P_i = \frac{i}{n} \quad (6)$$

where *i* is the rank and *n* is the total number of data. In this case *n* is the total number of data of measured fracture toughness. Other estimators such as $P_i = \frac{i}{n+}$; $P_i = \frac{i}{n+}$ and $P_i = \frac{i}{n+}$ have also been used [9-12].

4. Conclusions

The flexural strength of high purity alumina ceramics was determined by the three-point bend test. Measured values of flexural strength were in range from 266.7 to 372.2 MPa. It was found that a two-parameter Weibull distribution function may be employed to describe the statistical variability of the flexural strength measured by the three-point bend test. The

Weibull statistics has been widely used in the evaluation of the strength characteristics for brittle materials [5, 6]. The Weibull modulus of m = 16.6±1.06 and the scale parameter of σ_0 = 317 MPa were determined using linear regression analysis.

Acknowledgements

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PHOTOCATALYTIC COLOR REMOVAL OF REACTIVE CONGO RED DYE BY UV/NANO-TiO_2 PROCESS

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Izvorni znanstveni rad / Original scientific paper

Abstract:
Photooxidation with TiO_2 photocatalyst is a relatively new technique that can be used to remove various contaminants from water. In this investigation, the efficiency of color removal from aqueous diazo congo red dye solution has been investigated in TiO_2 nano-particles aqueous suspensions irradiated by artificial UV light. For this purpose, a series of batch photocatalytic tests were carried out with the same initial Congo red (CR) dye concentration by varying the amount of TiO_2 added and the irradiation time. The doses of TiO_2 were 0.25, 0.5 and 1.0 g/L. The wavelength of incident ultraviolet (UV) light for the photocatalytic oxidation was predominantly 254 nm. The decrease of CR concentration during photocatalytic decolorization was monitoring by means of UV-VIS spectrophotometer. It was observed that the degree of CR photodegradation increased as the dose of the photocatalyst increased with the best result achieved using a TiO_2 dose of 1.0 g/L.

Keywords: Photocatalytic oxidation, color removal; UV/TiO_2; Congo red dye

1. Introduction

Dyes are widely used in industries such as textile, rubber, paper, plastic, cosmetic etc. First usage of dyes belongs to textile industry for dyeing of textile materials. Dyes can be divided into several categories, based on their chemical nature: anionic or cationic and basic or reactive dyes. Azo dyes are the largest group of the synthetic colorants known and the most common group released in the environment. Wastewater containing dyes may be toxic, carcinogenic and even mutagenic and posses a serious hazard to aquatic living organisms [1]. Therefore, the removal of synthetic dyes with azo aromatic groups is extremely important. The removal methods of azo dyes can be divided into three groups: (i) physical methods (such as adsorption, nanofiltration, ion exchange, flocculation etc.), (ii) chemical methods (e.g. H_2O_2-UV radiation, NaClO, O_3, etc.) and (iii) biological degradation including aerobic and anaerobic degradation. Biodegradation processes are characterized by usually low degradation efficiency [2-9].

The development of new technologies for wastewater purification tends to reach complete destruction of the contaminants. Recently, advanced oxidation processes (AOPs) have been proposed as the alternative methods for water purification. Among AOPs, heterogeneous photocatalysis using TiO_2 as a photocatalyst is commonly used as destructive technology [10]. TiO_2 is widely used photocatalyst due to its stability during UV light exposure, high chemical resistance, non-toxicity and low cost. Titanium dioxide occurs in three crystalline polymorph forms: rutile (tetragonal), anatase (tetragonal) and brookite (orthorhombic). Rutile is known to be the most stable phase. Brookite and anatase are thermodynamically less stable than rutile. Generally, the TiO_2-based photocatalysts in anatase phase show usually best photocatalytic efficiency. The anatase phase can be transformed into the rutile phase at the temperatures above 800 °C.

Titanium dioxide can be used as a photocatalyst in various of applications, such as degradation of air pollutants (NO_x, aromates, chlorofluorocarbons) [5,11] and in the water purification processes, like degradation of various contaminants in waste water [12] or remediation of drinking [13] and surface water [14].

In this paper, photocatalytic color removal of aqueous solution of CR dye has been investigated using commercial form of titanium dioxide from Degussa (P-25). Degussa's P-25 product was identified in numerous of experiments as the best catalyst for heterogeneous photocatalytic oxidation of organic contaminants in water.

Congo red is used in medicine (as a biological stain) and as an indicator since it turns from red-brown (in basic medium) to blue in acidic one. It is also used to color textiles (initially cotton) and it could also be used as a gamma-ray dosimeter since its coloration decays with the intensity of the irradiation.

Congo red or the disodium salt of diphenyl diazo *bis*-1-naphthylaminesulphonic acid is brownish red powder having absorbance maxima between 497.0 and 500.0 nm in aqueous medium. It is water soluble (reactive) secondary diazo dye and contains an azo (-N=N-) chromophore and an acidic auxochrome (sulfonate: $-SO_3H$) (which, respectively, gives and reinforces the coloration) associated with the benzene structure (Fig. 1).

2. Experimental

2.1. Materials

Titanium dioxide (TiO_2) catalyst from Degussa (P-25), with purity 99.9 % was used as received, without further modification. It is mostly in the anatase form (75-80% anatase and 20-25% rutile), nonporous, with a reactive surface (BET) area of 50 to 54 m^2/g, corresponding to a mean particle size of around 30 nm [16, 17].
The structure of CR is illustrated in Fig. 1. Its molecular formula is $C_{32}H_{22}N_6Na_2O_6S_2$ and molecular weight 696.66 g/mol. Congo red (CR) was supplied by Acros, as high purity biological stain, and used as a model compound without further purification.

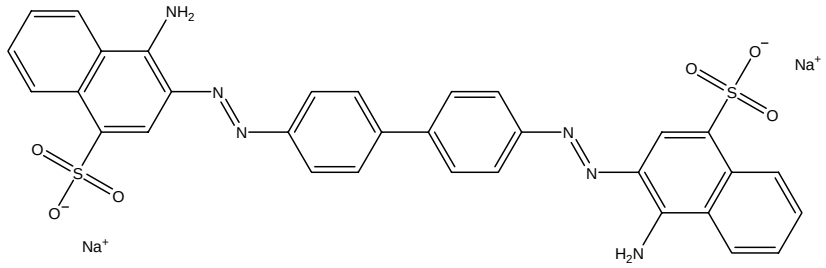

Figure 1. Molecular structure of Congo red dye.

2.2. Photocatalytic experiments

All experiments were carried out in a batch photoreactor (Figure 2) of 200 mL volume. The radiation source was mercury UV lamp, λ_{max} = 254 nm, model Pen-Ray 90-0012-01, manufactured by UVP. The removal of CR was investigated at the temperature (25±0.2) °C, with continuous purging with air (O_2) using three different conditions: (i) absorption in the dark (TiO_2 without UV), (ii) UV-irradiation (without TiO_2), and (iii) UV/TiO_2 by varying the amount of TiO_2. The reaction temperature was controlled by circulation of cooling water. The initial concentration of CR dye was 55 mg/L, concentrations of TiO_2 were 0.25, 0.5 and 1.0 g/L. The mixtures of aqueous solution of CR dye and TiO_2 nanoparticles were stirred with a magnetic stirrer at a constant speed of 300 rpm. Before turning on the UV lamp, the solution was placed in the dark, covered with aluminum foil, and kept stirring for 15 min to reach the adsorption equilibrium of the suspension. The samples were taken from the reactor for analysis at certain reaction intervals (60, 120, 240, 360 and 480 min), centrifuged (Sigma-Laborzentrifugen, Model 2-15) and remaining dye concentration was analyzed with UV-VIS spectrophotometer (HEWLETT PACKARD-8430) at 498 nm.

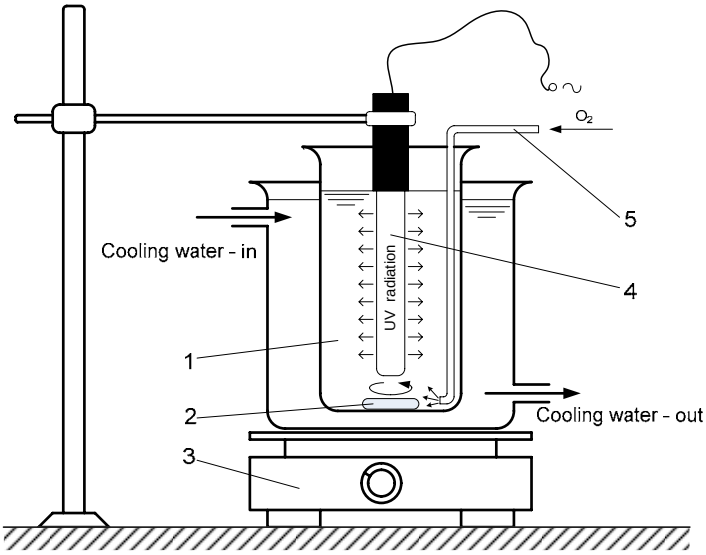

Figure 2. A batch photoreactor: 1 – reactor with examining solutions of CR dye, 2 – PTFE magnetic stir bar, 3 – magnetic stirrer, 4 – UV 254 nm mercury lamp, 5 – glass tube for bubbling the solution with compressed air (O_2).

3. Results and discussion

Figure 3 shows a time-dependent UV–VIS spectrum of 55 mg/L CR aqueous solution, as starting solution, during photocatalytic oxidation process. The spectrum of CR dye in the visible region has a maximum absorbance at 498 nm. Figure shows the change of absorbance spectrum of CR dye during the experiment with 1 g/L TiO_2, UV-irradiation and continuous O_2 purging. It is clear from this figure that absorption peaks has been decreasing under photocatalytic reaction, what implies that the CR dye is degraded. Almost complete degradation of CR dye was observed after 480 min. Experiments performed in the dark confirmed that the effects of adsorption of CR onto the TiO_2 nanoparticles catalysts were negligible in the overall color removal in comparison to photocatalytic oxidation process (Figure 4).

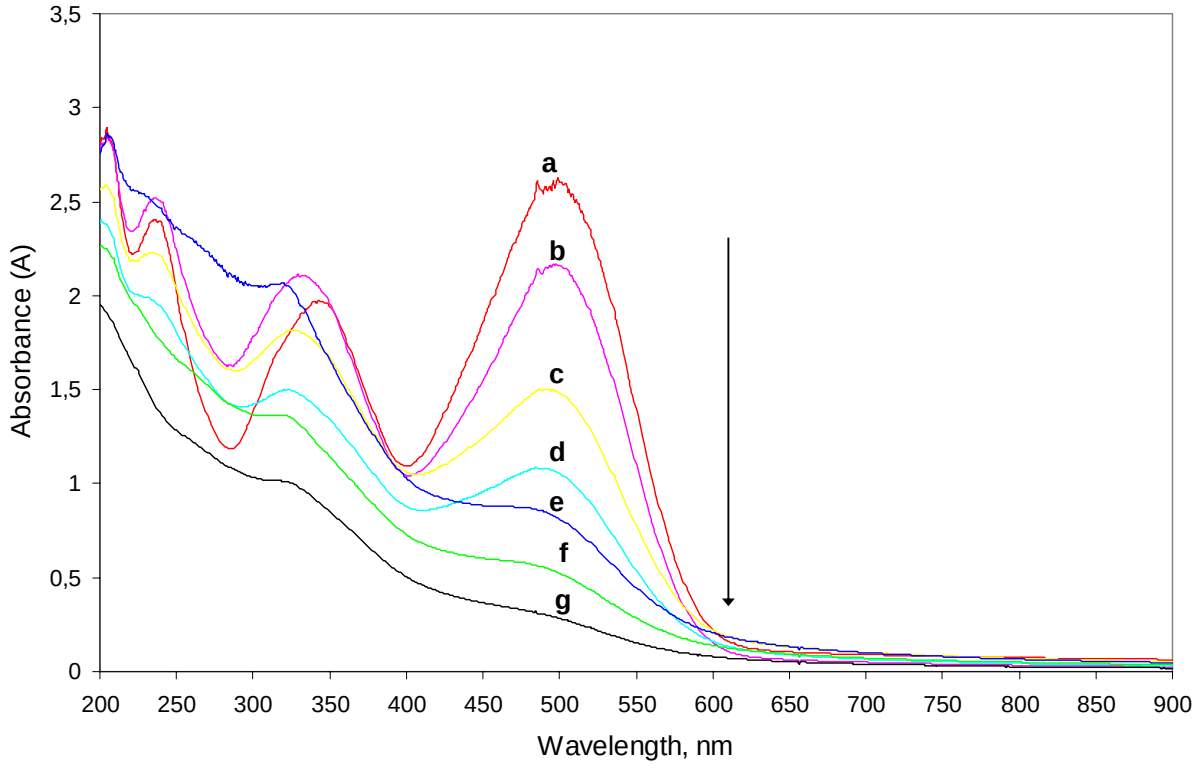

Figure 3. UV-VIS spectra of (a) 55 mg/L CR aqueous solution, (b) 15 minutes dark adsorption in the presence of 1 g/L TiO_2, ((c) – 60 min, (d) – 120 min, (e) – 240 min, (f) – 360 min and (g) – 480 min) in the presence of 1 g/L TiO_2 with UV-irradiation and continuous purging with air (O_2).

The degree of CR dye photodegradation (R) as a function of time is given by:

$$R = \frac{\gamma_0 - \gamma}{\gamma_0} \cdot 100,$$

where γ_0 and γ are the concentrations of CR dye at $t = 0$ and t, respectively.

The effects of amount of photocatalyst in suspension on the photodegradation of CR dye are shown in Figure 4. Obtained results indicate that amount of TiO_2 as well as duration of UV exposure influence the degree of CR dye photodegradation. The degree of photodegratation is increased with increased amount of TiO_2 and with irradiation time.

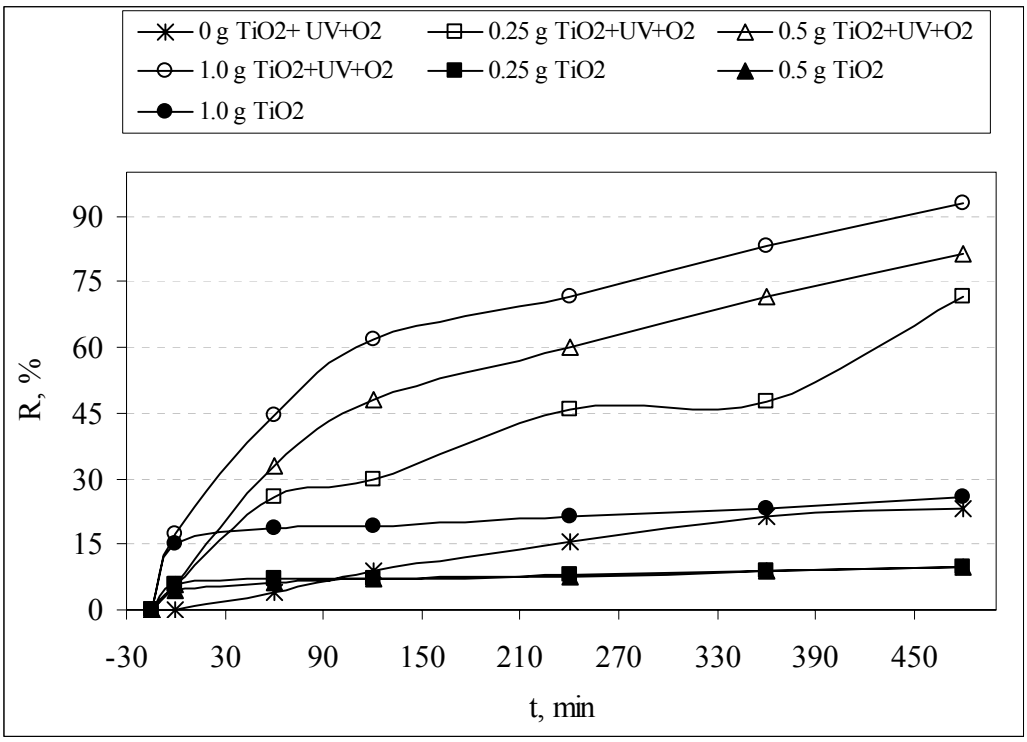

Figure 4. Influence of the UV exposure time on the degree of CR dye photodegradation for different experimental conditions. (Time marked as "-15" to time "0" means 15 minutes of mixing of the TiO_2 in dye solutions "in the dark" (e.g. UV lamp was switched off), and the time from 0 to 480 means that UV lamp was switched on).

The above results indicate that UV irradiation exposure of TiO_2 particles during 480 minutes continuously ensure degradation of CR dye. It is in accordance with the theoretical background that explains energetics of semiconductor photocatalysis: when TiO_2 is continuously illuminated by light $\lambda < 400$ nm, electrons are continuously promoted from the valence band to the conduction band to give electron-hole pairs, as could be seen in Figure 5. The valence band (h_{VB}) potential is positive enough to generate hydroxyl radicals at the surface, and the conduction band (e_{CB}) potential is negative enough to reduce molecular oxygen. The hydroxyl radical is a powerful oxidizing agent and attacks organic pollutants that are present at or near the surface of TiO_2. It causes photooxidation of the dye according to the following reactions [18-23]:

$$TiO_2 + h\nu \rightarrow TiO_2\left(e^-_{CB} + h^+_{VB}\right) \quad (1)$$

$$h^+_{VB} + H_2O_{ads} \rightarrow H^+ + {}^{\bullet}OH_{ads} \quad (2)$$

$$h^+_{VB} + OH^-_{ads} \rightarrow {}^{\bullet}OH_{ads} \quad (3)$$

$$e^-_{CB} + O_{2ads} \rightarrow {}^{\bullet}O^-_{ads} \quad (4)$$

$${}^{\bullet}OH_{ads} + \text{dye} \rightarrow \text{degradation of the dye} \quad (5)$$

$$h^+_{VB} + \text{dye} \rightarrow \text{dye}^{\bullet+} \rightarrow \text{degradation of the dye} \quad (6)$$

This mechanism is summarized in Fig. 5.

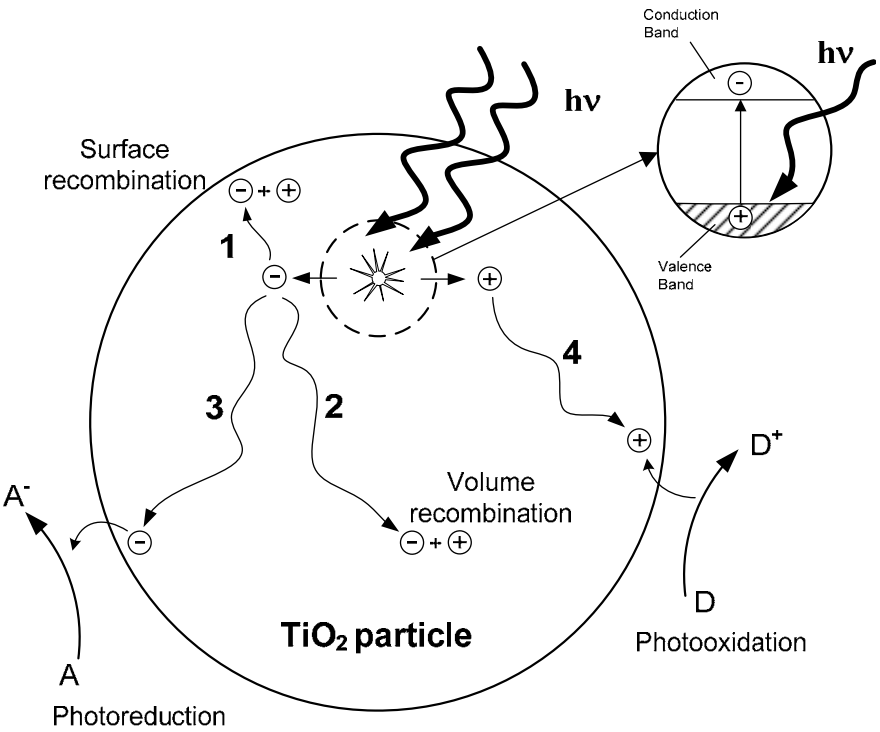

Figure 5. General mechanism of the photocatalytic process in TiO_2 water suspensions irradiated with UV light [24].

4. Conclusions

This paper presents the preliminary results of photodegradation of aqueous solution reactive diazo congo red dye by UV/TiO_2 nanoparticles.
The photocatalytic tests of Congo red (CR) dye degradation, as a model contaminant, show a good photocatalytic activity of the catalyst P25 TiO_2 from Degussa. It was observed that the degree of CR photodegradation increased as the dose of the photocatalyst increased achieving the highest color removal using a TiO_2 dose of 1.0 g/L.
Further investigation will include immobilizing TiO_2 catalyst onto inner surface of batch photoreactor by thin spray and sol-gel coatings and therewith lighten the process of separation of the photocatalyst from the suspension/solution.
The ranking of the degree of CR removal/degradation of different used methods is as follows:
0.25 g TiO_2 < 0.5 g TiO_2 < UV < 1.0 g TiO_2 < 0.25 g TiO_2/UV < 0.5 g TiO_2/UV < 1.0g TiO_2/UV.

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Interactive Robotics for Medical Rehabilitation

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Abstract:

The aim of this research is to develop robotic applications that can be used to take patients through a range of repetitive physiotherapy exercises that are currently performed manually by physiotherapists. The initial focus has been on the rehabilitation of people suffering from some level paralysis of the upper limbs as a result of suffering a stroke. To this end an apparatus has been developed to test one possible technical solution. The design and technical performance of this apparatus are the primary focus of this paper. This paper also contains a brief overview of how it is intended to take this research forward from this point.

Keywords:

control systems, paralysis, physiotherapy, robotics, strokes, upper limbs

1.0 Introduction

The aim of this research is to develop robotic applications that can be used to take patients through a range of physiotherapy exercises. The benefits of this would be two-fold. Firstly, it would allow patients greater access to physiotherapy treatments. Secondly, it would free physiotherapists from mundane, repetitive tasks, thus allowing them to focus more of their time on higher level activities. This should benefit both the speed and level of patient recovery.

The initial emphasis of the research has been on the rehabilitation of stroke sufferers. Paralysis or weakness in one side of the body is a common symptom of a stroke. This occurs due to a lack of blood flow to the brain which causes brain cells to die due to a lack of oxygen and nutrients. This can lead to a loss of muscle-memory. Hand-eye coordination can be badly affected. Muscle-memory is an important concept in the understanding of paralysis. When a person constantly repeats the same activity, physiological changes can occur which result in increased levels of accuracy. Examples of this can be seen in how people improve their golf technique or learn to cycle. In seeking to rehabilitate a person suffering from paralysis caused by a stroke, the aim is essentially to rebuild lost muscle-memory.

In a typical session for a stroke victim suffering from paralysis, a physiotherapist will execute simple exercises that involve hand on hand interaction. The patient is guided through exercises such as making circles, extending or retracting the arm or moving the hand in a diagonal motion. At present, in many cases, a patient may only receive a few hours per week with a physiotherapist. By developing a device that can carry out these exercises in the place of the physiotherapist the amount of therapy that each patient receives can be greatly increased, thus the rehabilitation rate of the patient may be increased. Using robotics as an aid in the rehabilitation of stroke sufferers has been quite well explored. Clinical trials carried out by MIT in 1994 showed the positive benefits of robotic rehabilitation in this regard. Further work has since been done in this area and a company in the United States currently offers rehabilitation robots for stroke sufferers on a commercial basis. While the initial focus of this research has been on this well-trodden area of the rehabilitation of stroke sufferers it is hoped that the technical expertise developed and the medical knowledge acquired will open up avenues for continued research in the area of applying interactive robotics to wider physiotherapy applications.

2.0 Types of Stroke

The range of medical conditions encountered by stroke sufferers is vast and it can have an impact on every aspect of the body from speech to the control of movements. 75% to 85% of stroke sufferers are over the age of 65, however in the UK and Ireland, 10,000 people under the age of 55 suffer a stroke each year. Strokes can be classified into two major categories, ischemic strokes and hemorrhagic strokes. Ischemic strokes are the most common type of stroke, accounting for about 80% of strokes suffered. They are caused by the blockage of a blood vessel in the brain or neck. These blockages can arise from three conditions;

1. Thrombosis - formation of a blood clot within a blood vessel in the neck or brain
2. Embolism - movement of a clot from another part of the body to the neck or brain
3. Stenosis - severe narrowing of an artery leading to the brain

Hemorrhagic stroke accounts for about 20% of strokes suffered. They result from the weakening of a blood vessel in the brain which then ruptures and bleeds into the surrounding tissue. The blood

accumulates and compresses the surrounding brain tissue. An aneurism is the ballooning of a weakened blood vessel which if left untreated can rupture and bleed into the brain.

Due to the complexity of the brain, a stroke can affect a sufferer in a number of different ways. The most common symptoms of a stroke include the following;

- Paralysis or weakness of one side of the body
- Dysarthria – muscles of speech impaired causing slurring
- Dysphagia – muscles of swallowing impaired
- Visual defects – double vision, decreased visual acuity
- Sensory impairment – absent or diminished response to touch, pain, pressure
- Dysphasia – difficulty in expression and/or comprehension
- Intellectual impairment –memory loss, poor judgement or reasoning

3.0 Principle of Operation

The initial phase of the research has focused on the rehabilitation of the upper limbs. A robot, based on a two dimensional planar co-ordinate system, has been built. A patient sits holding a handle and viewing a monitor that shows both the current position of the handle and the desired exercise path. The patient must use hand eye co-ordination to move the handle along the desired path. The robot has three distinct operation modes. In the first mode, the robot will take the handle, and thus the patients arm, through the desired exercise path. In the second mode, the robot will not offer any assistance but will ask the patient to move the handle along a desired path and record the result for the purpose of analysing the patients' progress. In the third mode, the patient will be asked to move the handle along a desired path as in the second mode. However, the robot will take measured corrective action if the patient deviates from the desired path by a given amount. To begin, the level of assistance would be high and can then be lowered as the patient improves.

The robot has been designed to operate with a range of different paths, each one working different regions of the arm. As shown in Figure 1. if the handle moves along the path of the green diagonal lines the patient uses their elbow, if the handle moves along the path of the yellow diagonal lines the patient uses their shoulder and if the handle moves along the path of the blue circle or the blue

square then the patient uses their elbow and shoulder together. Therefore, through careful path selection, the rehabilitation of one joint or the other can be emphasised.

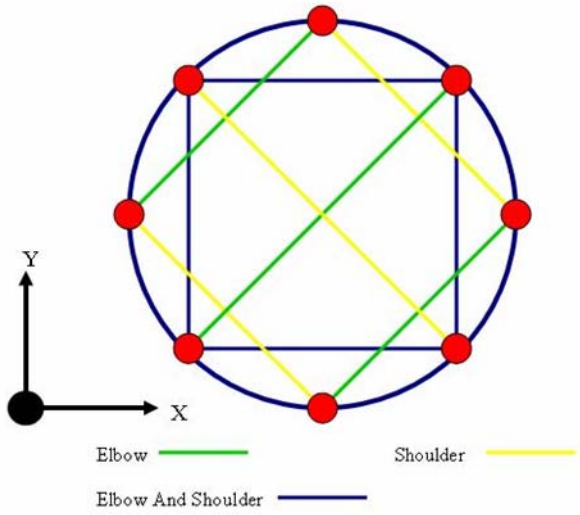

Figure 1. Paths of operation

4.0 Technical Details

4.1 Overview

The apparatus was developed to implement three distinct modes of operation, as outlined in the previous section. The current apparatus achieves this utilising a two degree of freedom Cartesian co-ordinate system. This has been achieved using linear guides, combined with timing belts driven by DC servo motors. Each axis is controlled by dedicated electronic controllers which, in turn, are connected to a PC. The desired operating parameters are inputted through an interactive screen displayed on the PC monitor. A second monitor has also been connected to the PC and positioned so that it is easy for patients to view while they are using the apparatus. It is used to display the current position of the handle and the desired path of motion of the handle. The desired path of motion is variable depending on the parameters entered using the interactive screen while the position of the handle is constantly updated on the second screen by information sent from the two dedicated electronic controllers to the PC. The different technical aspects of the apparatus will now be looked at in more detail, beginning with the mechanical components.

4.2 Mechanical Components

The mechanical system comprises the linear guides, timing belts, timing pulleys and the DC servomotors. Critical to the development of the rehabilitation robot was the need for positional accuracy and smooth motion. This was taken into account in the selection of the guide system and drive mechanism. The mechanical system was required to offer very little frictional resistance, smoothness and accuracy. As such, a track and wheel system, as illustrated in Figure 2. was selected. As well as offering good accuracy and smoothness, it is capable of withstanding the high loads and moments that are applied to it.

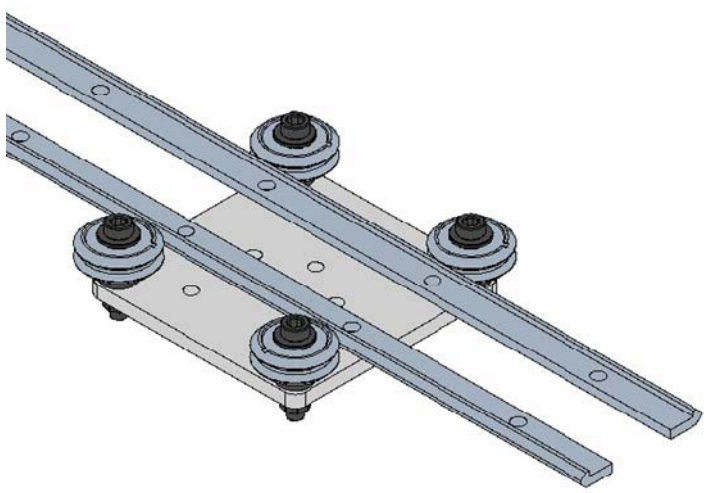

Figure 2. Track and Wheel system

For this application, the motors were required to constantly operate at very low speeds relative to their possible maximum speed. Relatively high stall torque was also required to resist and if necessary to overcome the external force produced by the patients hand. As such, digitally controlled, flat brushless DC servo-motors have been have been used in the apparatus. These motors came with built in hall sensors for detecting the angular position of the motor shaft. Brushless DC motors offer high torque, low wear, instant stall-torque and good power to weight ratios. As the motors are constantly at standstill, thermal considerations were also taken into account when choosing the motors. Most motors experience a cooling affect due to their speed of rotation which would mostly be unavailable for this application. Also, the brushless motors offer little resistance to motion because of their low frictional resistance. This is essential for the two operating modes where the patient is required to move the handle along a desired path. For these operation modes the patient is essentially driving the handle back against the motor and while bias electric currents have been introduced to counter any friction present in the mechanical system, it is still desirable to keep the overall level of friction as low as possible.

Furthermore, a three to one ratio has been implemented between the motor output shaft and the handle. This has the effect of increasing the speed that the motors operated at and the linear accuracy of the hall sensors built into the motors by a factor of three. It also means that the torque exerted by each motor on the handle is increased by a factor of three. This three to one ratio was implemented using timing belts and timing pulleys. The toothed timing belts and pulleys ensured good positional accuracy while still allowing the motors to be back-drivable.

4.3 Control Strategy

The motors used in the apparatus are digitally controlled. Each one is connected to a dedicated motor controller. The hall sensors incorporated into each of the motors also send information on the current position of the motor shaft back to the motor controller. Through monitoring the rates of change of the position of the motor shaft, the angular velocity and angular acceleration of the motor can be determined. The controllers are interlinked through a CAN field bus system and connected to a PC using a standard RS232 connection. Microsoft Windows based applications running on the PC can be used to input operating parameters into the controllers as well as the desired motor position, angular velocity or motor torque. The controllers utilise closed-loop PID control action to implement the desired motor position, angular velocity or motor torque. They also contain an auto-tuning function which can be used to determine the controller gains to give the best possible system performance without the need for developing a potentially complex mathematical model of the system.

The desired position, angular velocity or torque of each of the motors is constantly inputted to each of the digital controllers using a Microsoft Visual Basic programme that runs on the PC. Visual Basic was selected over other computer languages because of the ease with which it allowed interactive user interfaces to be created. The Visual Basic programme continuously changes the position controller's set point to execute the desired profile. The rate at which visual basic changes the set point determines the speed of the exercise. This, along with other parameters, can be adjusted using a Visual Basic interactive screen that is displayed on the PC monitor. The precise operation of the Visual Basic programme will vary depending on the operation mode that has been selected. For example, for the third control mode (when corrective action is taken only if the patient deviates from the desired path), the position of the handle is read from the individual motor controllers into the Visual Basic program. The distance from this point to the nearest point along the desired path is calculated and, from this, the magnitude and direction of the corrective force required to guide the

handle back towards the desired path are calculated. Commands are then sent by Visual Basic to each of the motor controllers to implement this.

5.0 Initial Results

The first operation mode, where the robot leads the patient through a specific profile, executes efficiently with the size of the profile and the speed of execution being easily adjustable. The smoothness of operation is good but could be improved by using more accurate position sensors and increasing the execution time through using a faster PC and upgrading the connection between the PC and the motor controllers to CANopen from RS232. This would allow a greater number of set points to be plotted around the profile path thereby increasing the accuracy of execution. Issues with the second operation mode revolve around the implementation of the bias currents to overcome friction in the system and improvements to this operation mode will come through the fine tuning of the implementation of these bias currents. Also, the development of software to accurately interpret the data received from the exercise and compare it to previous exercises would probably be beneficial. The third operation mode has significant room for improvement before reaching the standard required for the medical profession. As well as the same issues experience with the second operation mode there are a number of other issues specific to this mode of operation. At present, as the patient executes a desired path, the response is purely dependent on position. It would be much more desirable to have the response dependent on the rate of change of position as well as position. Another factor is the direction in which the guidance force is applied. At present, the guidance force is applied in the direction of the closest point on the desired path. This is satisfactory when the distance between actual position and desired position is small. However, in the case shown in Figure 3. the force is exerted in a direction that acts somewhat against the direction of motion, which is an unsatisfactory response. A possible solution to this problem is to take direction of motion in addition to position into account when calculating the direction in which the guidance force is applied.

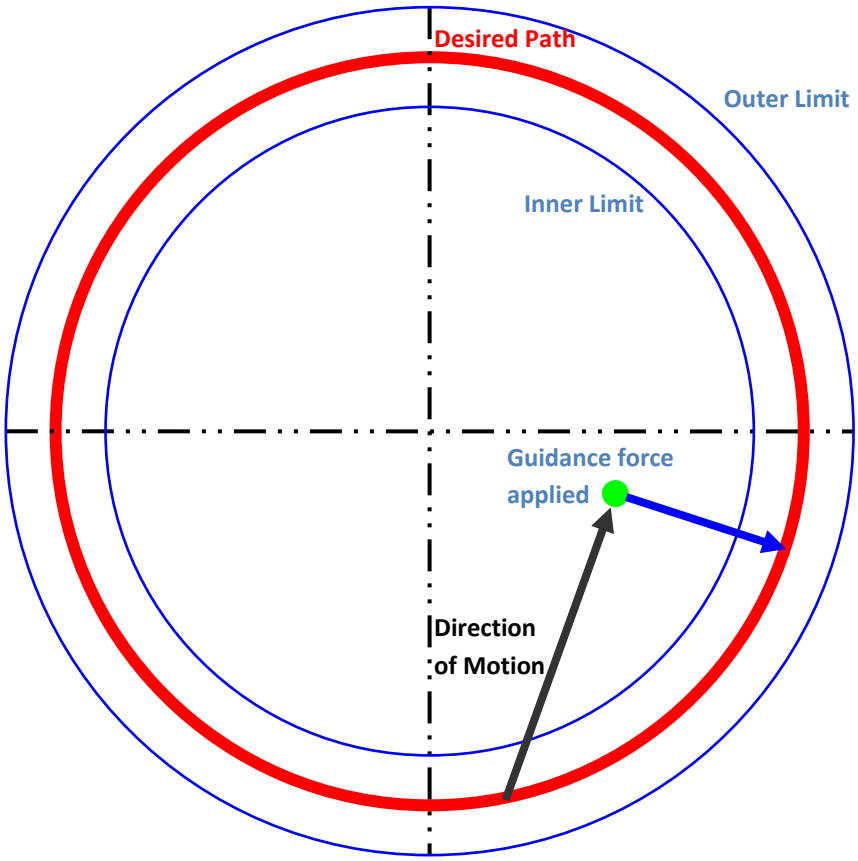

Figure 3. Direction of forces

6.0 Conclusion

This research is still at an early stage. The current apparatus works reasonably well but there is significant room for improvement to bring it up to the standards demanded by the medical profession. The immediate short term focus of the continuing research will be on improvements in these areas. To date, this research has been pursued purely from an Engineering perspective. However, longer term, for this research to achieve something tangible, the focus will have to move towards greater interaction with physiotherapy and other medical professionals. The purpose of this is two-fold. Firstly, to obtain feedback that can be used to determine the level of success of the current apparatus for the rehabilitation of stroke victims and thereby to ascertain what further work has to be done from a technical prospective. The second purpose is to gather information on the

more general needs of modern physiotherapists. This will be done with a view to exploring how the expertise developed through the creation of the rehabilitation robot for stroke victims can be tailored to other related but as yet relatively unexplored areas. As mentioned in section 1.0, the area of using interactive robotics as an aid in the rehabilitation of stroke victims, particularly focusing on the upper limbs, has been relatively well explored. From a technical point of view, our apparatus is unlikely to break significant new ground in this area. However, through developing a level of expertise in this area it is hoped that, with the aid of the physiotherapy profession, the focus of this research can be shifted onto new but related areas and thus make a positive contribution to patient welfare in the future.

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ELEKTROKEMIJSKA SVOJSTVA ALUMINIJSKE SLITINE EN AW-5083

ELECTROCHEMICAL PROPERTIES OF ALUMINIUM ALLOY EN AW-5083

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Izvorni znanstveni rad / Original scientific paper

Sažetak: Aluminijske slitine serije 5xxx najčešće se koriste u brodogradnji zbog svoje male specifične mase, dobrih mehaničkih svojstava i dobre otpornosti prema koroziji u uvjetima obične i morske atmosfere. U cilju proširenja saznanja i moguće interakcije ispitivane slitine EN AW-5083 u lijevanom (as-cast) stanju s kloridnim medijem, primjenom elektrokemijskih mjernih tehnika određena je korozijska otpornost navedene slitine u 0,01 M NaCl. Rezultati ispitivanja pokazali su da je slitina EN AW-5083 sklona jamičastoj (piting) koroziji, što se može povezati s mikrostrukturnim značajkama slitine.

Ključne riječi: aluminijska slitina EN AW-5083, lijevano stanje, kloridni medij, elektrokemijska svojstva

Abstract: The 5xxx series aluminium alloys are commonly used in shipbuilding due to low density, good mechanical properties and very good anticorrosion properties in general conditions and marine atmospheres. Aiming to enhance the knowledge of possible interactions of studied alloy EN AW-5083 in as- cast condition with chloride media, electrochemical measurements were used to determine the corrosion resistance in 0,01 M NaCl. The results of tests have shown that alloy EN AW-5083 is susceptible to pitting corrosion, which corresponds with the microstructural features of alloy.

Key words: aluminium alloy EN AW-5083, as – cast, chloride medium, electrochemical properties

1. Uvod

Piting korozija je jedan od najčešćih oblika korozije u aluminijskim slitinama, do kojeg dolazi zbog prisutnih heterogenosti u metalu, mediju ili okolišnim uvjetima [1]. Na ovaj oblik lokalne korozije mogu utjecati različiti eksperimentalni faktori kao što su pH, temperatura, tip prisutnih aniona u otopini ili fizikalno-kemijske karakteristike pasivnog sloja [2]. Na površini metalnih slitina dolazi do raznih fizikalnih nehomogenosti koje uzrokuju trajnu raspodjelu katodnih i anodnih mjesta i dovode do nastajanja lokalne korozije. Ove nehomogenosti su najčešće intermetalni spojevi ili uključci koji su raspoređeni na površini metalne osnove i stoga su najčešća mjesta za nukleaciju pitova u aluminiju i njegovim slitinama. Važan faktor koji utječe na osjetljivost aluminija prema piting koroziji i ostalim oblicima lokalne korozije je elektrokemijska priroda tih intermetalnih faza [3]. Nadalje, često su korozijska svojstva povezana sa razlikom potencijala između metalne osnove i intermetalnih faza u toj osnovi [2, 4].

Slitina EN AW-5083, kemijskog simbola AlMg4,5Mn0,7 je teško gnječiva, toplinski neočvrstiva slitina aluminija s magnezijem, koja se odlikuje visokim mehaničkim svojstvima, odličnom otpornošću na koroziju, čak i u slanoj vodi, visokom žilavošću, dobrom zavarljivošću različitim tehnikama. Aluminijske slitine serije 5xxx nalaze široku primjenu u proizvodnji traka i ploča, konstrukcijama cesta, uključujući mostove, automobilskoj industriji, brodogradnji, rezervoarima za skladištenje i posudama pod tlakom, a posebno u uvjetima gdje se zahtijeva velika otpornost na koroziju.

Dodatak magnezija aluminiju samo neznatno smanjuje galvanski potencijal, ali proizvodi oksidni sloj s većim specifičnim volumenom od metala od kojeg je nastao, i to rezultira nepropusnim zaštitnim slojem [5]. Zbog tog zaštitnog oksidnog filma, Al-Mg slitine imaju bolju korozijsku otpornost nego čisti aluminij u morskoj vodi i srednje lužnatim otopinama. Povećanjem sadržaja Mg iznad 3-4 mas.% povećava se sklonost interkristalnoj i napetosnoj koroziji. To je zbog formiranja Al-Mg intermetalnih faza na granicama zrna, pri čemu se ove površine ponašaju kao anode.

I mangan ima pozitivni utjecaj na otpornost prema koroziji [5]. Prije svega, on stvara komponente (Al_6Mn) sa elektrodnim potencijalom koji nije značajno različit od aluminijske osnove, bilo da je prisutan u krutoj otopini ili kao spoj. Intermetalni spojevi željeza i silicija su puno pozitivniji u usporedbi sa aluminijskom osnovom i mogu prouzrokovati njen jak piting. Međutim, kada je prisutan mangan, Fe i Si se mogu apsorbirati u Mn-čestice i tako smanjiti razliku potencijala, te praktički eliminirati piting. Prema tome slijedi da Al-Mn slitine imaju dobru otpornost prema napetosnoj, interkristalnoj i piting koroziji.

Prisutnost različitih intermetalnih faza u metalnoj osnovi slitine EN AW-5083 poboljšava njezina mehanička svojstva, ali vodi većoj osjetljivosti prema lokalnoj koroziji. Stoga su u ovom radu ispitana njena elektrokemijska svojstva i utjecaj mikrostrukture na sklonost jamičastoj koroziji.

2. Eksperimentalni dio

Eksperimentalni dio rada proveden je u Laboratoriju za fizikalnu kemiju i koroziju Metalurškog fakulteta. Za elektrokemijska ispitivanja je korišten uzorak lijevanog bloka aluminijske slitine EN AW-5083 (šarža oznake 3116), proizvedenog polukontinuiranim vertikalnim postupkom izravnog hlađenja u ljevaonici TLM-a Šibenik. Lijevani blok je imao dimenzije 1680x520x4809 mm, a ispitani uzorak je izrezan iz rubnog dijela poprečno izrezane ploče koja je prethodno odvojena s početka lijevanog bloka.

Taljevina je prije lijevanja rafinirana smjesom argona i klora u ALPUR-u. Usitnjavanje zrna provedeno je dodatkom predlegure Al-Ti5-B1 u obliku polugica (u ljevačku peć) i žice (u žlijeb ispred ALPUR-a), u prosječnoj količini 1,9 kg/t taljevine.

Ispitivani uzorak je Al-Mg slitina EN AW-5083, kemijskog simbola EN AW-AlMg4,5Mn0,7 (sukladno normi EN 573-3), čiji je kemijski sastav određen optičkim emisijskim spektrometrom (OES) dan u tablici 1.

Tablica 1. Kemijski sastav slitine EN AW-5083

Kemijski sastav [mas. %]									
Mg	**Mn**	**Si**	**Fe**	**Cr**	**Cu**	**Zn**	**Ti**	**Be**	**Na**
4,13	0,45	0,12	0,36	0,1	0,006	0,007	0,027	0,0036	0,0016

Za elektrokemijska ispitivanja Al-Mg uzorak je bio u obliku valjčića promjera 0,95 cm, a elektrodni kontakt je ostvaren pomoću izolirane bakrene žice. Slobodna površina koja je bila u kontaktu s elektrolitom iznosila je 2,83 cm^2. Prije mjerenja površina radne elektrode je mehanički i kemijski obrađena. Brušena je pod mlazom vode na uređaju za automatsku pripremu uzoraka (Vector LC, Buehler) brusnim papirom gradacije 400, 600 i 800. Na svakoj gradaciji brusnog papira uzorak je brušen 10 minuta kod sile opterećenja od 10 N i brzine okretanja rotacijskog diska 150 o/min. Nakon brušenja uzorak je poliran na platnu za poliranje Microcloth vodenom otopinom glinice granulacije 0,3 μm. Brušenje i poliranje je provedeno na istom uređaju, pri istim uvjetima. Nakon poliranja, površina uzorka se temeljito ispire vodom, potom alkoholom i suši. Da bi se odstranio površinski oksidni sloj i eventualno unesene nečistoće, elektroda je držana 1 minutu u alkalnoj otopini 0,1 M NaOH zagrijanoj na 40 °C, nakon čega je isprana destiliranom vodom, te što je moguće brže, postavljena u standardni elektrokemijski sistem. Mjerenja su se izvodila pri sobnoj temperaturi (T=20±2 m°C) u troelektrodnoj ćeliji koja se sastoji od tri elektrode: Al-Mg radne elektrode, zasićene kalomel elektrode (SCE), koja je služila kao referentna elektroda, te Pt mrežice koja je služila kao protuelektroda.

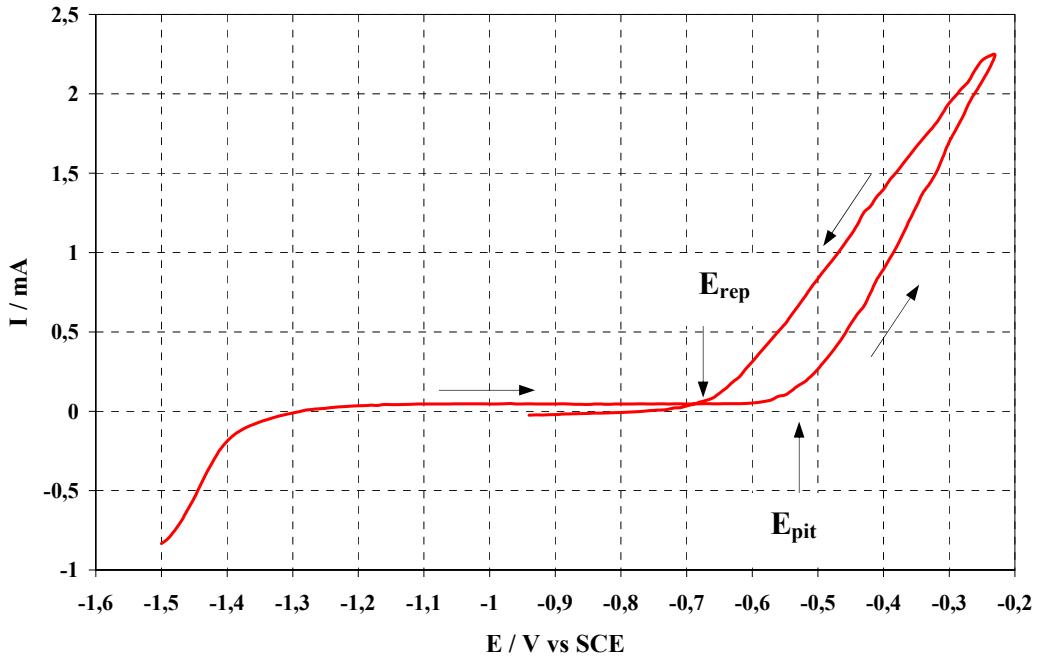
U ovom se radu za praćenje elektrokemijskih svojstava ispitanog materijala koristila metoda cikličke anodne polarizacije pomoću potenciostata („PARSTAT 2273“) vođenog računalom. Mjerenja su se provodila u otopini 0,01 M NaCl, u području potencijala od -1,5 do -0,3 V vs SCE, uz brzinu promjene potencijala od 5 mV/s.

Radi određivanja vrste i sastava intermetalnih spojeva uzorak je izbrušen i ispoliran, te je na jednom detalju provedena SEM analiza s energetsko disperzijskom spektrometrijom (EDS analiza).

Napredovanje korozije praćeno je optičkim mikroskopom Olympus GX51 s digitalnom kamerom Olympus DP70, pri različitim vremenima anodne polarizacije: 5, 10, 20, 40, 80 i 120 minuta pri potencijalu od -500 mV vs SCE. Nakon metalografske analize, a prije početka svake sljedeće elektrokemijske obrade uzorak je bio kemijski obrađen 1 minutu u 0,1 M NaOH pri 40 °C.

3. Rezultati i rasprava

Polarizacijom elektrode počevši od E_{kor} u anodnom smjeru i natrag, moguće je odrediti karakteristične parametre svojstvene za kovine i slitine sklone pasiviranju. To su piting potencijal, E_{pit} , kod kojeg dolazi do proboja pasivnog sloja i repasivacijski potencijal, E_{rep}, kod kojeg se ponovo uspostavlja pasivno stanje. Sposobnost repasivacije se manifestira postepenim smanjenjem struje polarizacije, što je uočljivo kao histereza ($E_{his} = E_{pit} - E_{rep}$) koja se zatvara pri E_{rep}, na slici 1.



Slika 1. Ciklički voltamogram za slitinu EN AW-5083 u 0,01 M NaCl

Vrijednosti elektrokemijskih parametara (E_{kor}, E_{pit} i E_{rep}) određene su iz cikličkog voltamograma i navedene u tablici 2. Iz krivulje na slici 1 se može uočiti da prilikom povratne polarizacije Al-Mg slitina pokazuje karakteristično cikličko ponašanje s uskom histereznom petljom širine 176 mV. Površina koju zatvara pozitivna histerezna petlja ukazuje na sposobnost repasivacije slitine: što je petlja uža, to je metal skloniji repasivaciji pri uvjetima mjerenja. To područje potencijala karakterizirano je metastabilnom ravnotežom na granici metal/elektrolit tj. neki se pitovi produbljuju, a neki repasiviraju.

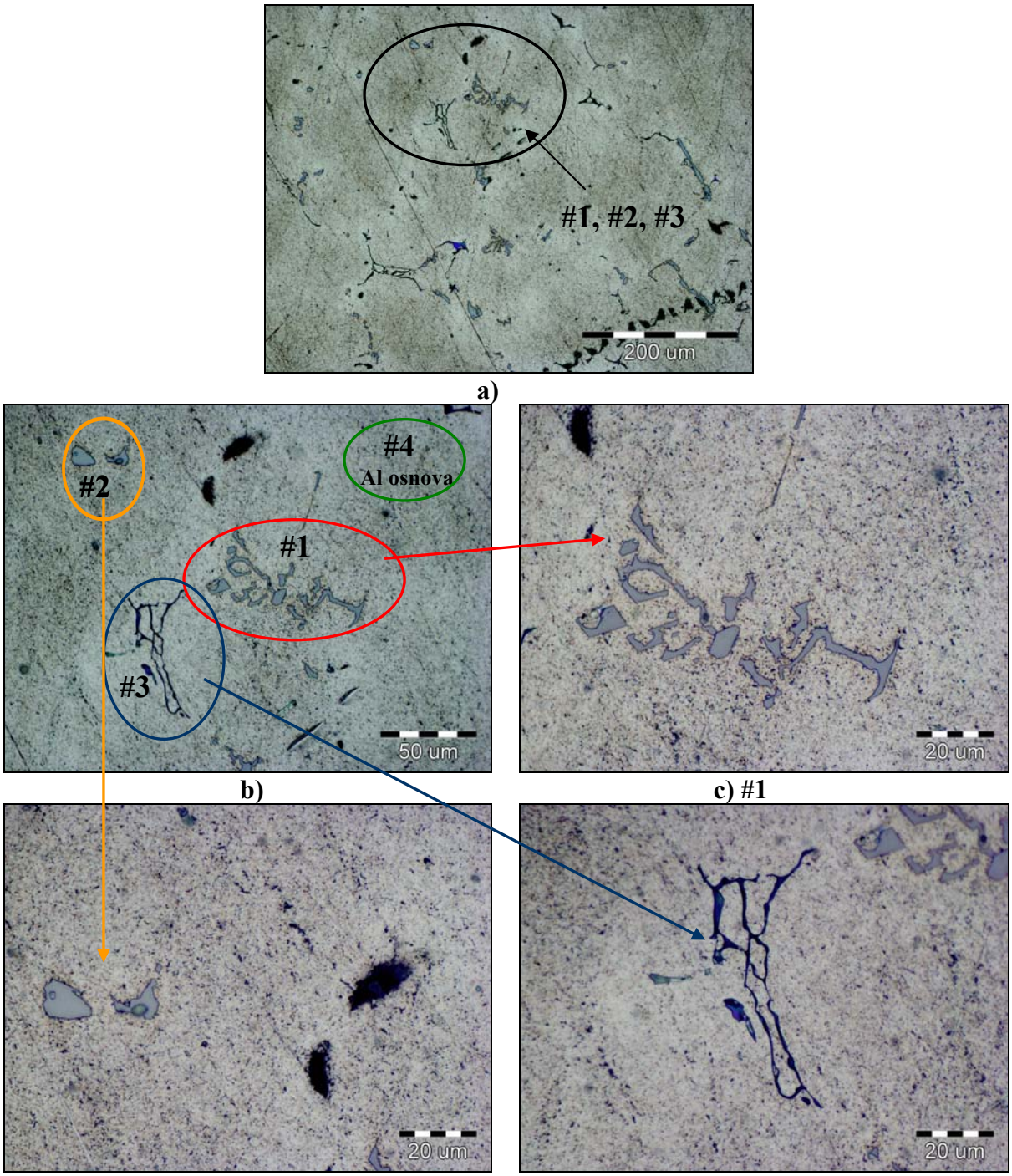
Tablica 2. Elektrokemijski parametri određeni iz cikličkog voltamograma za slitinu EN AW-5083

	E_{kor} [mV]	E_{pit} [mV]	E_{rep} [mV]	E_{his} [mV]
EN AW-5083	-902	-510	-686	176

Iz slike 1 se također vidi da Al-Mg slitina prilikom anodne polarizacije stvara pasivni sloj u području potencijala od cca -1,3 V do – 0,51 V vs SCE, a struja pasivacije iznosi cca 0,045 mA. Struja naglo poraste kod potencijala proboja pasivnog sloja – E_{pit}, jer počinje

intenzivna korozija na mjestima lokalnih galvanskih članaka raspoređenih po površini Al-Mg slitine. Da bi se uočila pojava i razvoj lokalnih korozijskih oštećenja, te su pojave praćene na optičkom mikroskopu.

Metalografski snimak na slici 2a prikazuje površinu detalja slitine EN AW-5083 prije izlaganja koroziji u 0,01 M NaCl snimljenog optičkim mikroskopom pri povećanju 200x. Radi lakšeg praćenja procesa piting korozije, na slikama 2b, 2c, 2d i 2e prikazani su pojedini detalji (#1, #2, #3) pri povećanju 500x i 1000x.

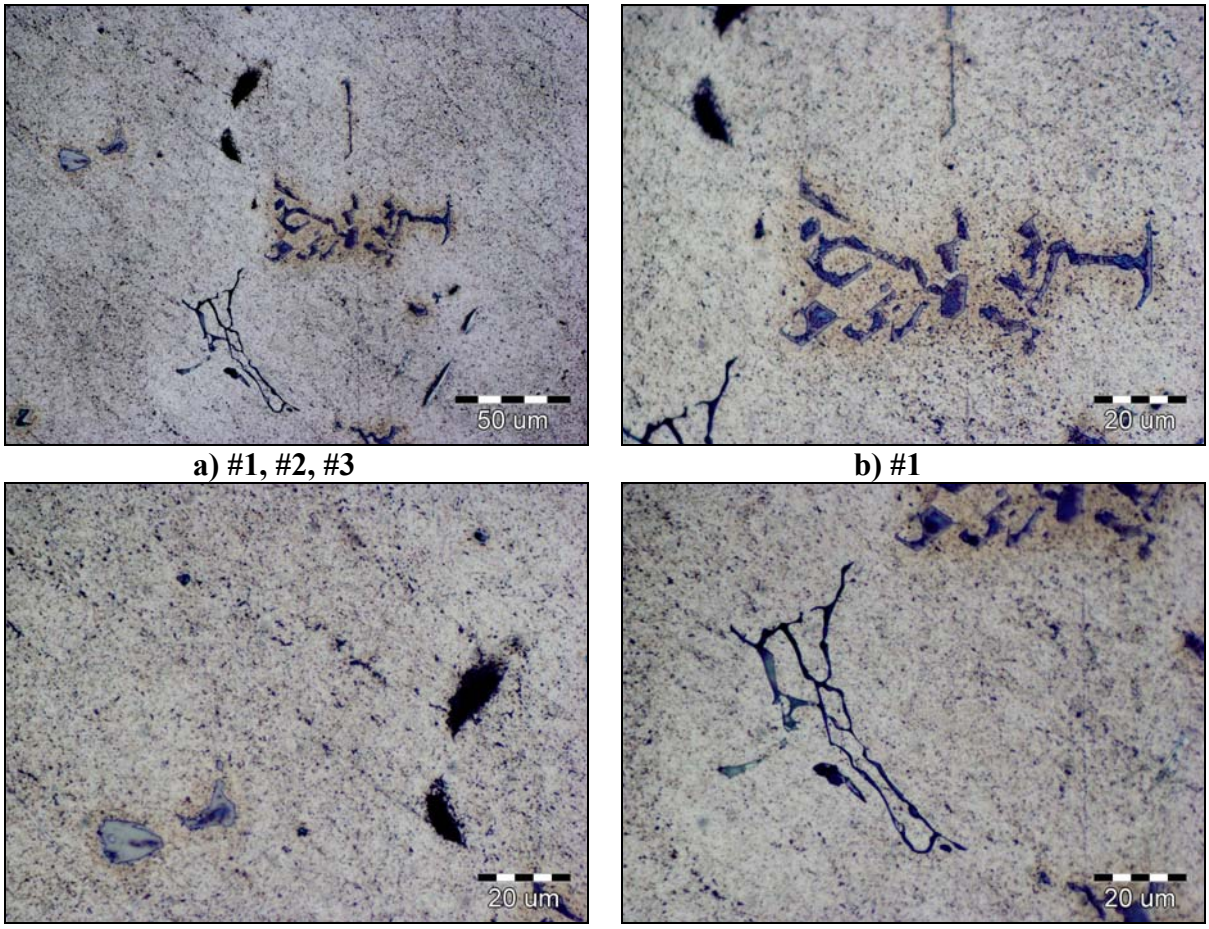


Slika 2. Metalografski snimak uzorka aluminijske slitine EN AW-5083 prije korozije promatran optičkim mikroskopom pri povećanjima:
a) 200x; b) 500x, c), d) i e) 1000x

Različite pozicije na slici 2 analizirane su EDS metodom da bi se odredila vrsta i sastav intermetalnih faza (#1, #2, #3), te metalne osnove (#4) na promatranom detalju. Dobiveni relativni odnosi elemenata ukazuju da su krupne svijetle čestice (detalj #1) u centralnom dijelu metalografskog snimka obogaćene željezom i manganom ako se uspoređuju s aluminijskom osnovom (#4), i one bi prema literaturi mogle biti opisane kao Al_6(Fe, Mn) [1, 2, 4]. Detalj #2 pokazuje da drugačiji oblik željezom obogaćenih čestica imaju one s dodatkom silicija i/ili kroma, tj. intermetalne faze Al-(Fe, Mn, Cr, Si) [6]. Drugi tip intermetalnih spojeva su čestice koje sadrže Mg i Si, a na slici 2 su tamne boje (#3). Te su čestice u literaturi poznate kao Mg_2Si faza [7, 8].

Dakle, osnovni tipovi mikrokonstituenata u ispitanoj Al-Mg slitini su željezne i magnezijske faze koje doprinose heterogenosti površine i nastajanju mikrogalvanskih članaka kad je slitina u kontaktu s elektrolitom. Naime, u literaturi se navodi da je faza Al_6(Fe,Mn) plemenitija u odnosu na aluminij [6], dok faza Mg_2Si pokazuje ili relativno sličnu vrijednost korozijskog potencijala ili niži korozijski potencijal u usporedbi s Al osnovom [9].

Izlaganje takvog uzorka agresivnom kloridnom mediju dovodi do promjene površinskih svojstava prisutnih faza, ovisno o anodnom potencijalu i vremenu kontakta s 0,01 M NaCl. Rezultati na slikama 3 i 4 pokazuju učinak anodne polarizacije na pojavu pitinga u području potencijala iznad E_{pit}.



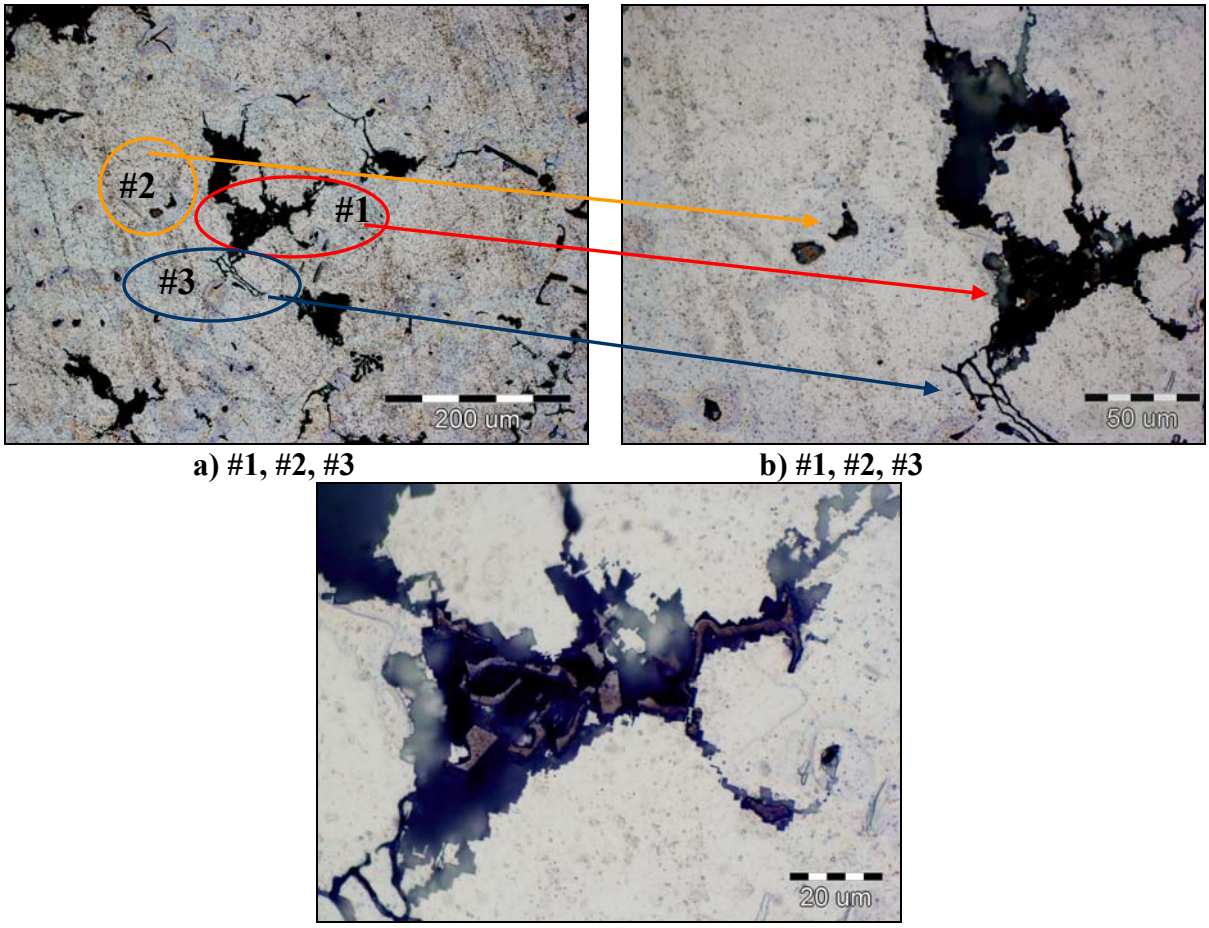
a) #1, #2, #3 **b) #1**

c) #2 **d) #3**

Slika 3. Metalografski snimak uzorka aluminijske slitine EN AW-5083 elektrokemijski polarizirane 10 minuta u 0,01 M NaCl pri potencijalu -500 mV v_s SCE, promatrane optičkim mikroskopom pri povećanjima: a) 500x; b), c) i d) 1000x

Već nakon kratkog vremena kontakta (10 minuta, slika 3), korozijski proces je jasno vidljiv u blizini svih čestica koje sadrže željezo. Dolazi do promjene u boji svijetlih Fe-faza (#1, #2), a posebno do promjene metalne osnove koja je poprimila tamniju žutu nijansu.

Daljnjim izlaganjem otopini 0,01 M NaCl u ukupnom vremenu od 120 minuta, slika 4, te promatranjem na optičkom mikroskopu, pojava lokalne korozije je sve uočljivija.



a) #1, #2, #3 **b) #1, #2, #3**

c) #1

Slika 4. Metalografski snimak uzorka aluminijske slitine EN AW-5083 elektrokemijski polarizirane 120 minuta u 0,01 M NaCl pri potencijalu -500 mV v_s SCE, promatrane optičkim mikroskopom pri povećanjima:
a) 200x; b) 500x; c) 1000x

Primjećuje se da je glavni korozijski napad fokusiran na metalnu osnovu koja okružuje Al-Fe intermetalne čestice, pri čemu dolazi do nastajanja pitova i njihova širenja. Do ovih lokaliziranih korozijskih napada dolazi zbog galvanskog spoja plemenitije željezne faze i aktivne osnove aluminijske slitine [6]. Osnovni anodni proces je otapanje aluminijske osnove:

$$Al \rightarrow Al^{3+} + 3e^-$$

Pored toga, do otapanja aluminija u blizini intermetalnih čestica koje sadrže Fe dolazi također zbog „lošijeg“ oksidnog sloja u toj zoni [7].

Istovremeno se na intermetalnim spojevima s Fe, koji su katodnog karaktera u odnosu na metalnu osnovu, odvija redukcija kisika prema jednadžbi:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

Ovo uzrokuje lokalno povišenje pH, rezultirajući kao prvo otapanjem oksidnog sloja oko precipitata, te odmah nakon toga i metalne osnove oko njih [9, 10]. Prema [6], statistička analiza velikog broja pitova formiranih u blizini Fe-čestica pokazala je da prisustvo Si i Cr u intermetalnoj fazi nema utjecaja na pojavu pitinga. To znači da i Al-(Fe, Mn, Cr, Si) i Al_6(Fe, Mn) faze pokazuju jednaku ulogu u inicijaciji lokalnih korozijskih oštećenja.

Nasuprot tome, intermetalna faza na bazi magnezija i silicija - Mg_2Si, ostaje nepromijenjena (slike 2e, 3d i 4b), tj. ne uočava se korozijska aktivnost, niti na njoj niti na metalnoj osnovi oko nje. Literatura [8] opisuje ovu intermetalnu česticu kao inaktivnu u korozijskim procesima. Međutim, detaljnijim ispitivanjima [6] utvrđeno je da, zbog njihovog anodnog karaktera, ipak dolazi do otapanja gornjeg sloja na ovim česticama, što dovodi do promjene kemijskog sastava. Naime, velika reaktivnost magnezija vodi ka otapanju i stoga brzom gubitku na magneziju tih intermetalnih faza. Te promjene u sastavu Mg_2Si spoja povezane su s dva procesa, tj. s njegovom kemijskom i elektrokemijskom (anodnom) aktivnošću. U početnoj fazi reakcije Mg_2Si može s vodom hidrolizirati stvaranjem različitih tipova silana, u osnovi mono-silana prema sljedećoj reakciji:

$$Mg_2Si + 4\ H_2O \rightarrow 2Mg(OH)_2 + SiH_4$$

Simultano, veoma brzom hidrolizom silana dolazi do razvijanja vodika i nastajanja silicijevog hidroksida na površini Mg-Si čestica:

$$SiH_4 + mH_2O \rightarrow SiO_2{\cdot}nH_2O + H_2\uparrow$$

Istodobno, zbog anodičke aktivnosti Mg_2Si faze, elektrokemijskim otapanjem magnezija iz tih intermetalnih čestica, može doći do obogaćivanja na Si ili do izlučivanja SiO_2:

$$Mg_2Si + 2H_2O \rightarrow 2Mg^{2+} + SiO_2 + 4H^+ + 8e^-$$

Iz toga proizlazi da obogaćivanje na siliciju, kao i stvaranje hidroksidnih naslaga ($Mg(OH)_2$ i $SiO_2{\cdot}nH_2O$) na Mg_2Si fazi, djeluje kao dodatna difuzijska barijera koja sprječava nastajanje i propagaciju (širenje) pitova.

Iz slike 4c jasno je vidljivo da se najveći napad lokalne korozije događa u metalnoj osnovi oko Al_6(Fe, Mn) čestica, što je su u skladu s njihovom katodnom prirodom. Pored toga, metalografske analize su pokazale da je korozijski proces lokaliziran na granici između tih čestica i metalne osnove, zbog formiranja mikrogalvanskih članaka na tim mjestima. Također jednako vrijedi i za Al-(Fe, Mn, Cr, Si) faze (slike 2d, 3c i 4b). Kao posljedica toga, uzorci s većim sadržajem Al_6(Fe, Mn)/Al-(Fe, Mn, Cr, Si) faza, imaju veću gustoću pitova na svojoj površini.

4. Zaključak

Na osnovi elektrokemijskih i metalografskih istraživanja Al-slitine EN AW-5083 u lijevanom stanju, ustanovljeno je da spontano nastali pasivni film formiran na zraku, gubi svoja zaštitna svojstva kad je slitina u kontaktu s otopinom 0,01 M NaCl u uvjetima anodne polarizacije. Do proboja sloja dolazi kod potencijala pitinga E_{pit} = – 0,51 V vs SCE, uz brzinu promjene potencijala od 5 mV/s.

Sklonost piting koroziji može se povezati s prisustvom intermetalnih faza koje na površini slitine stvaraju brojne mikrogalvanske članke. Faze Al_6(Fe, Mn) i Al-(Fe, Mn, Cr, Si) djeluju kao katode, dok Mg_2Si faza ima anodna svojstva u odnosu na Al-osnovu. Sukladno tome Mg_2Si čestice nisu se pokazale kao inicijalna mjesta stvaranja pitova u Al-osnovi.

Pokazalo se da je otapanje aluminija lokalizirano na granici faza između Al-Fe čestica i metalne osnove, a gustoća pitova veća je na površini uzorka koji ima veći broj tih intermetalnih faza.

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ODREĐIVANJE SADRŽAJA UGLJIKA I SILICIJA U PRIMARNOJ TALJEVINI ZA PROIZVODNJU NODULARNOG LIJEVA RAČUNALOM POTPOMOGNUTOM TOPLINSKOM ANALIZOM

DETERMINING THE CONTENT OF CARBON AND SILICON IN THE PRIMARY MELT FOR THE PRODUCTION OF DUCTILE IRON USING COMPUTER-AIDED THERMAL ANALYSIS

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Izvorni znanstveni rad / Original scientific paper

Sažetak: U radu je prikazana primjena računalom potpomognute toplinske analize za određivanje sadržaja ugljika i silicija u primarnoj taljevini za proizvodnju nodularnog lijeva. Toplinska analiza, odnosno snimanje krivulja hlađenja provedeno je na 150 taljevina. Pomoću višestruke regresijske analize formirane su jednadžbe za određivanje sadržaja ugljika i silicija na osnovi karakterističnih temperatura s krivulja hlađenja dobivenih ulijevanjem uzoraka taljevina u standardizirane lončiće (Quik-cup®) s telurom. Dobiveno visoko slaganje između izmjerenih sadržaja ugljika, odnosno silicija optičkim spektrometrom i sadržaja navedenih elemenata određenih pomoću jednadžbi potvrđuje uspješnu primjenu toplinske analize za brzo određivanje sadržaja ugljika i silicija u primarnim taljevinama za proizvodnju nodularnog lijeva.

Ključne riječi: nodularni lijev, toplinska analiza, kemijski sastav

Abstract: The paper shows the application of computer-aided thermal analysis for determining the content of carbon and silicon in the primary melt for the production of ductile iron. Thermal analysis and recording cooling curves have been carried out on 150 melts. With multiple regressions analysis formed the equation for determining the content of carbon and silicon on the basis of the characteristic temperatures from the cooling curve obtained by pouring samples of melts in standardized cups (Quik-cup®) with tellurium. Obtained a high correlation between the measured contents of carbon and silicon using the optical spectrometer and the contents of these elements obtained using the equations confirms the successful application of thermal analysis for rapid determination of the content of carbon and silicon in the primary melts for the production of ductile iron.

Key words: ductile iron, thermal analysis, chemical composition

Uvod

Nodularni lijev pripada skupini željeznih ljevova kod kojih je ugljik izlučen u obliku grafita u metalnoj osnovi [1 - 4]. Najčešće se proizvodi obradom primarne (polazne) taljevine određenog kemijskog sastava predlegurama na bazi magnezija čime se postiže modifikacija oblika izlučenog grafita, odnosno izlučivanje grafita u nodularnom (kuglastom) obliku.

Mikrostruktura i svojstva nodularnog lijeva ovise o kemijskom sastavu primarne i obrađene taljevine te uvjetima pri hlađenju i skrućivanju taljevine u kalupu. Ugljik i silicij stalni su elementi u nodularnom lijevu i imaju značajan utjecaj na izlučivanje ugljika u obliku grafita, odnosno postizanje mikrostrukture bez karbida u lijevanom stanju, a samim tim i na ostvarena svojstva lijeva. Zbog toga se često u ljevaonicama nodularnog lijeva primjenjuje brza provjera sadržaja ugljika i silicija u primarnoj taljevini pomoću toplinske analize.

Toplinska analiza je brza i pouzdana metoda za „on-line“ kontrolu kvalitete taljevine, zbog čega ima široku primjenu u ljevaonicama željeznih ljevova. Primjena toplinske analize u ljevaonicama ide u smjeru utvrđivanja korelacije između pojedinih karakterističnih točaka s krivulje hlađenja s kemijskim sastavom, mikrostrukturnim i mehaničkim svojstvima [5 - 18]. Na taj način moguće je izgraditi sustav kontrole koji će na osnovi snimljene krivulje hlađenja moći procijeniti navedena svojstva, što omogućava eventualne korekcije taljevine u cilju postizanja propisanih svojstava.

Toplinskom analizom može se odrediti sadržaj ugljika i silicija s relativno visokom točnošću, ukoliko se skrućivanje odvija metastabilno, tj. ako se ugljik izluči u obliku karbida (Fe_3C) a ne grafita [19]. Na taj se način može jasno uočiti zastoj koji odgovara likvidus temperaturi ϑ_L i temperaturi eutektičkog skrućivanja ϑ_E pri metastabilnom skrućivanju. Metastabilno skrućivanje postiže se lijevanjem uzorka taljevine u standardizirani lončić za toplinsku analizu koji pored termoelemenata sadrži i telur. Telur nema izravan utjecaj na iznos navedenih temperatura. Primjenom višestruke regresijske analize moguće je dobiti jednadžbe za određivanje sadržaja ugljika i silicija na osnovi izmjerenih prethodno navedenih temperatura, a samim tim i provesti korekcije sadržaja ovih elemenata u cilju postizanja propisanog kemijskog sastava.

U ovom je radu sadržaj ugljika i silicija u primarnim taljevinama za proizvodnju nodularnog lijeva određen pomoću računalom potpomognute toplinske analize na osnovi izmjerenih karakterističnih temperatura s krivulja hlađenja.

Metodologija ispitivanja

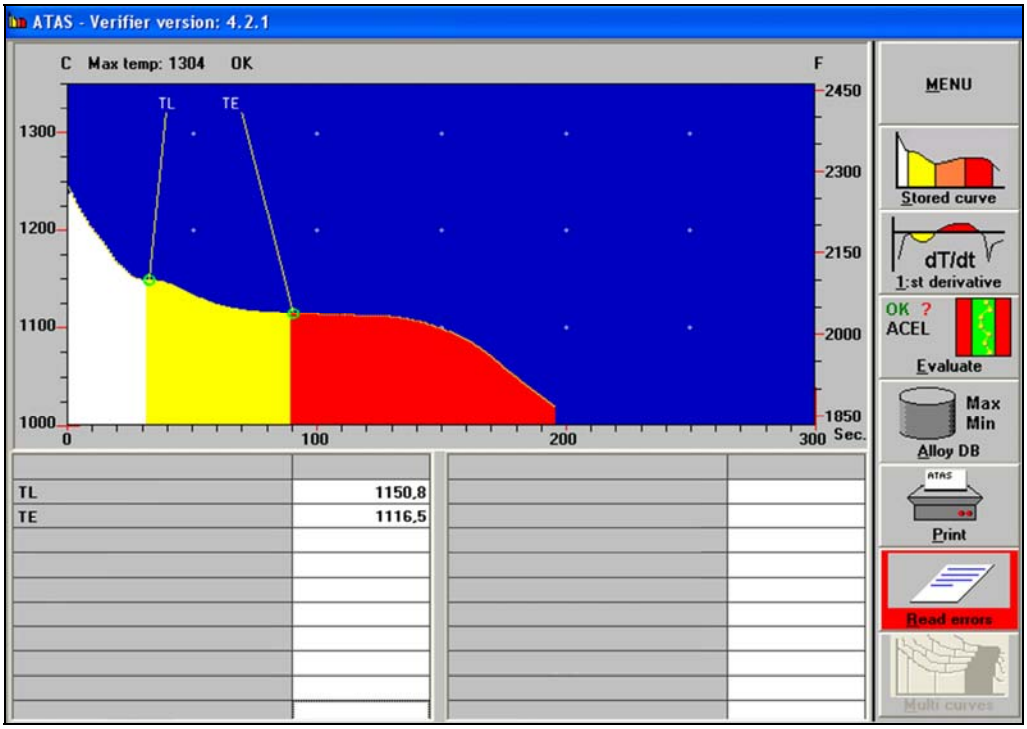
Taljevine za proizvodnju nodularnog lijeva izrađene su u kupolnoj peći. Potom su prenesene u mrežno-frekventnu indukcijsku peć gdje je provedena korekcija temperature i kemijskog sastava. Odsumporavanje taljevina provedeno je u loncu dodatkom CaC_2 uz snažno miješanje inertnim plinom. Nakon odsumporavanja i uklanjanja troske taljevine su ulivene u receptor (indukcijska peć kanalnog tipa).

Primarne taljevine za proizvodnju nodularnog lijeva sukcesivno su uzimane iz receptora. Toplinska analiza primarnih taljevina provedena je suvremenim sustavom za toplinsku analizu ATAS® (engl. *Adaptive Thermal Analysis System*). Uzorci taljevina lijevani su u standardizirane lončiće s termoelementom (Quik-cup®) koji sadrže telur. Paralelno s tim lijevani su uzorci za određivanje kemijskog sastava na spektrometru.

Pomoću višestruke regresijske analize formirane su jednadžbe za određivanje sadržaja ugljika i silicija u primarnim taljevinama za proizvodnju nodularnog na osnovi karakterističnih temperatura s krivulja hlađenja.

Rezultati i diskusija

Na slici 1 prikazana je krivulja hlađenja za jednu od primarnih taljevina dobivena ulijevanjem uzorka taljevine u standardizirani lončić (Quik-cup®) s telurom, čime je postignuto metastabilno skrućivanje, odnosno izlučivanje ugljika u obliku karbida (Fe_3C).



Slika 1. Krivulja hlađenja primarne taljevine br. 1 dobivena ulijevanjem uzorka taljevine u standardizirani lončić (Quik-cup®) s termoelementom

Pomoću višestruke regresijske analize formirane su slijedeće jednadžbe za određivanje sadržaja ugljika i silicija u primarnim taljevinama na osnovi izmjerenih likvidus temperatura ϑ_L i temperatura eutektičkog skrućivanja ϑ_E s krivulja hlađenja:

$$C = 4{,}840913 - 0{,}005153 \cdot \vartheta_L + 0{,}004298 \cdot \vartheta_E, \quad \text{mas. \%} \qquad (1)$$

$$Si = 31{,}55963 - 0{,}005950 \cdot \vartheta_L - 0{,}020260 \cdot \vartheta_E, \quad \text{mas. \%} \qquad (2)$$

U tablici 1 prikazane su izmjerene vrijednosti likvidus temperatura ϑ_L i temperatura eutektičkog skrućivanja ϑ_E, sadržaji ugljika i silicija izmjereni spektometrom te sadržaji ugljika i silicija određeni na osnovi jednadžbi 1 i 2.

Tablica 1. Karakteristične temperature s krivulja hlađenja te sadržaji ugljika i silicija određeni na spektrometru (SP) i pomoću toplinske analize (TA)

Broj taline	ϑ_L, °C	ϑ_E, °C	% C, SP	%C, TA	Razlika, % C	% Si, SP	% Si, TA	Razlika, % Si
1	1150,8	1116,5	3,69	3,71	0,02	2,15	2,09	0,06
2	1151,3	1116,2	3,68	3,71	0,03	2,23	2,10	0,13
3	1152,4	1117,6	3,63	3,71	0,08	2,20	2,06	0,14
4	1153,7	1117,8	3,67	3,70	0,03	2,11	2,05	0,06
5	1154,2	1118,4	3,66	3,70	0,04	2,08	2,03	0,05
6	1153,5	1118,1	3,64	3,70	0,06	2,09	2,04	0,05
7	1151,2	1116,5	3,69	3,71	0,02	2,10	2,09	0,01
8	1151,2	1116,5	3,69	3,71	0,02	2,10	2,09	0,01
9	1154,3	1116,8	3,67	3,69	0,02	2,11	2,07	0,04
10	1152,0	1117,1	3,70	3,71	0,01	2,15	2,07	0,08
11	1151,2	1117,1	3,74	3,71	0,03	2,20	2,08	0,12
12	1152,5	1119,1	3,74	3,71	0,03	2,14	2,03	0,11
13	1147,7	1116,8	3,67	3,73	0,06	2,10	2,10	0,00
14	1155,0	1116,2	3,76	3,69	0,07	2,12	2,07	0,05
15	1149,0	1116,3	3,72	3,72	0,00	2,19	2,11	0,08
…..	…..	…..	…..	…..	…..	…..	…..	…..
85	1164,7	1119,7	3,64	3,65	0,01	2,00	1,94	0,06
86	1162,3	1119,0	3,66	3,66	0,00	1,95	1,97	0,02
87	1162,9	1120,4	3,67	3,66	0,01	1,94	1,94	0,00
88	1162,3	1118,3	3,66	3,66	0,00	1,90	1,99	0,09
89	1158,0	1120,1	3,67	3,69	0,02	1,92	1,98	0,06
90	1158,9	1119,4	3,64	3,68	0,04	1,92	1,99	0,07
91	1161,9	1118,8	3,70	3,66	0,04	1,96	1,98	0,02
92	1161,7	1118,9	3,65	3,66	0,01	1,95	1,98	0,03
93	1161,1	1115,4	3,71	3,65	0,06	1,94	2,05	0,11
94	1154,7	1119,2	3,67	3,70	0,03	1,92	2,01	0,09
95	1149,0	1118,6	3,70	3,73	0,03	1,92	2,06	0,14
96	1156,6	1117,1	3,71	3,68	0,03	1,98	2,05	0,07
97	1154,8	1119,7	3,69	3,70	0,01	1,98	2,00	0,02
98	1159,1	1118,3	3,66	3,67	0,01	1,88	2,01	0,13
99	1157,5	1118,3	3,68	3,68	0,00	1,87	2,02	0,15
100	1161,2	1118,7	3,67	3,67	0,00	1,90	1,99	0,09
…..	…..	…..	…..	…..	…..	…..	…..	…..
140	1150,2	1118,4	3,71	3,72	0,01	2,18	2,06	0,12
141	1146,8	1117,5	3,73	3,73	0,00	2,16	2,10	0,06
142	1137,0	1115,6	3,78	3,78	0,00	2,34	2,19	0,15
143	1146,4	1115,4	3,72	3,73	0,01	2,40	2,14	0,26
144	1142,6	1116,6	3,77	3,75	0,02	2,27	2,14	0,13
145	1148,9	1122,3	3,72	3,74	0,02	2,04	1,99	0,05
146	1152,8	1123,5	3,74	3,73	0,01	1,89	1,94	0,05
147	1154,6	1117,4	3,66	3,69	0,03	2,04	2,05	0,01
148	1150,6	1118,0	3,69	3,72	0,03	2,09	2,06	0,03
149	1157,5	1116,1	3,66	3,67	0,01	1,98	2,06	0,08
150	1155,9	1118,3	3,66	3,69	0,03	1,97	2,03	0,06

Iz tablice 1 može se vidjeti da je ostvareno vrlo dobro slaganje sadržaja ugljika i silicija određenih na osnovi parametara s krivulja hlađenja s vrijednostima dobivenim analizom na spektrometru. Veća točnost (veće slaganje) postignuto je u slučaju određivanja sadržaja ugljika. U slučaju sadržaja silicija prisutna su manja odstupanja.

Na temperaturu eutektičkog skrućivanja pri metastabilnom skrućivanju ϑ_E najznačajniji utjecaj imaju silicij, fosfor i krom. Povećanjem sadržaja silicija i fosfora snižava se, a povećanjem sadržaja kroma povisuje temperatura ϑ_E. U cilju dobivanja veće točnosti određivanja sadržaja silicija pomoću toplinske analize potrebno je uzeti u obzir utjecaj navedenih elemenata (prvenstveno fosfora), odnosno svesti varijacije sadržaja fosfora i kroma na što je moguće nižu mjeru. Međutim, ostvarena točnost u određivanju sadržaja silicija (tablica 1) je zadovoljavajuća za realne uvjete proizvodnje nodularnog lijeva.

Zaključak

Dobiveni rezultati potvrđuju da je pomoću računalom potpomognute toplinske analize moguće odrediti sadržaj ugljika i silicija u taljevinama sivih željeznih ljevova s zadovoljavajućom točnošću. Pri tome je važno da se skrućivanje uzorka odvija metastabilno, odnosno da se ugljik izluči u obliku karbida (Fe_3C) da bi se eliminirao utjecaj nukleacijskog potencijala taljevine na temperaturu eutektičkog skrućivanja. U cilju postizanja veće točnosti, u jednadžbu za određivanje sadržaja silicija u taljevini potrebno je, pored parametara s krivulje hlađenja, uvrstiti i sadržaje elemenata (prvenstveno fosfora) koji utječu na temperaturu eutektičkog skrućivanja pri metastabilnom skrućivanju ϑ_E, ili svesti njihove varijacije na što je moguće manju mjeru.

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SVOJSTVA I MIKROSTRUKTURA CrMoNb ČELIKA NAKON PLINSKOG ZAVARIVANJA

PROPERTIES AND MICROSTRUCTURE OF CrMoNb STEEL AFTER GAS WELDING

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Sažetak: U radu su prikazani rezultati ispitivanja mehaničkih svojstava i mikrostrukture lima iz niskolegiranog CrMoNb čelika prije i nakon zavarivanja. Zavarivanje lima debljine 18 mm provedeno je plinskim postupkom uz uporabu elektrode Böhler DCMS ϕ2,5 mm. Tvrdoća i udarna radnja loma zavarenog spoja ispitivani su standardnim metodama. Mikrostrukturna i fraktografska analiza provedene su pomoću optičkog i elektronskog mikroskopa opremljenog sustavom za energetsko disperzijsku spektrometriju (EDS). Utvrđeno je da se mikrostruktura zavarenog spoja CrMoNb čelika sastoji od ferita i perlita, te mjestimično precipitiranih karbida.

Ključne riječi: zavarivanje, niskolegirani CrMoNb čelik, mehanička svojstva, mikrostruktura

Abstract: In this work the results of mechanical and microstructural testing of sheet made from low alloyed CrMoNb steel before and after welding are shown. Welding of sheet thickness 18 mm was carried out using gas method with Böhler DCMS ϕ2.5 mm electrode. The hardness and impact energy testing were performed with standard methods. The analyses of microstructure and fracture surfaces were carried out with optical and electron microscopy equipped with the energy dispersive spectrometry (EDS). It is found that microstructure of CrMoNb steel welded join were consisted from ferrite and pearlite with sporadically precipitated of carbides.

Key words: welding, low alloyed CrMoNb steel, mechanical properties, microstructure

1. UVOD

Niskolegirani feritni čelici pripadaju skupini čelika koji pored zadovoljavajućih mehaničkih svojstava, dobre zavarljivosti imaju i visoku korozijsku otpornost. Pored odgovarajuće otpornosti na puzanje odlikuje ih trajna vremenska čvrstoća i vatrootpornost. Krom-molibden čelici mikrolegirani niobijem često zamjenjuju standardne 2.25Cr-1Mo i modificirane 9Cr-1Mo čelike [1]. Svoju primjenu CrMoNb čelici pronalaze u proizvodnji tlačnih posuda, kompresora, turbinskih rotora, elektrana, te u ostalim konstrukcijskim komponentama koje su izložene naprezanju u uvjetima povišenih temperatura [2]. Optimalan sastav niskolegiranih CrMo čelika predviđenih za zavarivanje uključuje nizak sadržaj ugljika, kisika, dušika i mangana, uz mikrolegiranje s vanadijem i niobijem.

Poznato je da su mikrostrukturne promjene izazvane unosom topline tijekom zavarivanja odgovorne za promjenu mehaničkih svojstava zavarenog spoja [3]. Zato je veoma važno znati do kakvih promjena mikrostrukture zavarivanjem može doći i kako one utječu na mehanička svojstva gotovog proizvoda. Tijekom uporabe niskolegiranih čelika u kemijskim i procesnim postrojenjima može doći do neočekivanih prijeloma. Stoga je fraktografska analiza prijelomnih površina, nakon ispitivanja mehaničkih svojstava, postala obvezatna budući da omogućava utvrđivanje uzroka prijeloma [4, 5].

U radu je dana analiza mikrostrukture i mehaničkih svojstava niskolegiranog CrMoNb čelika nakon zavarivanja plinskim postupkom, te je objašnjen mehanizam nastanka prijeloma.

2. EKSPERIMENTALNI DIO

Za istraživanje je korišten lim debljine 18 mm proizveden iz niskolegiranog CrMo čelika mikrolegiranog niobijem (tablica 1). Zavarivanje pripremljenog V-spoja provedeno je plinskim postupkom uz primjenu odgovarajućeg dodatnog materijala. Prije zavarivanja ploče (300x300x18 mm) iz CrMoNb čelika su predgrijane (~150°C). Dodatni materijal za zavarivanje bila je žica Böhler DCMS EN 12536-OV (W. Nr.: 1.7346) promjera 2,5 mm.

Tablica 1. Kemijski sastav osnovnog materijala (OM) i zone taljenja (ZT) niskolegiranog CrMoNb čelika, mas.%

	C	Mn	P	S	Si	Mo	Al	Cr	Ni	Cu	Nb
OM	0,05	1,41	0,019	0,006	0,44	0,42	0,04	1,36	0,47	0,07	0,05
ZT	0,06	0,89	0,038	0,005	0,22	0,45	0,01	1,27	0,28	0,05	0,03

Nakon zavarivanja provedena su ispitivanja mikrostrukture, mehaničkih svojstava i prijelomnih površina (nakon ispitivanja udarne radnje loma). Ispitivanja mikrostrukture i prijelomnih površina provedena su optičkom i pretražnom elektronskom mikroskopijom (SEM) koja ima mogućnost uporabe energetsko disperzijske spektrometrije (EDS). Uzorci su prije mikrostrukturnih ispitivanja pripremljeni (brušenje i poliranje) i nagriženi u nital otopini.

Ispitivanje udarne radnje loma provedeno je Charpy metodom na standardnim uzorcima (10x10x55 mm) osnovnog materijala i zone taljenja s V-zarezom dubine 2 mm u sredini zone taljenja kod sobne temperature [6]. Tvrdoća je ispitana Vickers metodom (HV_{20}).

3. REZULTATI I RASPRAVA

Rezultati ispitivanja mehaničkih svojstava istraživanog CrMoNb čelika prije i nakon zavarivanja navedeni su u tablici 2. Može se zamijetiti da je udarna radnja loma zone taljenja

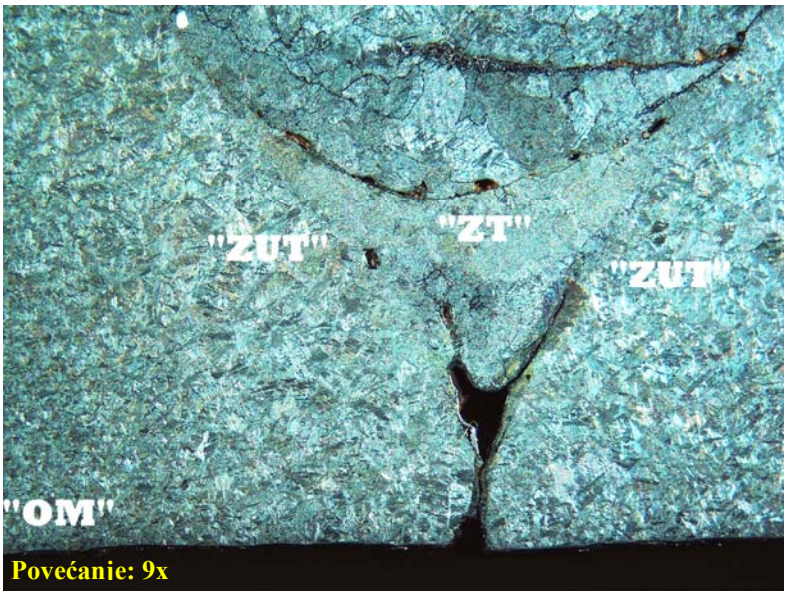
za 24,4 J manja od udarne radnje loma osnovnog materijala (31,9 J). Nasuprot tome, vrijednost tvrdoće zone taljenja je neznatno viša od tvrdoće osnovnog materijala. Povećana vrijednost tvrdoće u zoni taljenja posljedica je unosa topline tijekom zavarivanja i taljenja, te mikrostrukture nastale ponovnim skrućivanjem toga područja. Budući da plinski postupak zavarivanja spada u postupke zavarivanja taljenjem tijekom zavarivanja dolazi do miješanja osnovnog i dodatnog materijala u zoni taljenja. Zavarljivost CrMo čelika znatno ovisi o kemijskom sastavu, tj. ekvivalentu ugljika [2]. Na osnovi kemijskog sastava istraživanog čelika (tablica 1) prema jednadžbi 1 izračunati ekvivalent ugljika (C_E) iznosio je 0,695.

$$C_E = \%C + \frac{\%Mn}{6} + \frac{\%Cr + \%Mo + \%V}{5} + \frac{\%Ni + \%Cu}{10} \qquad (1)$$

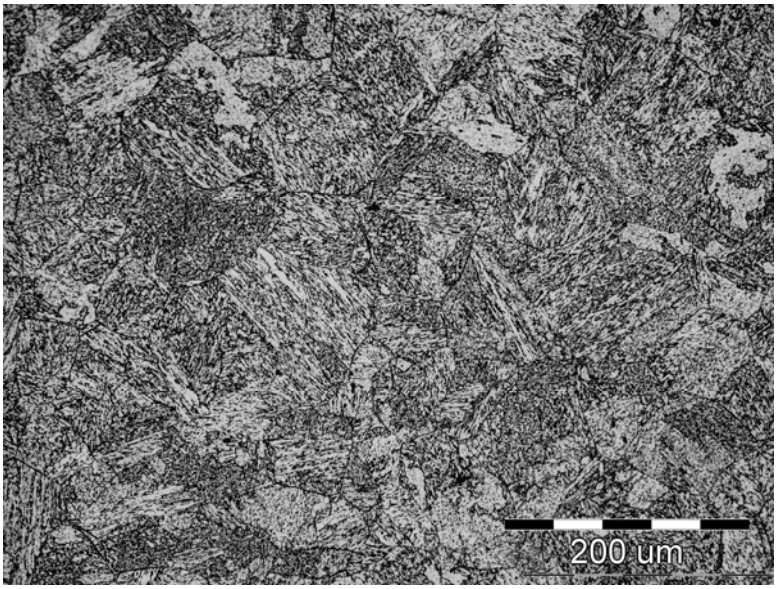
Tablica 2. Mehanička svojstva niskolegiranog CrMoNb čelika prije i nakon zavarivanja

	Granica razvlačenja, MPa	Vlačna čvrstoća, MPa	Udarna radnja loma, J	Tvrdoća, HV 20
Osnovni materijal	800	923	31,9	261,3
Zona taljenja	-	-	7,5	264,0

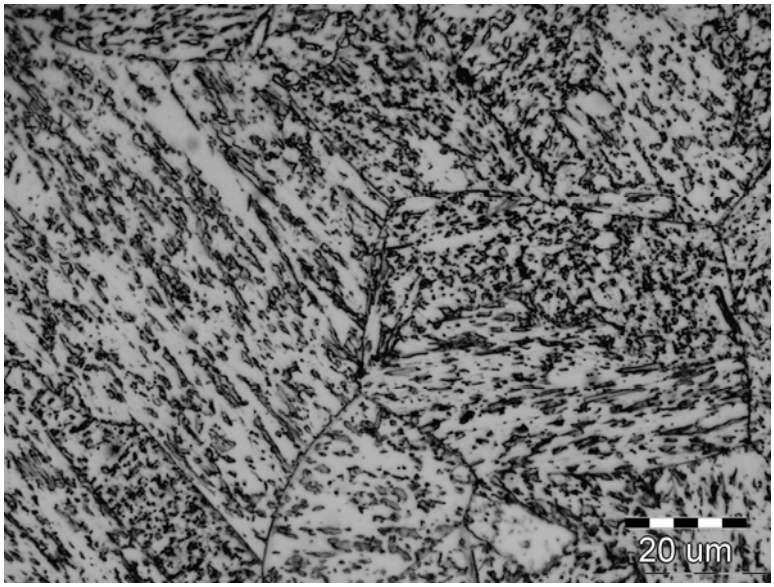
Kemijski sastav i mikrostruktura zone taljenja i zone utjecaja topline odlučujući su čimbenici koji utječu na mehanička svojstva zavarenih konstrukcija. Općenito su mehanička svojstva zavara lošija od svojstava osnovnog materijala [7]. Zbog temperaturnog i kemijskog gradijenta tijekom i nakon zavarivanja dolazi do pojave različitih zona heterogenih mikrostruktura kroz zavareni spoj. To se može zapaziti iz snimaka dobivenih optičkom mikroskopijom. Optičkom mikroskopijom provedeno je promatranje makrostrukture (slika 1) i mikrostrukture (slike 2-4). Na makrosnimku se zapažaju pojedini prijelazi, zona utjecaja topline, zona taljenja i osnovni materijal. Mikrostrukturni snimci osnovnog materijala ukazuju da se radi o feritno-perlitnoj mikrostrukturi (slika 2). Nakon zavarivanja u zoni taljenja je nastala igličasta bainitna mikrostruktura (slika 3). Zbog neposrednog utjecaja topline u dijelu osnovnog materijala uz zonu taljenja (zona utjecaja topline) dolazi do ogrubljivanja mikrostrukture (slika 4), te je ona podložnija pojavi izlučivanja nepoželjnih faza.



Slika 1. Makrosnimak zavarenog spoja CrMoNb čelika

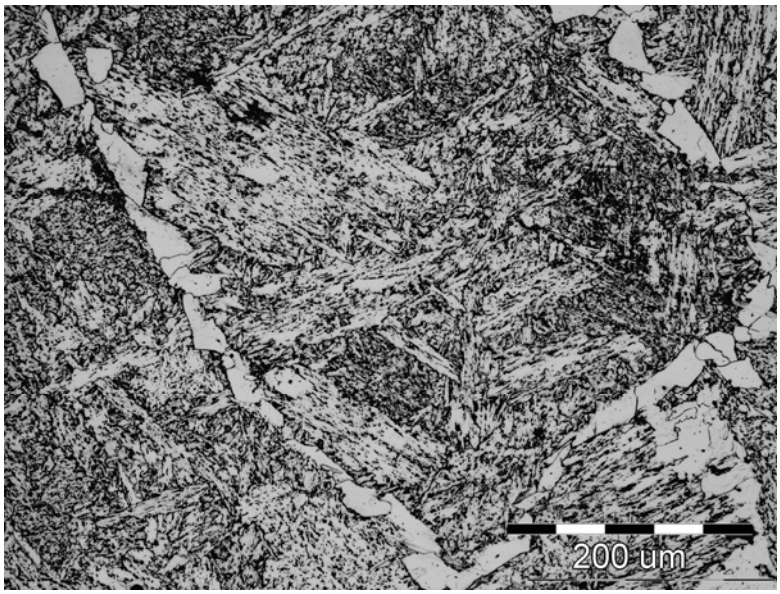


(a)

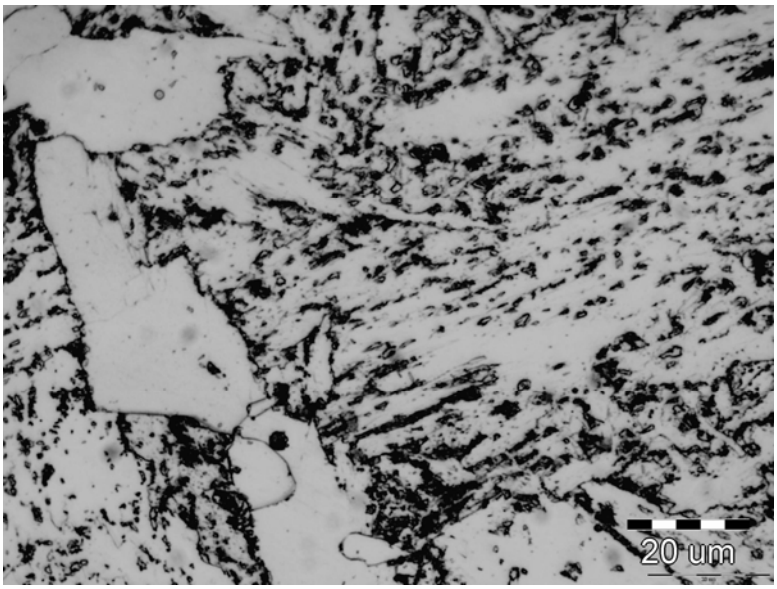


(b)

Slika 2. Optička mikrografija osnovnog materijala CrMoNb čelika
a) povećanje 200X
b) povećanje 1000X

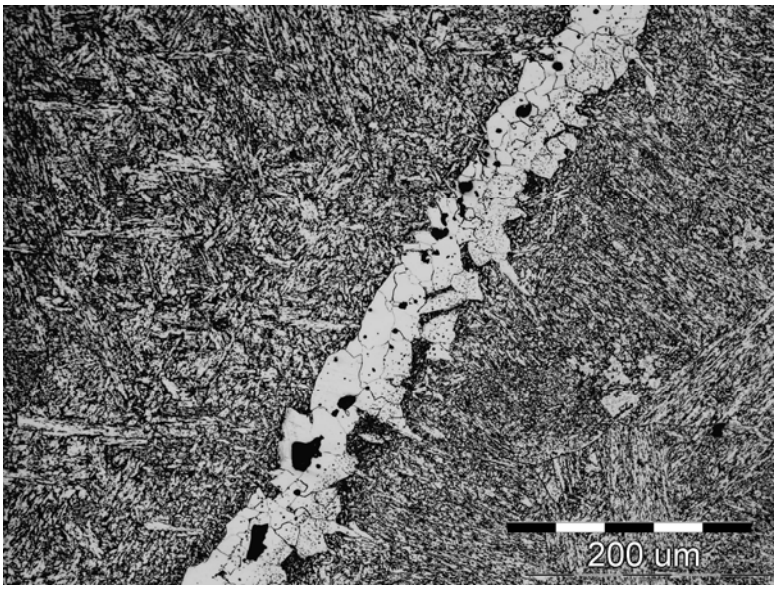


(a)

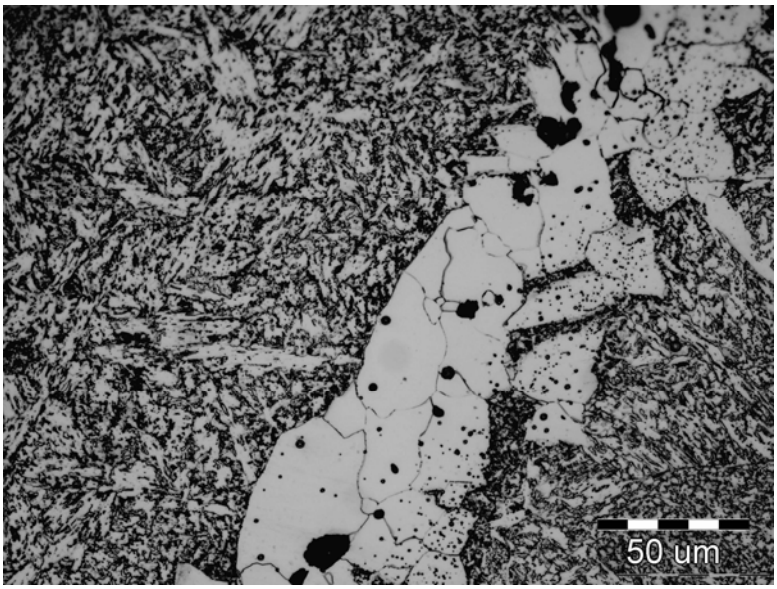


(b)

Slika 3. Optička mikrografija zone taljenja CrMoNb čelika
a) povećanje 200X
b) povećanje 1000X



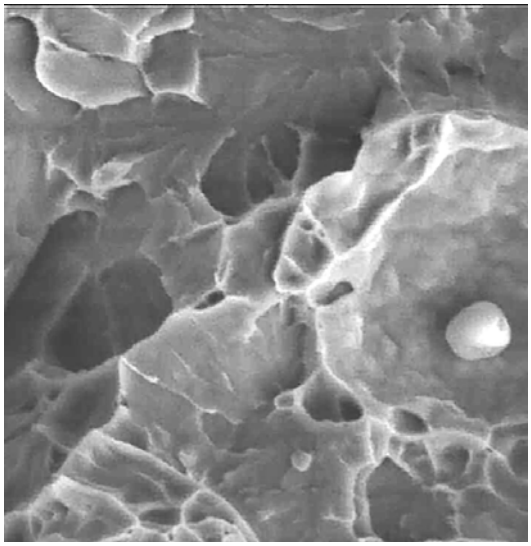
(a)



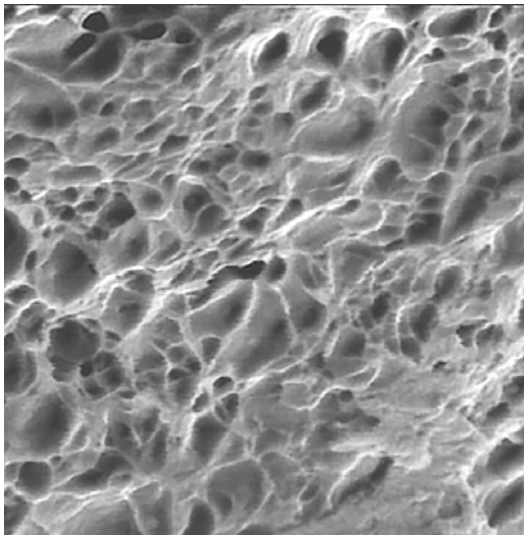
(b)

Slika 4. Optička mikrografija zone utjecaja topline CrMoNb čelika
a) povećanje 200X
b) povećanje 1000X

Poznato je da se fraktografskom analizom može opisati proces prijeloma, te ponuditi vjerodostojni dokaz načina prijeloma čeličnog proizvoda ili njegovog propadanja tijekom uporabe. Prijelomne površine CrMoNb čelika analizirane su nakon ispitivanja udarne radnje loma Charpy metodom kod sobne temperature. Reprezentativne mikrofraktografije snimljene pretražnim elektronskim mikroskopom u struji sekundarnih elektrona prikazane su na slikama 5-8. Osnovni materijal uglavnom karakterizira sitnojamičasti prijelom (slike 5a i 6) s transkristalnim područjima. Prijelomna površina zone taljenja sastoji se od kombinacije transkristalnog krhkog i sitnojamičastog duktilnog prijeloma (slike 5b i 7). Mjestimično je u jamicama duktilnog prijeloma uočena prisutnost čestica različitog sastava (slike 6c i 7c). Prijelom je započinjao na međupovršinama uključak/metalna osnova i/ili karbid/metalna osnova (slike 6 i 7). Dobiveni rezultati fraktografske analize se podudaraju s rezultatima Ahila i sur. [4] koji su utvrdili da prijelom započinje oko sferičnih čestica promjera 3-8 μm. Prijelomne površine zone utjecaja topline karakterizirane su primarno transkristalnim ravnim prijelomom (slika 8).

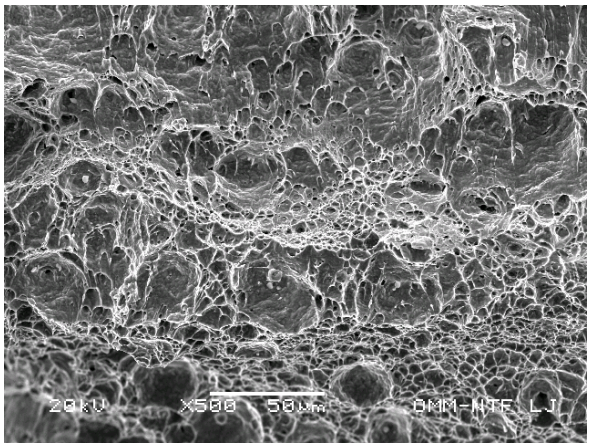


(a)

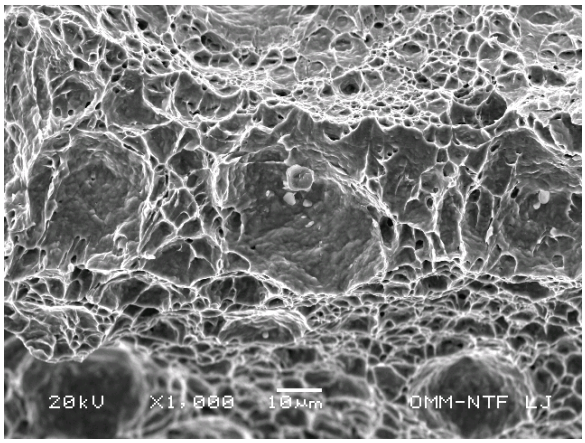


(b)

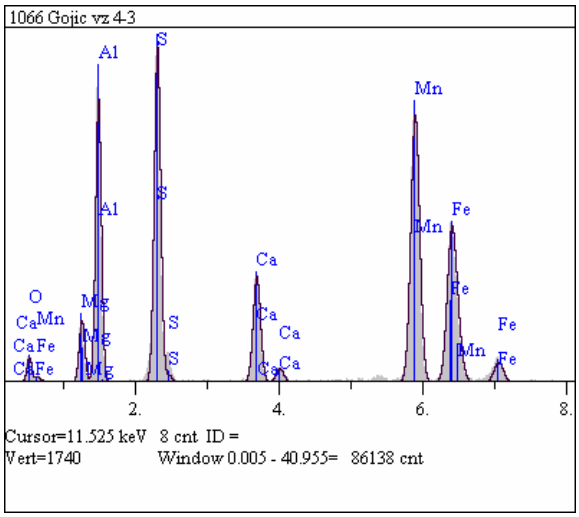
Slika 5. SEI mikrofraktografije prijelomne površine osnovnog materijala (a) i zone taljenja (b) CrMoNb čelika nakon ispitivanja udarne radnje loma; povećanje 1000X



(a)



(b)

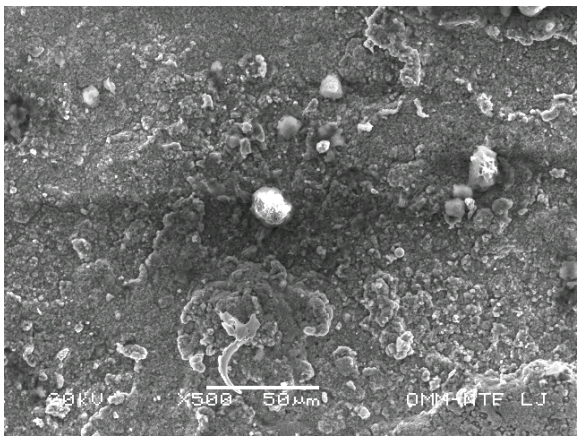


Elt.	Line	Intensity (c/s)	Error 2-sig	Atomic %	Conc	
O	Ka	10.07	0.635	8.056	3.324	wt.%
Mg	Ka	29.35	1.084	6.061	3.799	wt.%
Al	Ka	139.07	2.358	21.936	15.261	wt.%
S	Ka	182.67	2.703	18.743	15.498	wt.%
Ca	Ka	66.29	1.628	5.910	6.108	wt.%
Mn	Ka	199.97	2.828	24.375	34.529	wt.%
Fe	Ka	109.85	2.096	14.918	21.482	wt.%
				100.000	100.000	wt.%
						Total

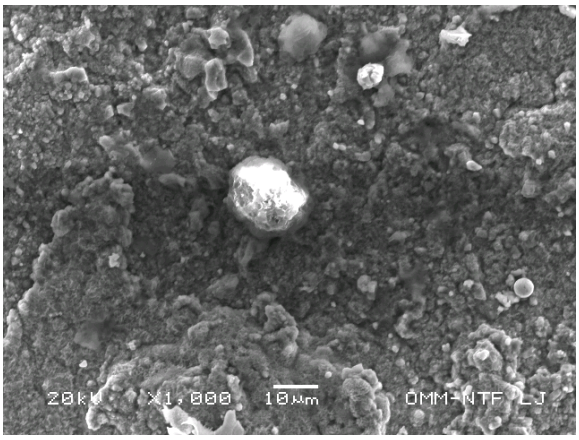
kV	20.0
Takeoff Angle	35.0°
Elapsed Livetime	100.0

(c)

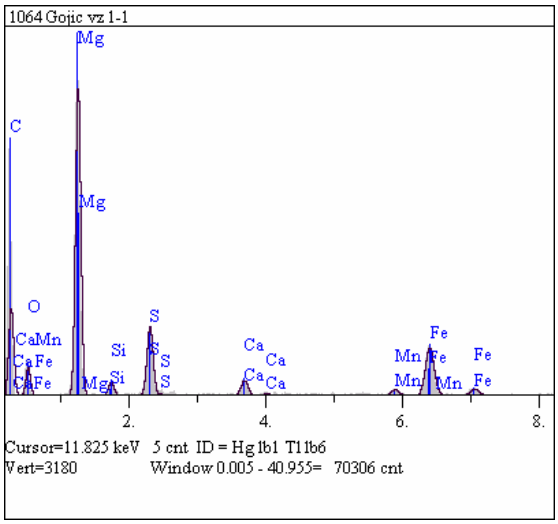
Slika 6. SEM mikrofraktografije (a, b) i EDS spektar (c) uključka na prijelomnoj površini osnovnog materijala CrMoNb čelika nakon ispitivanja udarne radnje loma



(a)



(b)

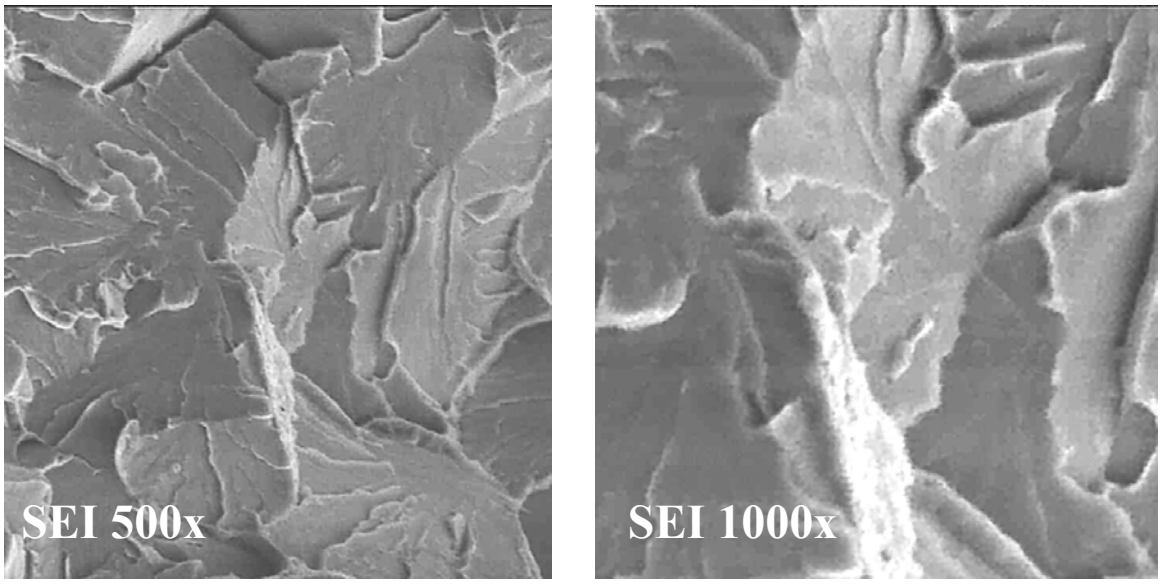


Elt.	Line	Intensity (c/s)	Error 2-sig	Atomic %	Conc		
C	Ka	69.39	1.666	66.748	47.893	wt.%	
O	Ka	20.43	0.904	10.803	10.325	wt.%	
Mg	Ka	260.37	3.227	14.900	21.634	wt.%	
Si	Ka	11.99	0.693	0.596	1.000	wt.%	
S	Ka	66.13	1.626	2.456	4.705	wt.%	
Ca	Ka	16.53	0.813	0.572	1.369	wt.%	
Mn	Ka	7.43	0.545	0.364	1.195	wt.%	
Fe	Ka	64.32	1.604	3.561	11.879	wt.%	
				100.000	100.000	wt.%	Total

kV	20.0
Takeoff Angle	35.0°
Elapsed Livetime	100.0

(c)

Slika 7. SEM mikrofraktografije (a, b) i EDS spektar (c) karbidne čestice na prijelomnoj površini zone taljenja CrMoNb čelika nakon ispitivanja udarne radnje loma



Slika 8. SEI mikrofraktografije prijelomne površine zone utjecaja topline CrMoNb čelika nakon ispitivanja udarne radnje loma

4. ZAKLJUČCI

Na temelju provedenih istraživanja mehaničkih svojstava i mikrostrukture prije i nakon plinskog zavarivanja niskolegiranog CrMoNb čelika može se zaključiti slijedeće:

- Nakon zavarivanja lima debljine 18 mm postignuta je vrlo niska udarna radnja loma zone taljenja (7,5 J) u odnosu na osnovni materijal (31,9 J).
- Osnovni materijal istraživanog čelika ima feritno-perlitnu mikrostrukturu. Nakon zavarivanja u zoni taljenja nastaje igličasta bainitna mikrostruktura.
- Fraktografskom analizom utvrđeno je da prijelomne površine osnovnog materijala uglavnom karakterizira sitnojamičasti prijelom s transkristalnim područjima. Mjestimično je u jamicama duktilnog prijeloma uočena prisutnost uključaka. Prijelom je započinjao na međupovršinama uključak/metalna osnova.
- Prijelomne površine zone taljenja sastoje se od kombinacije transkristalnog krhkog i sitnojamičastog duktilnog prijeloma. Prijelom je započinjao na međupovršinama karbid/metalna osnova. Zona utjecaja topline pokazuje primarno transkristalni ravni prijelom.

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THE EFFECT OF HARD SEGMENT CONTENT AND POLYOL TYPE ON THERMAL AND MECHANICAL PROPERTIES OF TPU/PC BLENDS

UTJECAJ UDJELA TVRDOG SEGMENTA I VRSTE POLIOLA NA TOPLINSKA I MEHANIČKA SVOJSTVA PU/PC MJEŠAVINA

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Izvorni znanstveni rad / Original scientific paper

Abstract: The miscibility of polyurethane / polycarbonate ,PU/PC, blends prepared by mixing of PU elastomers based on polyether and polyester polyol as a soft segments and different hard segments content with an amorphous PC was investigated.

Neat thermoplastic polyurethane (TPU), polycarbonate (PC) and TPU/PC blends with different weight ratios prepared in a Brabender mixer were investigated by differential scanning calorimetry (DSC) and by the universal tester for mechanical investigation. Differential scanning calorimetry (DSC) indicated partial crystalinity structure of the PU elastomers. PU elastomers based on polyether-type polyol show the higher degree of crystalization. Dynamic mechanical analysis (DMA) and tensile testing indicated partial miscibility of PU/PC blends. The miscibility obtained with polyester-type PU and with higher hard segment content was higher than that observed with polyeter-type PU, what was attributed to better interactions between ester groups from soft segments and urethane groups from the hard segments. In the blends with 70 wt. % of PC the formation of PU–PC copolymer by –OH of PC and ~NCO groups of PU interchange reaction was observed.

Keywords: polyurethane elastomers, polymer blends, polycarbonate, thermal properties, mechanical properties

Sažetak: Istražena je mješljivost PU/PC mješavina pripravljenih miješanjem PU elastomera s polieter i poliester poliolom uz različite udjele tvrdog segmenta i amorfnog PC. Mješavine su priređene miješanjem u talini u Brabender gnjetilici uz različit udio poliuretana i polikarbonata. Provedena je karakterizacija toplinskih i mehaničkih svojstava. Tehnikom diferencijalne pretražne kalorimetrije (DSC) dobivena je djelomična kristalna struktura PU elastomera. Veću kristalnost imaju PU elastomeri eterskog tipa poliola. Rezultati dinamičko mehaničke analize (DMA) i rasteznih svojstava ukazuju na djelomičnu mješljivost PU/PC mješavina. Dobivena je bolja mješljivost u PU/PC mješavinama esterskog tipa i uz veći udio tvrdog segmenta, zbog boljih interakcija između esterskih i uretanskih skupina.Kod mješavina sa 70 mas% PC dobiven je PU–PC kopolimer reakcijom –OH skupine od aromata iz PC-a i uretanske, ~NCO, skupine iz PU-a.

Ključne riječi: poliuretanski elastomeri,polimerne mješavine,polikarbonat,toplinska svojstva,mehanička svojstva

Introduction

Blending has been widely and effectively used to modify or control the properties of polymer by appropriately compounding miscible polymers. Miscible polymer blends can create new materials with completely different properties, and fabricated articles may possess good mechanical properties (1). Because the physical properties of polymer blends are influenced strongly by the blending conditions and processes that, in turn, affect the level of mixing of the blends, there is a growing interest in studying the miscibility and phase behaviour of polymer blends.

Polyurethanes (PU) are versatile materials used in a large number of application (2,3).Segmented polyurethanes are composed of alternating soft (low glass transition) segments and more rigid, polar urethane (hard) segments. The soft segments are generally polyethers (4-6) or polyesters (7,8) and the hard segments are formed from the extension of a diisocyanate terminated prepolymer with a low molecular weight diol. Depending on the soft segment or hard segment concentration the polymer has a continuous hard phase with a dispersed soft phase, a continuous soft phase with dispersed hard phase (9,10). The morphology developing during production, the miscibility of the phases, the size of the dispersed particles and their characteristics affect strongly the final properties of the polymer. Polycarbonate (PC) is a tough, transparent, impact-resistant thermoplastic polymer with a very wide range of service temperature. However, it suffers from its high melt viscosity, which causes difficulties in processing (e.g., injection molding), and its low fatigue strength, which generates cracks at points of concentrated residual stress. For these resons, blends of PU and PC are expected to usefully combine the properties of the parent polymers. The objectives of the present work is the study of the thermal and mechanical behaviour of neat polyurethane (PU),neat polycarbonate (PC) and their blends PU/PC.

Experimental

Synthesis of PUR prepolymers

The PUR prepolymer was prepared at 80°C under a nitrogen atmosphere in a stirred-glass reaction kettle. The diisocyanates (MDI) was charged into the kettle first and heated up to 80°C. Then an appropriate amount of polyol (PTMO) was added, NCO/OH ratios of 2/1 (35 % NCO/OH) and 4/1 (52% NCO/OH) were employed. The reaction was considered competed when the experimental value of the NCO concentration and the calculated value, were within one percent. The NCO content of isocyanates and prepolymers was measured by the di-(n-butyl) amine titration method.

Preparation of polyurethane elastomers

A chain extender 1,4-butanediol (1.4-BD) was added to the prepolymer with intensive mixing at a temperature of 90°C. After 60 s of mixing, the reaction mixture was immediately poured into a preheated teflon-coated aluminium mould This mixture was then heated to 100°C in a Carver hydraulic platen press for about 30 min. The elastomers were postcured in an oven for 24h at 105°C immediately after molding.

Preparation of polyurethane /polycarbonate blends

The neat polymers (TPU and PC) and their blends (TPU/PC blends) were prepared in a Brabender mixer using a temperature of 210 ; 180 and 190°C for PC, PU and PU/PC blends, respectively with a screw speed of 45 rpm. Then, the specimens were compression moulded in a hydraulic press (Dake Model 44-226) at 230 ^{o}C .

Dynamic Mechanical measurements

Dynamic Mechanical measurements were performed on a Dynamic Mechanical Analyser DMA 983, TA Instruments, at a frequency of 1 Hz. The changes of loss (E'') moduli were measured over the temperature range of -100 to 250°C at a heating rate of 5°C/min. The sample length between the clamps was approximately 25 mm. All the samples were cooled to –100°C using liquid nitrogen. The miscibility of the PU/PC blends is characterized also by employing DMA technique.

Mechanical measurements

Mechanical measurements were performed on a Zwick Universal testing machine (model 1445) in uniaxial tension mode at 23°C and 65% of relative humidity.
Tests were performed at a crosshead speed of 50.00 mm / min. At least five test specimens of 30.00 mm x 13.0 mm x 3.5 mm were tested for each blend and average values were calculated.

RESULTS AND DISCUSSION

Dynamic mechanical analysis of the blends

DMA spectra on binary blends can provide information on the degree of polymer-polymer interaction and interphase mixing.
The DMA curves for the loss modulus versus temperature (E"/T) of neat PU elastomers ,neat PC and PU/PC blends prepared from the polyether (PU ET) and polyester (PU ES) as the soft segment with varying isocyanate content (NCO/OH 2/1 and 4/1) and with various compositions (PU/PC 30/70; 50/50 and 70/30) are shown in Figures 1 and 2, the DMA results are summerized for various compositions in Table 1.

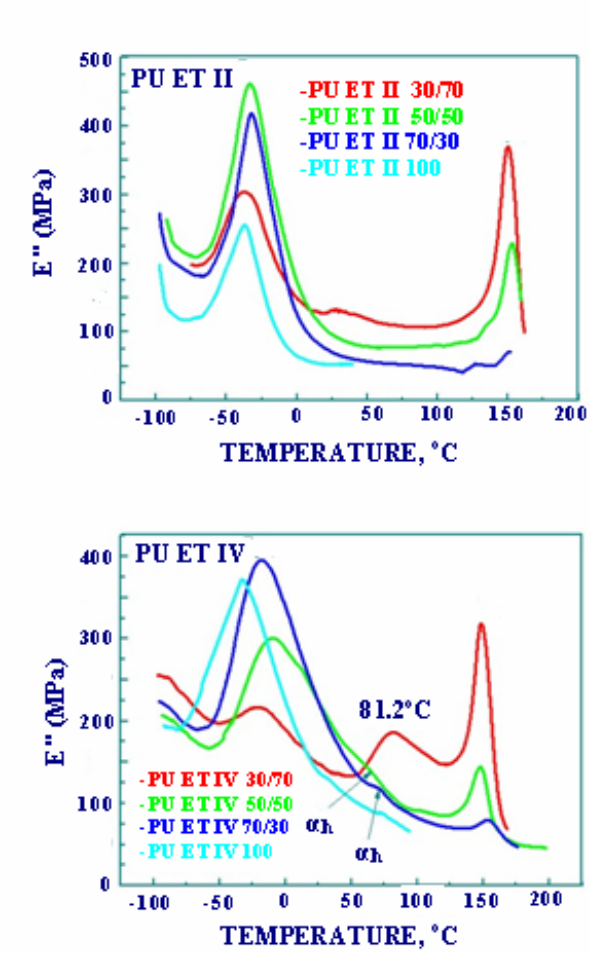


Fig.1. Curves of loss (E") versus temperature for PU/PC blends.

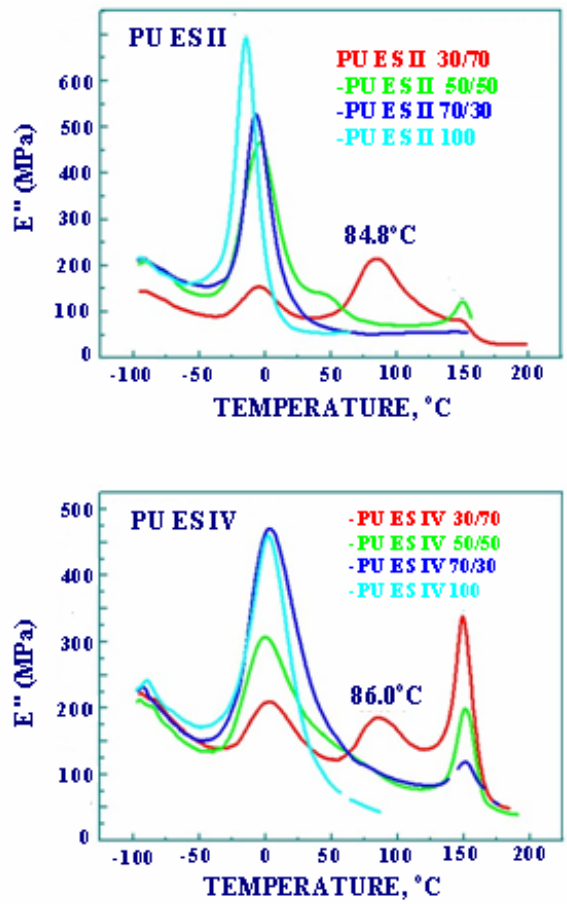


Fig.2. Curves of loss (E") versus temperature for PU/PC blends

The soft segment T_g in neat PU elastomers was found below 0°C and depends on the hard segment content and type of the soft segment.

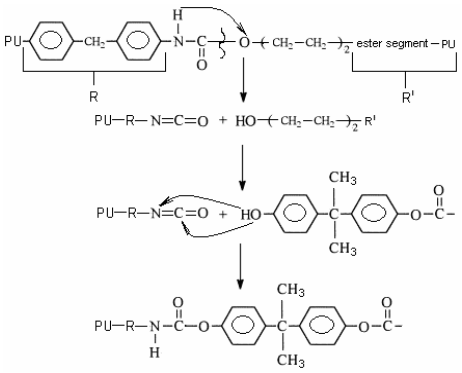
The T_g value for the polyether PU elastomers with lower hard segment content (PU ET II) remains the same value as that of the polyether PU elastomer with higher hard segment content (PU ET IV) -37.0°C. This was attributed to the restricted chain mobility of the soft segments with the increasing NCO/OH ratio (11). The weak interactions between the ether oxygen in the soft segment and the urethane groups in the hard segment of the polyurethane may lead to the phase separation between the hard and soft segments in the polyurethane. On the other hand, the interactions between the urethane groups and the ester carbonyl groups in the polyester polyurethane (PU ES) are higher and therefore the T_g increases, also T_g increased with increasing content of the hard segments (PU ES IV). As we can see in Figures 1 and 2 is a relaxation of neat PC at 154.4 °C while neat PU ET II, ET IV, ES II and ES IV show a T_g at -37.1 , -37.7 , -14.6 and 2.2 °C, respectively, as shown by the temperature dependence plots of the loss modulus E'' . The curve of PU/PC blends show primary relaxations intermediate between those of neat components. As we can see in Table 1, there is a systematic shift of the T_g of the blends with the composition, the T_g values increases with increasing NCO/OH and PC content in the PU/PC blends of polyether (PU ET) and polyester (PUES) soft segments compared to neat polyether and polyester PU. The T_g's maxima of the PU broadened and decreased its intensity more in polyether than in polyester PU (Figure 1).The PC glass transition temperature in all investigated PU/PC blends

were shifted to lower temperature. In general, the shift in the polyurethane T_g is more significant than the shift for the polycarbonate (Table1). According to the obtained results the changes are much higher for PU/PC blends with polyester polyurethane (Fig. 2, Table 1). One possible explanation can be that urethane groups of PU may interact with carbonyl groups from PC (12). The T_g's maxima of the PU and PC phases shift towards to each other as the composition changes. This shift of the T_gs gives an indication of possible partial miscibility of the PU and PC chains.

Table 1. Dynamic mechanical properties of neat components and PU/PC blends.

PU elastomers	T_{gPC} (°C)	T_{gPU} (°C)	$I_{E"PC}$ (MPa)	$I_{E"PU}$ (MPa)
PU ET II		**-37.1**		**255.8**
PU ET IV		**-37.7**		**376.7**
PU ES II		**-14.6**		**693.1**
PU ES IV		**2.2**		**459.8**
PC 100	**154.4**		**1001**	
PU/PC Blends				
PU ET II				
PU/PC 70/30	**151.8**	**-32.1**	**71.07**	**417.8**
PU/PC 50/50	**152.9**	**-33.2**	**227.7**	**461.5**
PU/PC 30/70	**150.1**	**-35.7**	**369.9**	**304.1**
PU ET IV				
PU/PC 70/30	**152.8**	**-18.4**	**79.79**	**395.4**
PU/PC 50/50	**147.8**	**-7.9**	**144.4**	**300.7**
PU/PC 30/70	**148.7**	**-16.3**	**316.3**	**216.4**
PU ES II				
PU/PC 70/30	**147.5**	**-7.1**	**56.67**	**527.3**
PU/PC 50/50	**150.1**	**-4.0**	**121.9**	**465.8**
PU/PC 30/70	**148.3**	**-4.2**	**154.4**	**214.4**
PU ES IV				
PU/PC 70/30	**151.4**	**3.4**	**118.7**	**471.0**
PU/PC 50/50	**151.2**	**0.0**	**198.4**	**307.3**
PU/PC 30/70	**149.1**	**3.1**	**209.5**	**333.1**

The new relaxation maxima around 80°C was detected only in DMA curves of PU ET IV 30/70; PU ES II 30/70 and PU ES IV 30/70 blends. This new relaxation maxima was attributed to interactions (chemical) at the interface of PC-PU and partial miscibility of the PU and PC . In this PU/PC blends the PC-PU copolymer was result of reaction between the –OH groups from aromatic of PC and the –NCO– groups of PU. The sequence of reactions that may take place is summarized in Sheme 1.



The results of stress-strain behavior of neat components (PU elastomers and PC) and their blends (PU/PC; 70/30, 50/50 and 30/70) with various NCO/OH ratio and polyether and polyester polyol are listed in Table 2.

Table 2 shows that for the blends, the tensile strength (σ_R) increase and elongation at break (ε_R) decrease as the hard segment content is increased compared with the neat PU elastomers (Table 2). The tensile strength was higher and elongation at break was lower for PU/PC polyester blends (PU ES) than those of PU/PC polyether blends (PU ET) for both NCO/OH ratio (2/1 and 4/1), except for PU/PC 70/30 blend. The Young modulus (E) increases as the hard segment content increases in both type of PU elastomers.The obtained results ndicate that the PU/PC blends with higher NCO/OH ratio and with the polyester soft segment shows better miscibility, these mechanical results are in good agreement with those obtained by DMA.

Table2.Tensile properties of neat components and PU/PC blends.

PU elastomers	σ_R **(MPa)**	ε_R **(%)**	**E(MPa)**
PU ET II	**3.5**	**36.0**	**22.92**
PU ET IV	**14.1**	**25.0**	**260.12**
PU ES II	**2.3**	**38.0**	**18.10**
PU ES IV	**13.6**	**36.0**	**181.11**
PC	**28.3**	**2.0**	**1716.8**
PU/PC blends			
PU ET II			
PU/PC 70/30	**3.6**	**12.0**	**124.10**
PU/PC 50/50	**4.8**	**6.0**	**480.86**
PU/PC 30/70	**16.6**	**3.0**	**1090.79**
PU ET IV			
PU/PC 70/30	**13.0**	**19.0**	**180.95**
PU/PC 50/50	**18.7**	**4.0**	**692.10**
PU/PC 30/70	**20.4**	**2.0**	**1222.44**
PU ES II			
PU/PC 70/30	**12.8**	**22.8**	**136.08**
PU/PC 50/50	**10.8**	**3.0**	**424.46**
PU/PC 30/70	**21.3**	**2.0**	**950.23**
PU ES IV			
PU/PC 70/30	**13.6**	**36.0**	**181.11**
PU/PC 50/50	**13.3**	**5.0**	**457.85**
PU/PC 30/70	**24.8**	**2.0**	**1239.11**

Conclusions

In this study, the blends of PU and PC were prepared by melt mixing in Brabender mixer. DMA study revealed that higher concentration of the hard segment results in increased T_g and decreased mobility of the soft segment in PU elastomers.

The results also indicate an increase of T_g of polyester -based PU elastomers (PU ES) in comparasion with T_g of polyether- based PU elastomers (PU ET) because of better interactions between the urethane groups and the ester carbonyl groups in the polyester polyurethane.

The results from DMA measurements showed that the PU/PC blends exhibited two separate T_gs which shift towards to each other demonstrating that PU and PC formed a partial miscible blend, these results may be explained in terms that urethane groups of PU may interact with carbonyl groups from PC.

The results of mechanical properties measurements showed that the higher hard segment content and PC concentration increased tensile strength but decreased elongation

at break of the all investigated PU elastomers (PU/ET and PU/ES) and PU/PC blends (70/30, 50/50 and 30/70).

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TLAČNO ISPITIVANJE ALUMINIJSKIH PJENA

COMPRESSION TESTING OF ALUMINIUM FOAMS

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Stručni članak / Professional paper

Sažetak: Pjene općenito, kao i aluminijske pjene imaju mnoga povoljna svojstva zahvaljujući njihovoj poroznoj strukturi što ih čini pogodnima za mnoge primjene. Mogućnost apsorpcije energije je jedno od najzanimljivijih uporabnih svojstava pjena. Primjena lakih poroznih materijala visoke čvrstoće u transportnoj industriji je sve zanimljivija u pogledu povećanja sigurnosti. Aluminijske pjene se sve češće koriste kao različiti apsorberi kinetičke energije (odbojnici automobila, vlakova, tramvaja). U ovom radu istraživan je utjecaj kemijskog sastava, gustoće i oblika aluminijske pjene na ponašanje pri tlačnom opterećenju.

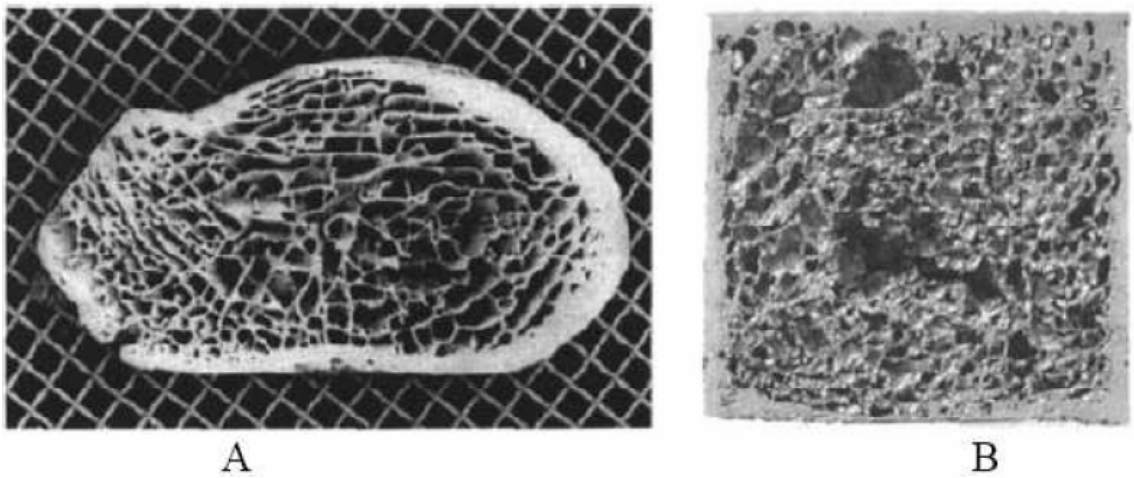
Ključne riječi: aluminijska pjena, tlačno ispitivanje, apsorpcija energije

Abstract: Foamed materials in general, and aluminium foams in particular, demonstrate a number of interesting properties due to their porous structure, which makes them usable in a wide range of applications. Possibility of absorbing the energy is one of the most interesting properties of foams. The use of lightweight porous materials with high specific strength has attracted much interest in the transportation industry in order to improve safety. Recently, foamed aluminium is frequently used in various absorbers of kinetic energy (buffers of automobiles, trains, trams). This paper studies the influence of chemical composition, density and shape of aluminium foams on compression behaviour.

Keywords: aluminium foam, compression test, absorption of energy

1. UVOD

Metalne pjene predstavljaju potpuno novi oblik metalnih materijala koji je još uvijek relativno nepoznat inženjerima. Iako su prvi patenti na ovom području prijavljeni prije 50-tak godina intenzivna istraživanja metalnih pjena počela su tek unazad 10-tak godina. To su porozni metalni materijali ispunjeni šupljinama (ćelijama) koje mogu varirati po obliku (otvorene, zatvorene) i veličini.
Kao što je već prije navedeno mogućnost apsorpcije energije udara jedno je od najvažnijih uporabnih svojstava metalnih pjena. Posebno je izražen interes u transportnoj industriji jer mnogi dijelovi vozila mogu biti izloženi udarnim opterećenjima. Ovo svojstvo zanimljivo je i kod pakirne ambalaže koja je prilikom transporta također izložena udarnim opterećenjima, [1].



Slika 1 - Prikaz strukture kosti (A) i metalne pjene (B), [2]

Metalne pjene mogu se proizvesti iz gotovo svih vrsta metala koji postoje u obliku praha, no zbog ranog stadija istraživanja komercijalno su danas najčešće dostupne metalne pjene na bazi aluminija (Al) i nikla (Ni). Po posebnoj narudžbi proizvode se i pjene na bazi magnezija (Mg), olova (Pb), cinka (Zn), bakra (Cu), bronce, titana (Ti), čelika pa čak i zlata (Au), [1]

Osnovna svojstva metalnih pjena su:

- niska gustoća (masa),
- relativno visoka krutost,
- dobra izolacijska svojstva (zvuk, toplina),
- negorivost,
- odlična apsorpcija energije udara itd.

2. APSORPCIJA ENERGIJE UDARA

Primjena lakih poroznih materijala visoke čvrstoće u transportnoj industriji je sve zanimljivija u pogledu povećanja sigurnosti, [3]. Aluminijske pjene se sve češće koriste kao različiti apsorberi kinetičke energije (odbojnici automobila, vlakova, tramvaja) [4]

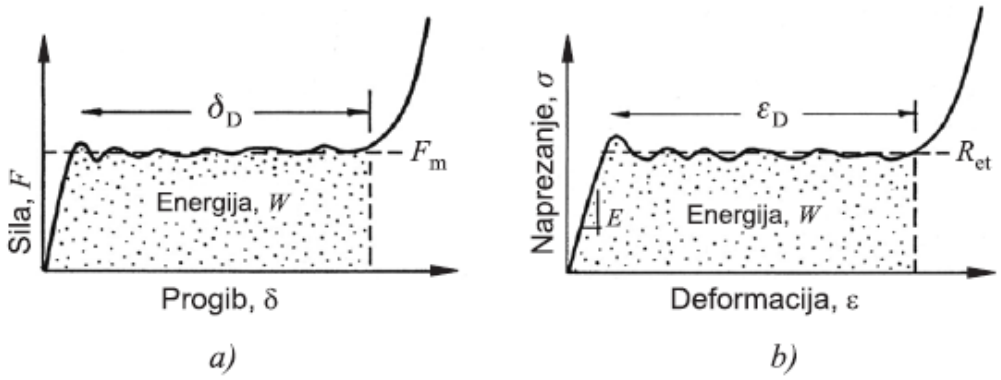
Apsorpcija energije udara po jedinici volumena (W) može se prikazati sljedećom relacijom:

$$W = \int_0^{\varepsilon} \sigma(\varepsilon) d\varepsilon$$

Gdje je:

W – apsorbirana energija udara po jedinici volumena (MJ/mm^3) ili (N/mm^2)
σ – tlačno naprezanje (N/mm^2)
ε – deformacija (%)

Tu je bitno da granica stlačivanja (R_{et}) bude tek nešto manja od naprezanja pri kojem dolazi do loma materijala, odnosno do dosizanja kritične deformacije zgušnjavanja (ε_D). Površina ispod krivulje R_{et} – ε_D pokazuje kolika se količina energije udara može apsorbirati (slika 2).



Slika 2 - Krivulje koje prikazuju apsorpciju energije pri savijanju a) i tlaku b), [1]

3. EKSPERIMENTALNI DIO

U radu su ispitivane dvije vrste aluminijskih pjena sa zatvorenim ćelijama:

- ALULIGHT AlSi 10 TiH_2 -0,8
- ALULIGHT AlMgSi 0,6 TiH_2 -0,4

Za izradu uzoraka korištena je tehnologija plinom oslobonenih čestica rastvorenih u polučvrstoj fazi. Uzorci su izrađeni u Laboratoriju za toplinsku obradu Fakulteta strojarstva i brodogradnje u Zagrebu, a korištena je elektrootporna peć snage 10 kW
Slika 3 prikazuje uzorke aluminijskih pjena.

Slika 3 - Uzorci aluminijskih pjena različite gustoće i materijala stjenke

Tablica 1 - Uzorci aluminijskih pjena kvadratnog presjeka

Naziv	470 MAT x 1	470 MAT x 2	470 MAT x 3	470 SJAJ x 1	470 SJAJ x 2	470 SJAJ x 3	600 SJAJ x 1	600 SJAJ x 2	600 SJAJ x 3
Dimenzije (mm)	76 x 76 x 100								
Materijal	ALULIGHT AlSi 10 TiH_2 – 0,8			ALULIGHT AlMgSi 0,6 TiH_2 – 0,4					
Masa (kg)	0,47	0,47	0,47	0,47	0,47	0,47	0,60	0,60	0,60
Gustoća (g/cm^3)	0,81	0,81	0,81	0,81	0,81	0,81	1,04	1,04	1,04

Tablica 2 - Uzorci aluminijskih pjena okruglog presjeka

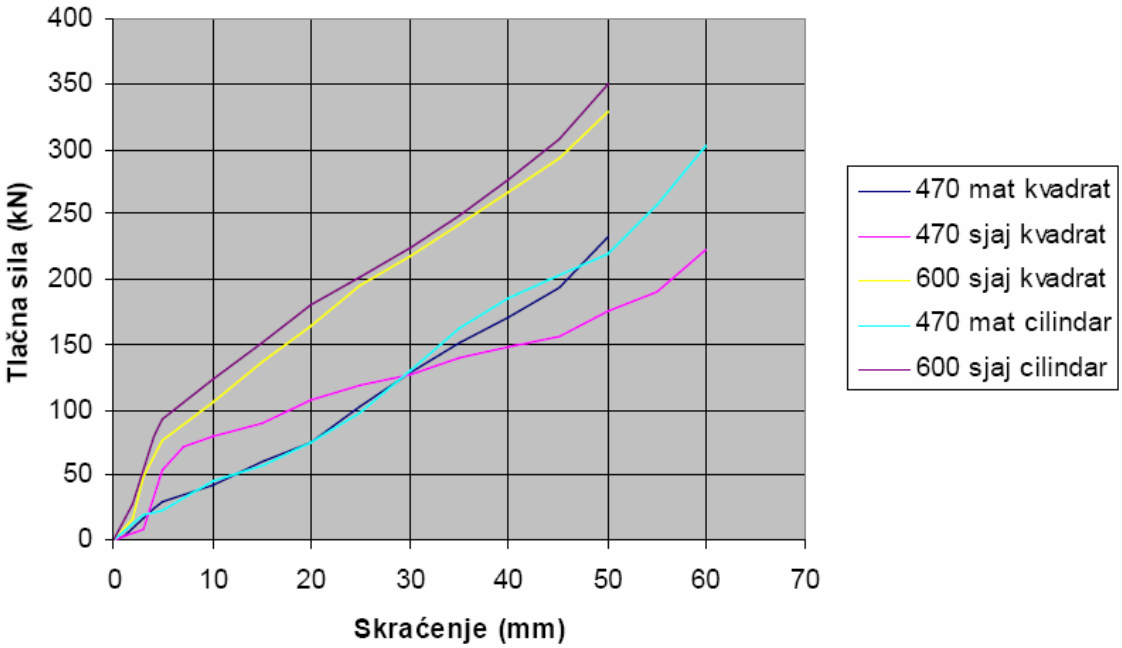
Naziv	470 MAT x 1	470 MAT x 2	470 MAT x 3	600 SJAJ x 1	600 SJAJ x 2	600 SJAJ x 3
Dimenzije (mm)	Ø 84,9 x 100					
Materijal	ALULIGHT AlSi 10 TiH_2 – 0,8			ALULIGHT AlMgSi 0,6 TiH_2 – 0,4		
Masa (kg)	0,47	0,47	0,47	0,60	0,60	0,60
Gustoća (g/cm^3)	0,83	0,83	0,83	1,07	1,07	1,07

Ispitivanje je provedeno u Laboratoriju za ispitivanje mehaničkih svojstva na Fakultetu strojarstva i brodogradnje u Zagrebu. Za ispitivanje se koristila kidalica marke WPM, model EU 40 mod., maksimalne tlačne sila od 400 kN. Brzina ispitivanja iznosila je 6 mm/min. Na slici 4 prikazan je tijek ispitivanja uzorka.

Slika 4 – Ispitivanje uzoraka

Slika 5 – Uzorci nakon statičkog tlačnog pokusa

Na slici 6 prikazane su srednje vrijednosti dobivenih dijagrama „tlačno naprezanje – relativno skraćenje“ svih uzoraka.



Slika 6 – Srednje vrijednosti dijagrama „tlačno naprezanje – relativno skraćenje“

Iz slike 6 vidljivo je podudaranje krivulja naprezanje – skraćenje za uzorke oznaka 600 sjaj cilindar i 600 sjaj kvadrat, kao i za krivulje uzoraka oznaka 470 mat kvadrat i 470 mat cilindar. Budući da ti uzorci imaju međusobno različite oblike poprečnog presjeka može se zaključiti da oblik poprečnog presjeka uzoraka aluminijske pjene ne utječe na rezultate tlačnog ispitivanja. Krivulje uzoraka oznaka 470 sjaj kvadrat i 470 mat kvadrat se međusobno razlikuju pri čemu krivulja uzorka 470 sjaj kvadrat ima oblik koji pokazuje bolju mogućnost apsorpcije energije. Uzorci oznaka 600 sjaj kvadrat i 600 sjaj cilindar imaju krivulje koje dostižu više vrijednosti naprezanja nego je to prisutno kod ostalih uzoraka.

4. ZAKLJUČAK

Statičkim tlačnim pokusom utvrđeno je različito ponašanje aluminijskih pjene pri tlačnom opterećenju u ovisnosti o njihovoj gustoći i kemijskom sastavu. Prema obliku krivulja naprezanje – skraćenje ustanovljeno je da pjene niže gustoće pri jednakom naprezanju mogu apsorbirati više energije uz veće relativno skraćenje kao i da ALULIGHT AlMgSi 0,6 TiH_2 - 0.4 pjena ima oblik krivulje naprezanje - skraćenje koji pokazuje bolju mogućnost apsorpcije energije od ALULIGHT AlSi 10 TiH_2 – 0,8 pjene iste gustoće. Prema dobivenim rezultatima nema značajnijeg utjecaja oblika poprečnog presjeka.

Zahvala

Prikazani rezultati su nastali u okviru projekta „Prototip uređaja za zaštitu od stražnjeg i bočnog podlijetanja na teretnim vozilima" programa TEST – Tehnologijski istraživačko-razvojni projekti. Zahvaljujemo na potpori Ministarstvu znanosti, obrazovanja i športa.

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[3] S:Y: Kim, B.Y. Hur, K.C. Kwon, S.H. Cho, C.Y. Lim, Y.M. Yoo, M.H. Lee: "Mechanical and sound absorption properties of closed cell Al foam by pot furnace method", International Conference on Cellular Metals and Metal Foaming Technology METFOAM 2003, Berlin

[4] V.I. Lebedev, V.I. Komov, D.A. Andreev: "Ability of constructions from foamed aluminium to absorb different konds of energy", International Conference on Cellular Metals and Metal Foaming Technology METFOAM 2003, Berlin

PONAŠANJE ALUMINIJSKIH PJENA I RAZLIČITIH ČELIČNIH CIJEVI PRI TLAČNOM OPTEREĆENJU

BEHAVIOUR OF ALUMINIUM FOAMS AND DIFFERENT STEEL TUBES DURING COMPRESSION

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[2] PLIVA Hrvatska d.o.o., Prilaz baruna Filipovića 25, Zagreb
[3] Tehnička škola Zadar, Nikole Tesle 9c, Zadar

Pregledni članak / Subject review

Sažetak: Pjene općenito, kao i aluminijske pjene imaju mnoga povoljna svojstva zahvaljujući njihovoj poroznoj strukturi što ih čini pogodnima za mnoge primjene. Mogućnost apsorpcije energije udara je jedno od najzanimljivijih uporabnih svojstava pjena. Pri tlačnom naprezanju metalne pjene pokazuju specifičnu ovisnost naprezanja i deformacije pri čemu tijekom opterećivanja postoji gotovo konstantno naprezanje pri velikom dijelu deformacije. U ovom radu prikazani su dijagrami "sila - skraćenje" za nekoliko oblika uzoraka čiji su sastavni dijelovi i aluminijske pjene.

Ključne riječi: aluminijska pjena, tlačno ispitivanje, apsorpcija energije

Abstract: Foamed materials in general, and aluminium foams in particular, demonstrate a number of interesting properties due to their porous structure, which makes them usable in a wide range of applications. The capability of absorbing the impact energy is one of the most interesting properties of foams. Under compression, foamed materials show a unique stress – strain response with a plateau region in which the stress is nearly constant over a wide range of strain. This paper studies the behaviour of aluminium foams and different steel tubes during compression.

Keywords: aluminium foam, compression test, absorption of energy

1. UVOD

U prirodi postoji mnogo ćelijastih materijala, kao što su drvo, kamen, kost, koralj i sl. Metalne pjene su pokušaj oponašanja takvih građa i struktura za tehničke uvjete primjene. Njihova glavna karakteristika je visoka poroznost koja se kreće od 40 do 90%. Uz to, oblik, veličina i vrsta osnovnog materijala bitno određuju njihova svojstva.
Metalne pjene predstavljaju relativno novi oblik metalnih materijala koji su još uvijek nedovoljno poznati inženjerima i znanstvenicima. Intenzivna istraživanja počela su unatrag 10 – tak godina, iako su prvi patenti prijavljeni još 50 – tih godina prošlog stoljeća. Metalne pjene izrađuju se novim procesnim tehnikama koje se iz dana u dan razvijaju i unapređuju. Neki od tih postupaka još nisu u potpunosti dorađeni i kvantitativno opisani, te nije usavršeno upravljanje procesima izrade [1].

2. APSORPCIJA ENERGIJE UDARA

Primjena lakih poroznih materijala visoke čvrstoće u transportnoj industriji je sve zanimljivija u pogledu povećanja sigurnosti [2]. Aluminijske pjene se sve češće koriste kao različiti apsorberi kinetičke energije (odbojnici automobila, vlakova, tramvaja) [3].

Apsorpcija energije udara po jedinici volumena (W) može se prikazati sljedećom relacijom:

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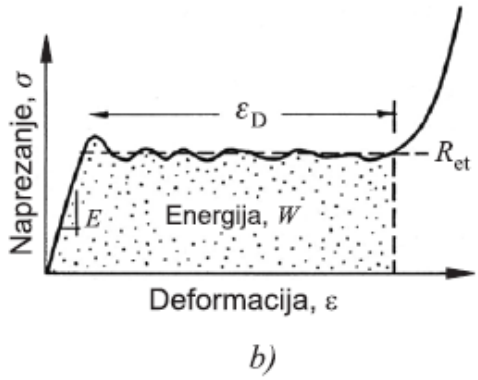
gdje je:

W – apsorbirana energija udara po jedinici volumena (MJ/mm^3) ili (N/mm^2)
σ – tlačno naprezanje (N/mm^2)
ε – deformacija (%)

Tu je bitno da granica stlačivanja (R_{et}) bude što izraženija odnosno da se postigne stlačivanje pri gotovo konstantnom naprezanju i da granica stlačivanja bude tek nešto manja od naprezanja pri kojem dolazi do loma materijala, odnosno do dosizanja kritične deformacije zgušnjavanja (ε_D). Površina ispod krivulje $R_{et} - \varepsilon_D$ pokazuje kolika se količina energije udara može apsorbirati, slika 1.



Slika 1 - Krivulja koje prikazuju apsorpciju energije pri tlačnom opterećenju [1]

3. EKSPERIMENTALNI DIO

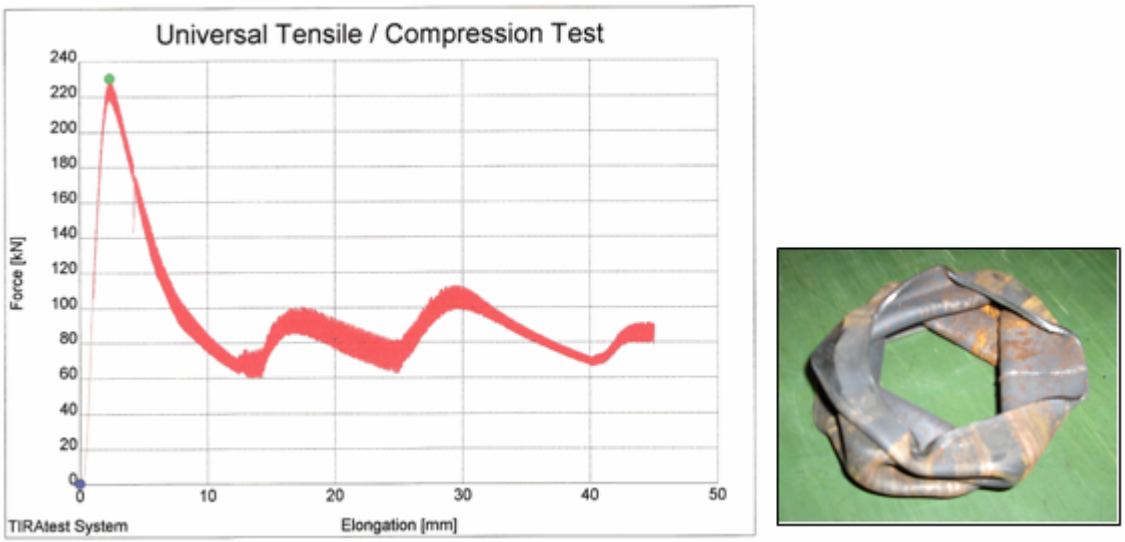
Za izradu uzoraka aluminijske pjene korištena je elektrootporna peć snage 2,5 kW koja se nalazi u Laboratoriju za nemetale, Fakulteta strojarstva i brodogradnje u Zagrebu. Na slici 2 je prikazan postupak izrade uzoraka aluminijske pjene. Određena masa prekursora se stavlja u kalup, a kalup se stavlja u peć na temperaturu od 850°C gdje se drži određeno vrijeme koje je potrebno za upjenjavanje.

Slika 2 – Postupak izrade uzoraka metalne pjene

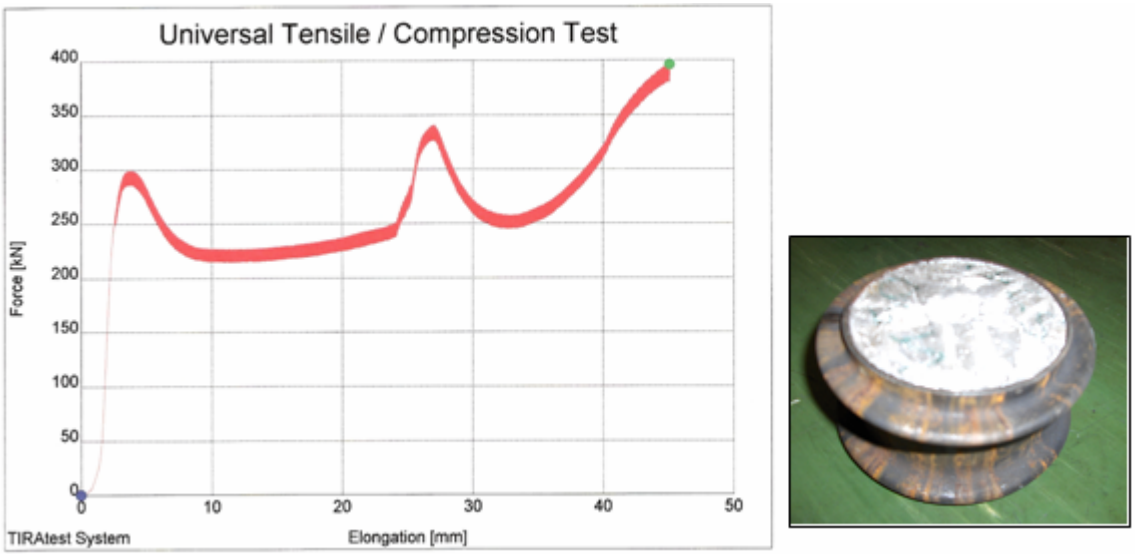
Određivanje apsorpcije energije provedeno je u Laboratoriju za ispitivanje mehaničkih svojstva na Fakultetu strojarstva i brodogradnje u Zagrebu. Za ispitivanje se koristila kidalica proizvođača WPM, Njemačka, model EU 40 mod, nazivne sile od 400 kN, slika 3. Brzina pomaka iznosila je 6 mm/min.

Slika 3 – Kidalica na kojoj su stlačivani uzorci

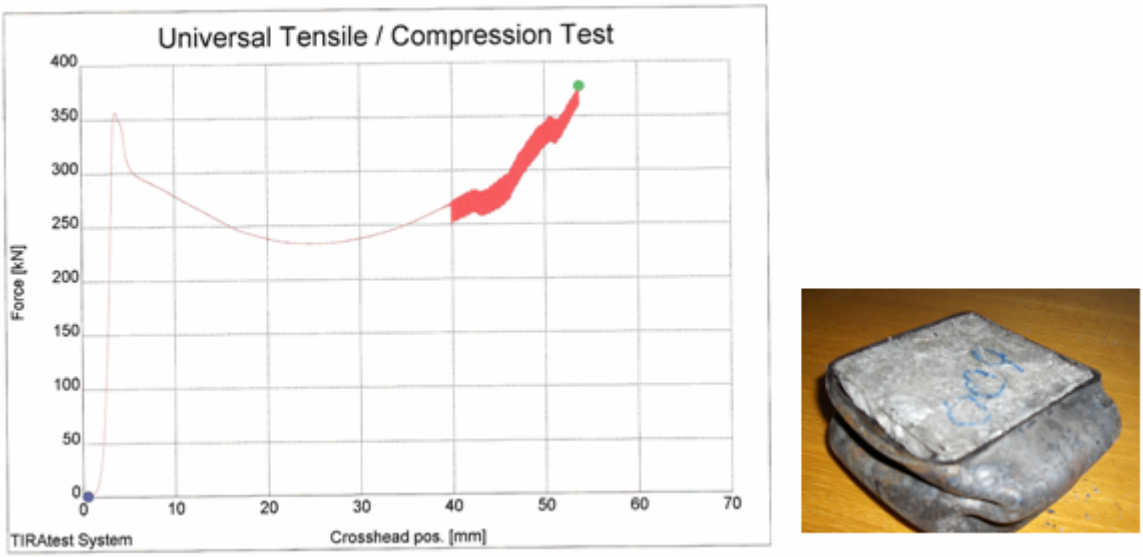
Da bi se pokazala sposobnost apsorpcije energije metalnih pjena provedeno je tlačno ispitivanje čelične cijevi, čelične cijevi ispunjene aluminijskom pjenom te same aluminijske pjene. Na slikama 4 do 10 prikazani su dijagrami sila – skraćenje i oblik različitih uzoraka nakon stlačivanja.



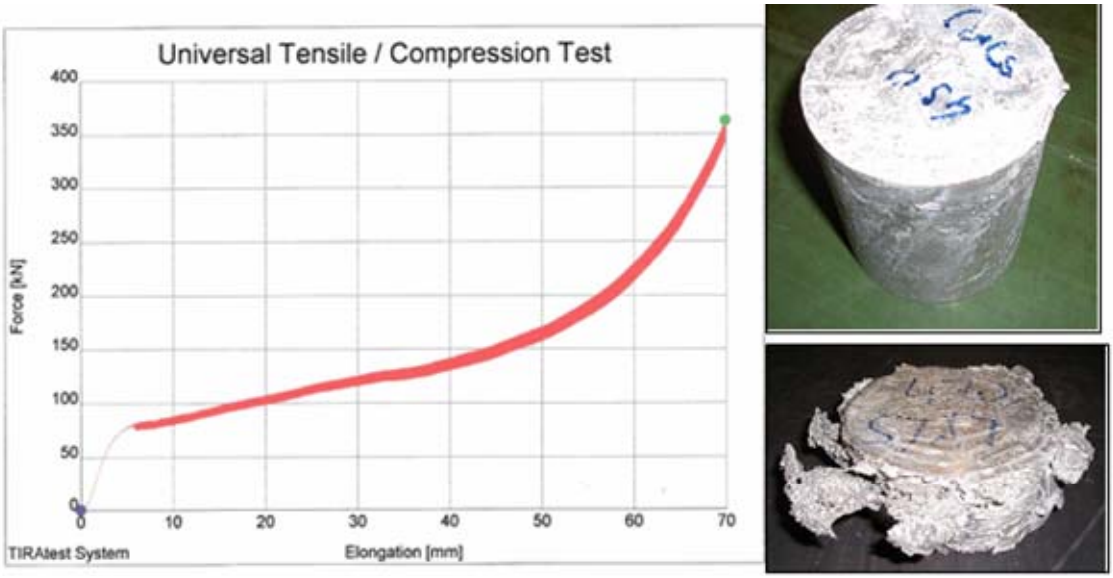
Slika 4 - Dijagram sila – skraćenje čelične cijevi (sila djeluje aksijalno)



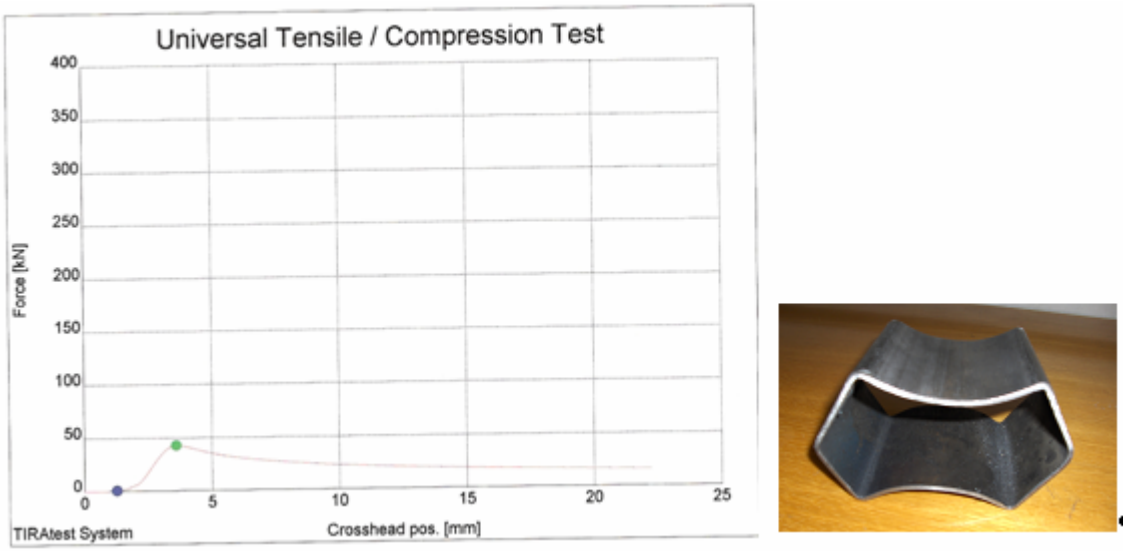
Slika 5 - Dijagram sila – skraćenje čelične cijevi (okrugla) s Al pjenom (sila djeluje aksijalno)



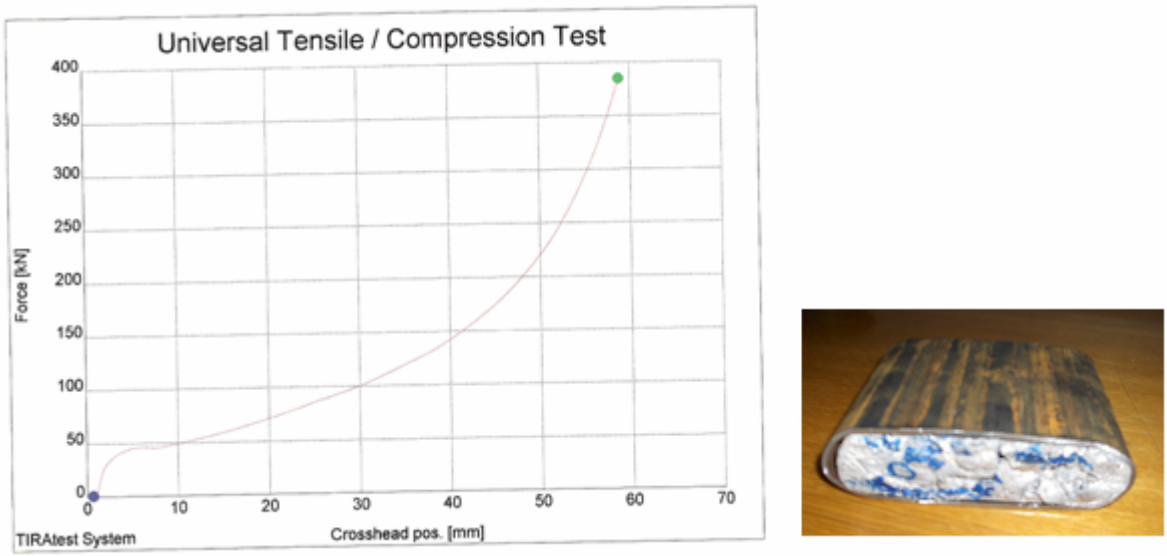
Slika 6 - Dijagram sila – skraćenje čelične cijevi (kvadratna) s Al pjenom (sila djeluje aksijalno)



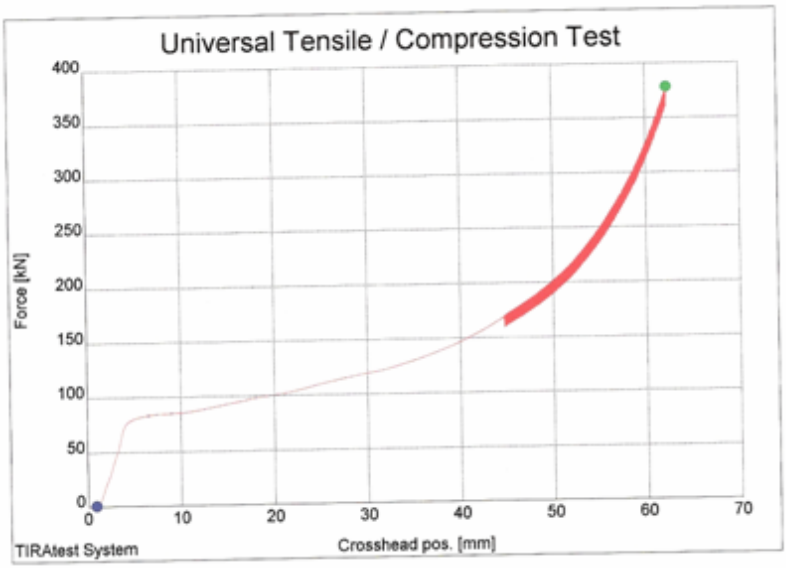
Slika 7 - Dijagram sila – skraćenje Al pjene (sila djeluje aksijalno)



Slika 8 - Dijagram sila – skraćenje čelične cijevi (sila djeluje radijalno)



Slika 9 - Dijagram sila – skraćenje čelične cijevi (okrugla) s Al pjenom(sila djeluje radijalno)



Slika 10- Dijagram sila – skraćenje čelične cijevi (kvadratna) s Al pjenom (radijalna sila)

Na slikama 5 i 6 vidljivo je da pri aksijalnom tlačenju aluminijske pjene, čelična cijev u kojoj se pjena nalazi u apsorpcijskom smislu nepovoljno utječe na oblik dijagrama sila – skraćenje. Pri radijalnom opterećenju i uz prisutnost čelične cijevi zadržan je oblik dijagrama koji pokazuje dobro apsorpcijsko svojstvo.

4. ZAKLJUČAK

Statičkim tlačnim pokusom utvrđeno je da aluminijske pjene imaju dobra svojstva pri apsorpciji energije. Pri statičkom tlačnom pokusu niti jedan ispitani uzorak nije imao u potpunosti istaknutu fazu deformacije pri konstantnom opterećenju. Tome konstantnom opterećenju najviše se približio uzorak koji se je sastojao samo od aluminijske pjene. Pri aksijalnom tlačenju aluminijske pjene, čelična cijev u kojoj se pjena nalazi u apsorpcijskom smislu nepovoljno utječe na oblik dijagrama sila – skraćenje. Pri radijalnom opterećenju i uz prisutnost čelične cijevi zadržan je oblik dijagrama koji pokazuje dobro apsorpcijsko svojstvo.

Zahvala

Prikazani rezultati su nastali u okviru projekta „Prototip uređaja za zaštitu od stražnjeg i bočnog podlijetanja na teretnim vozilima" programa TEST – Tehnologijski istraživačko-razvojni projekti. Zahvaljujemo na potpori Ministarstvu znanosti, obrazovanja i športa.

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ABRAZIJSKA I UDARNA EROZIJA IZOTERMIČKI POBOLJŠANOG NODULARNOG LIJEVA

ABRASION AND IMPACT EROSION OF AUSTEMPERED DUCTILE IRON

Krešimir Grilec, Tomislav Sabolić
Faculty of Mechanical Engineering and Naval Architecture, Ivana Lučića 5, Zagreb

Prethodno priopćenje / Preliminary note

Sažetak: Erozija česticama je gubitak materijala s površine krutog tijela zbog relativnog gibanja (strujanja) fluida u kojem se nalaze krute čestice. Erozija kod koje je strujanje pod malim kutom u odnosu na površinu (manjim od 30°) naziva se abrazivna erozija, a kad čestice udaraju o površinu gotovo okomito (60° do 90°) to je udarna erozija.
Jedna od prednosti nodularnog lijeva u odnosu na druge ljevove je njegova dobra otpornost na trošenje. Ipak treba imati na umu da ta otpornost ovisi i o uvjetima trošenja. Kad se govori o otpornosti na erozijsko trošenje krutim česticama, ta otpornost značajno ovisi o kutu udara čestica. U ovom radu ispitivana je otpornost na erozijsko trošenje pri dva kuta upada čestica (15 i 90°) te s tri vrste abraziva (kvarcni pijesak, čelične kuglice promjera 700 μm i 1100 μm).

Ključne riječi: nodularni lijev, izotermički poboljšani nodularni lijev, abrazivna erozija, udarna erozija

Abstract: Particle erosion is a wear loss from surface of solid body caused by a relative motion of fluid with solid particles. When impact angle is low (between 0° and 30°) this kind of erosion is called the abrasive erosion. On the other side, if the impact angle is between 60° and 90°, it is considered the impact erosion.
One of the advantages of ductile cast iron in relation to other cast irons is his good wear resistance. However, we must consider that wear resistance depends on wear conditions. Solid particle erosion resistance is a function of an impact angle. In this paper, samples of austempered ductile iron were eroded with quartz sand and angular steel erodent particles of two different sizes (700 μm i 1100 μm) at two different angles of impact (15° and 90°).

Key words: ductile cast iron, austempered ductile iron, abrasive erosion, impact erosion

1. UVOD

Nodularni lijev je ljevačka pseudobinarna slitina željeza i ugljika, koji se pretežnim dijelom izlučio u kuglastom obliku, [1]. Približni kemijski sastav lijeva prema [2] iznosi: 3,2…3,8 %C, 2,4…2,8 %Si, < 0,5 % Mn, < 0,045 % P i < 0,01 %Si. Metalna osnova u lijevanom stanju može biti monofazna: feritna i perlitna te dvofazna feritno-perlitna.

Legiranjem ili toplinskom obradom mogu se postići i druge strukture. Nodularni lijev je materijal koji osvaja tržište i zamjenjuje druge ljevove na bazi željeza. Mehanička svojstva su mu između čeličnog i sivog lijeva: bolje se obrađuje od čelika, ima bolju sposobnost prigušivanja i bolja ljevačka svojstva od čelika.

Izotermičko poboljšavanje nodularnog lijeva spada u skupinu postupaka kojima se mijenja struktura cijelog volumena, a provodi se u cilju povišenja mehaničkih svojstava odljevaka (čvrstoće, istezljivosti, žilavosti, dinamičke izdržljivosti itd.). Uobičajno se za izotermički poboljšani nodularni lijev koristi kratica ADI (austempered cast iron)

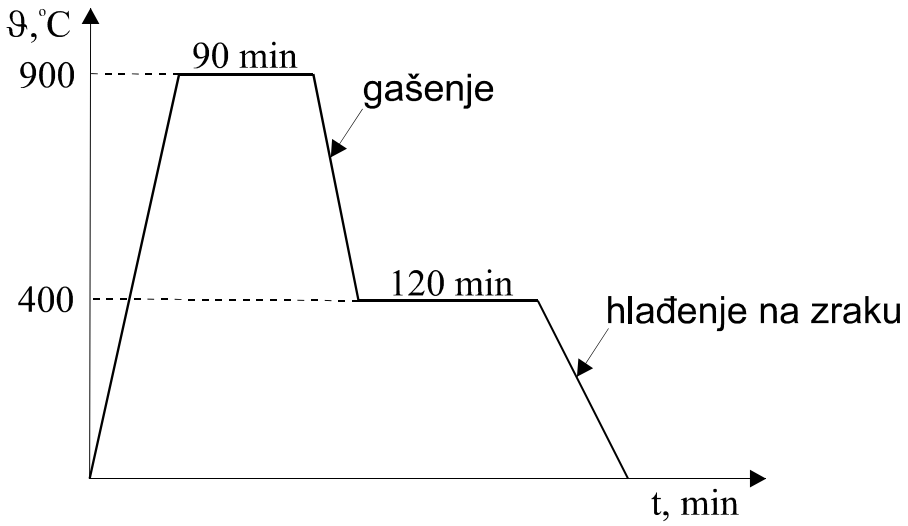
2. EROZIJA ČESTICAMA

Erozija česticama je gubitak materijala s površine krutog tijela zbog relativnog gibanja (strujanja) fluida u kojem se nalaze krute čestice. Od velike je važnosti kut pod kojim čestice udaraju o površinu. Erozija kod koje je strujanje pod malim kutom u odnosu na površinu naziva se abrazivna erozija, a kad čestice udaraju o površinu gotovo okomito to je udarna erozija, [3].

Valja napomenuti da je erozija česticama različita od ostalih vrsta erozije, tj. erozije fluidima i kavitacijske erozije. Razlog tome leži u činjenici da je vremenski period kontakta između erozivne čestice i materijala jako kratak, što eroziju česticama čini potpuno drugačijim procesom od abrazije i adhezije gdje je kontakt između reaktivnih površina relativno konstantan.

3. EKSPERIMENTALNI DIO

Uzorci nodularnog lijeva izliveni su u brodogradilištu Brodosplit u Splitu. Postupak izotermičkog poboljšavanja proveden je u Laboratoriju za toplinsku obradu Fakulteta strojarstva i brodogradnje. Postupak izotermičkog poboljšavanja prikazan je na slici 1.



Slika 1 – Postupak izotermičkog poboljšavanja

3.1. Kemijska analiza

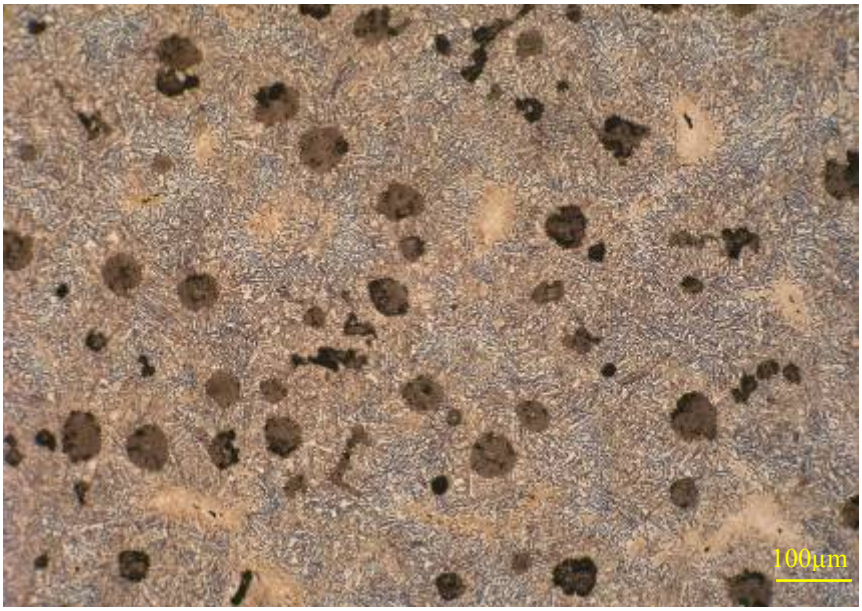
Uzorci za kemijsku analizu su izrezani iz odljevka te analizirani u Laboratoriju za analizu metala Fakulteta strojarstva i brodogradnje. Nakon analize dobiveni su sljedeći rezultati:

Tablica 1 – Kemijski sastav uzorka

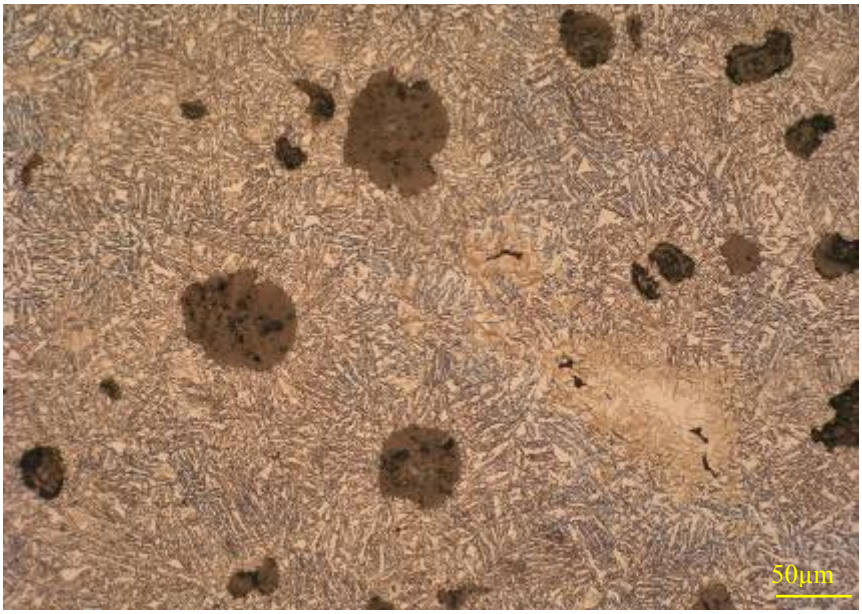
	Maseni udjeli, %								
	C	Si	Mn	P	S	Cu	Ni	Mo	Mg
Nodularni lijev	2,34	2,72	0,72	0,054	0,011	1,14	0,095	0,016	0,033

3.2. Metalografska analiza

Metalografska analiza provedena je u Laboratoriju za materijalografiju Fakulteta strojarstva i brodogradnje u Zagrebu. Na slikama 2 i 3 vidljive su nodule grafita u bainitnoj matrici.



Slika 2 – Mikrostruktura uzorka izotermički poboljšanog nodularnog lijeva u nagriženom stanju, povećanje 100x



Slika 3 – Mikrostruktura uzorka izotermički poboljšanog nodularnog lijeva u nagriženom stanju, povećanje 200x

3.3. Ispitivanje tvrdoće

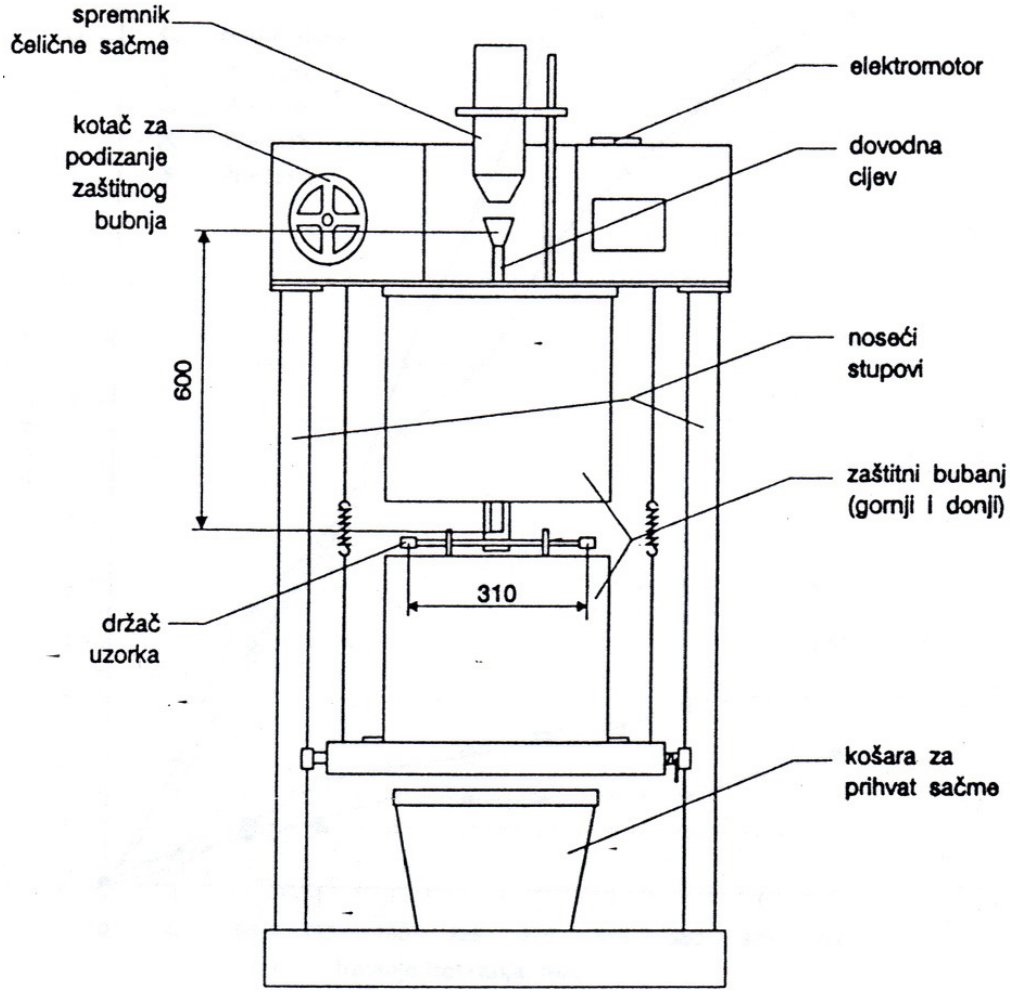
Mjerenje tvrdoće provedeno je u Laboratoriju za ispitivanje mehanička svojstva Fakulteta strojarstva i brodogradnje. Za mjerenje je korištena metoda po Rockwellu C. U tablici 2 su prikazani dobiveni rezultati.

Tablica 2. Tvrdoća po Rockwellu C

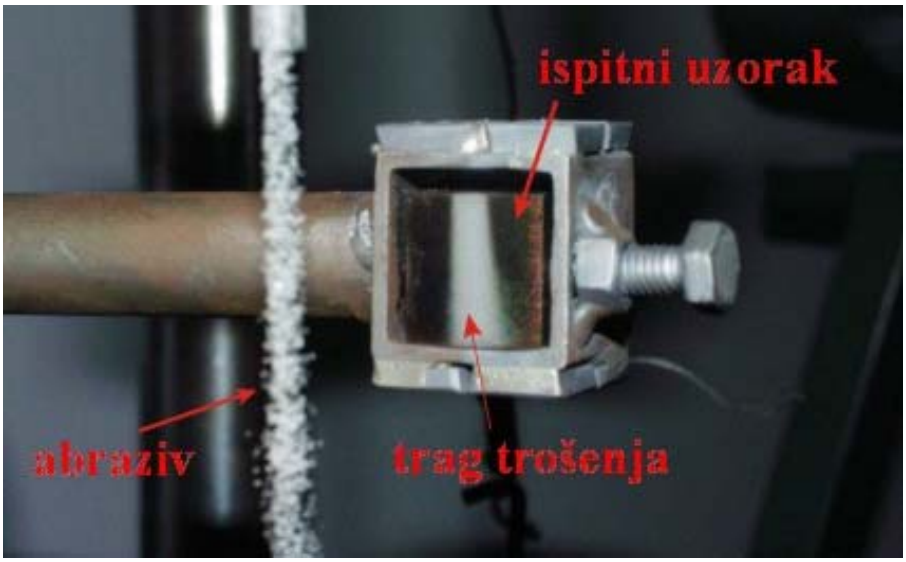
Broj mjerenja	HRC
1.	25
2.	27
3.	27
4.	26
5.	26
srednja vrijednost	26

3.4. Ispitivanje otpornosti na erozijsko trošenje

Ispitivanje otpornosti na erozijsko trošenje provedeno je u Laboratoriju za tribologiju Fakulteta strojarstva i brodogradnje u Zagrebu. Uređaj za ispitivanje je prikazan na slici 4, a detalj ispitivanja na slici 5.



Slika 4 – Uređaj za ispitivanje otpornosti na eroziju



Slika 5 – Ispitivanje otpornosti na erozijsko trošenje

Parametri ispitivanja:

- Abraziv: kvarcni pijesak, čelične kuglice srednjih promjera 700μm i 1100μm
- Brzina vrtnje: 1440 okr/min
- Vrijeme trajanja ispitivanja: 13min 53 sec
- Broj udara uzorka u mlaz kuglica: ~20000
- Kutovi udara uzorka u mlaz kuglica: 15°, 90°
- Dimenzije uzorka: 18×18×18 mm

Srednje vrijednosti tri mjerenja gubitaka mase pri ispitivanju izotermički poboljšanog nodularnog lijeva dane su u tablicama 3 i 4, zajedno s rezultatima ispitivanja otpornosti nodularnog lijeva koji nije toplinski obrađen.

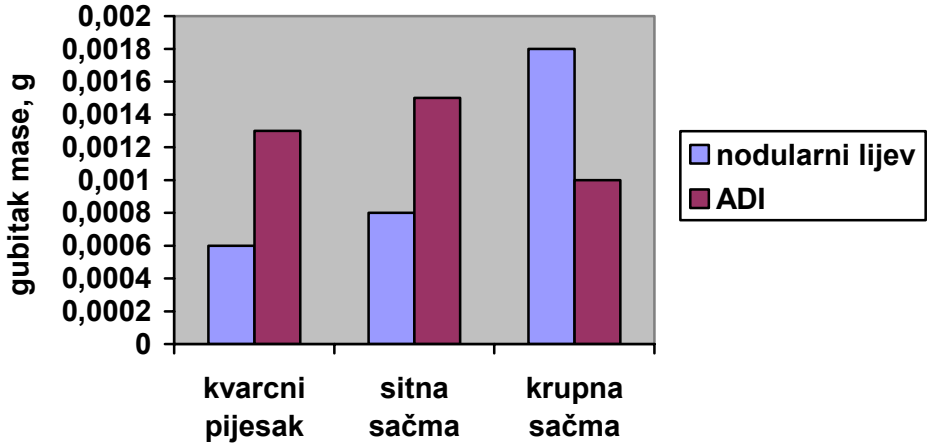
Tablica 3 - Gubitak mase pri abrazivnoj eroziji (kut upada 15°)

Vrsta abraziva	Gubitak mase Δm, g	
	Nodularni lijev	ADI
Kvarcni pijesak	0,0006	0,0013
Čelične kuglice 700μm	0,0008	0,0015
Čelične kuglice 1100μm	0,0018	0,0010

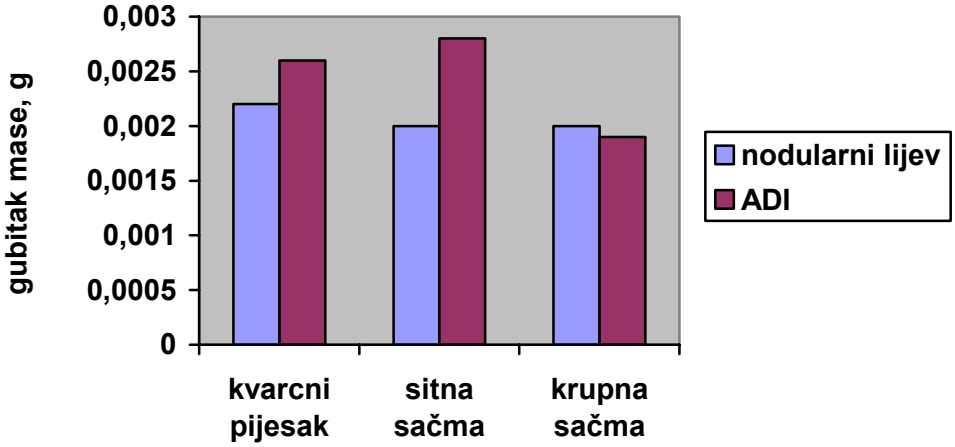
Tablica 4 - Gubitak mase pri udarnoj eroziji (kut upada 90°)

Vrsta abraziva	Gubitak mase Δm, g	
	Nodularni lijev	ADI
Kvarcni pijesak	0,0022	0,0026
Čelične kuglice 700μm	0,0020	0,0028
Čelične kuglice 1100μm	0,0020	0,0019

Na slikama 6 i 7 prikazane su srednje vrijednosti gubitaka mase ovisno o kutu upada i vrsti abraziva.



Slika 6 - Gubitak mase pri kutu upada od 15° ovisno o vrsti abraziva



Slika 7 - Gubitak mase pri kutu upada od 15° ovisno o vrsti abraziva

4. ZAKLJUČAK

Erozija kod koje je strujanje pod malim kutom u odnosu na površinu (manjim od 30°) naziva se abrazivna erozija, a kad čestice udaraju o površinu gotovo okomito (60° do 90°) to je udarna erozija. Tablice 3 i 4, odnosno slike 6 i 7 pokazuju da nodularni lijev ima bolju otpornost na eroziju česticama od izotermički poboljšanog nodularnog lijeva kada je abraziv kvarcni pijesak ili čelična sačma manje veličine.Kada je abraziv čelična sačma većeg promjera izotermičko poboljšavanje povećava otpornost na eroziju česticama. Isti rezultati vrijede kod oba ispitana kuta.

Zahvala
Prikazani rezultati su nastali u okviru znanstveno-istraživačkog projekta „Modificiranje površine izotermički poboljšanog nodularnog lijeva" Zahvaljujemo na potpori Ministarstvu znanosti, obrazovanja i športa.

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BRUŠENJE, PROCES I MOGUĆNOST MODELIRANJA

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Prethodno priopćenje / Preliminary note

Sažetak:

Povećanjem obodne brzine brusa povećava se i temperatura u zoni brušenja, što je posebno izraženo kod legura Ti poznatih kao materijala loše „brusivosti”. Istraživanja pokazuju da zahvatna sila pojedinih zrna, kod dubokog brušenja pokazuje tendenciju pada s porastom dubine brušenja. Ovo je zato jer je porast broja reznih oštrica u zahvatu veći od porasta ukupne sile brušenja. Zbog smanjenja zahvatne sile na jednom brusnom zrnu i povećanje luka zahvata, oštrice su kod dubokog brušenja podvrgnute intentzivnom trošenju radi trenja, koje kod čvrstog držanja zrna u vezivu ili male sposobnosti pucanja zrna vodi do stvaranja izrazitog trošenja vrhova oštrice brusa. U radu su dani rezultati mjerenja sile.

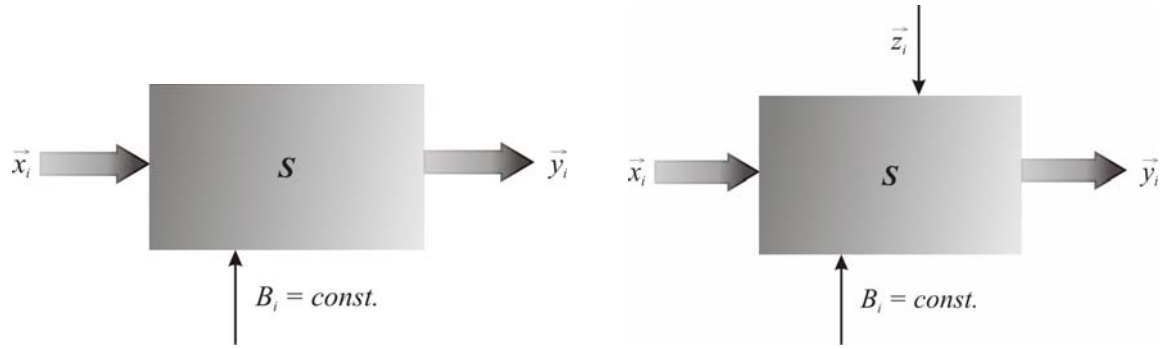
UVOD

Projektiranju procesa obrade uvijek treba prethoditi određeno modeliranje kako bi se tako dobiveni modeli mogli koristiti u definiranju viševarijantnih rješenja iz kojih je moguće definirati optimalni proces, postupak, opterećenje ili geometriju alata, vrijeme obrade i slično.

Rezultati procesa modeliranja su modeli koji mogu biti analitički, stohastički, numerički, grafički, statistički i drugi. Znači, modeliranje predstavlja opis zakona promjene parametara procesa u određenom vremenskom trenutku i prostoru imajući u vidu definirani skup ulaznih parametara, njihove međusobne interakcije kao i početne uvjete. Tako dobiveni modeli koji na matematički način definiraju odnos ulazno-izlaznih parametara procesa nazivaju se matematičkim modelima.

Metode modeliranja u svojoj osnovi moguće je podijeliti na dvije opće skupine i to:

- determinističke i
- stohastičke.



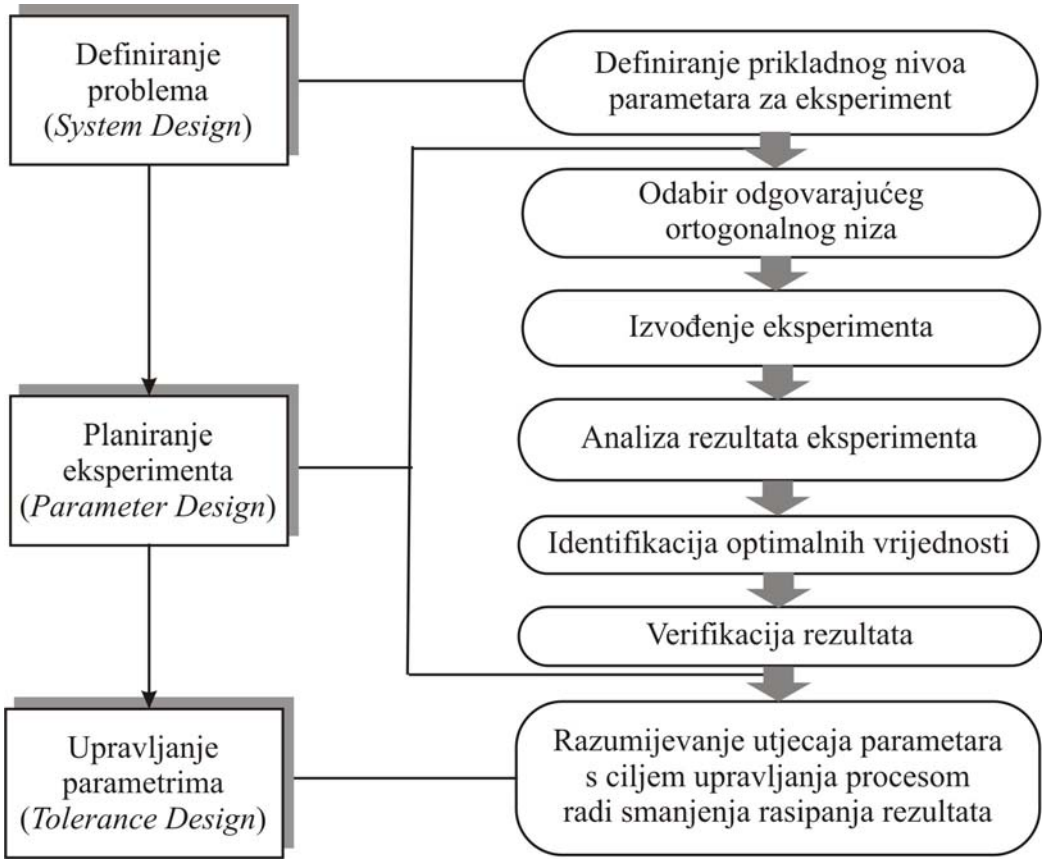
Slika 1. Blok shema: determinističkog i stohastičkog modela

Osnovna je svrha modeliranja procesa ili sustava izgradnja pouzdanih matematičkih modela, koji će s odgovarajućim stupnjem točnosti adekvatno opisati proces ili sustav.

Proizvodi i procesi mogu biti tako oblikovani da su što manje pod utjecajem okoline. Takav se pristup oblikovanju proizvoda i procesa naziva robusnim planom (dizajnom), a po idejnom tvorcu cijeli je ovaj pristup danas poznat pod nazivom Taguchi metoda.

Ideja na kojoj počiva robusni dizajn je minimalna varijacija ciljane vrijednosti proizvoda ili ciljane performanse procesa. Dakle, robusnim se dizajnom namjerava smanjiti potencijalna zavisnost procesa tj. omogućiti takvu stabilnost (robusnost) procesa na koji će ograničeni utjecaj imati promjene nastale u procesu oblikovanja i proizvodnje, a u cilju smanjenja mogućih gubitaka do kojih mogu dovesti neželjene promjene ili odstupanja parametara od unaprijed definiranih vrijednosti.

Broj ulaznih parametara kao i u potpunom faktorskom planu je ostao tri, a mijenjaju se nivoi vrijednosti ulaznih parametara.



Slika 2. Taguchi metoda – procedura

REZULTATI EKSPERIMENTA

Eksperimentalni je dio rada izveden na Institutu za strojarstvo, Fakulteta strojarstva i računarstva, Sveučilišta u Mostaru. Cilj je istraživanja bio dobiti rezultate mjerenja koji će omogućiti definiranje modela za tri izlazna parametra procesa brušenja: temperatura procesa brušenja, radijalna i transverzalna sila brušenja, kvalitet obrađene površine - mikrogeometrija obrađene površine iskazana kroz površinsku hrapavost (R_a, R_z, R_{max}).

Eksperimentalni podaci dobijeni su pomoću odgovarajuće mjerne opreme bez upotrebe sredstava za hlađenje i podmazivanje.

✓ ***Stroj***

Eksperimenti su izvedeni na univerzalnoj brusilici „Красний Борац 3 71" u radionici Instituta za strojarstvo u Mostaru. Osnovne tehničke karakteristike mašine su:

- pogonska snaga elektromotora – 2,2 kW;
- broj obrtaja glavnog vretena 2860 min^{-1};
- maksimalno kretanje stola – 200x630 mm;
- maksimalno brzina stola – 18 m/min;
- najveće dimenzije obratka – 630x200x320 mm.

✓ ***Alat - brus***

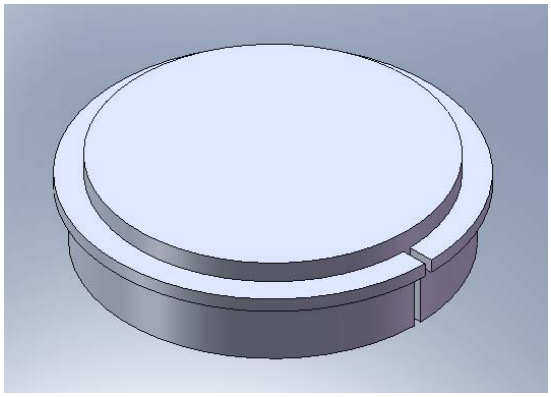
Korišten je brus oznake 2B 46 J 6V, proizvođača „SWATY“ Tovarna umetnih brusov, ISO 525. Dimezije brusa su: 250x35x26.

✓ **Epruvete**

Za ispitivanje sile brušenja korištene su epruvete od legure titana T-A6V dimenzija ϕ51 mm, debljine 10 mm.

Tablica 1. Mehaničke karakteristike i kemijski sastav legure T-A6V

Titanova legura T-A6V	Mehaničke karakteristike						
	zatezna čvrstoća N/mm^2		granica razvlačenja N/mm^2		tvrdoća HB		istezljivost A_5 %
	400-900		500-600		200-220		20-25
	Kemijski sastav %						
	Al	V	Fe	C	N_2	O_2	Ti
	6,87	4	0,13	0,08	0,07	0,02	ostalo



Slika 3. Epruveta korištena pri ispitivanju

✓ ***Mjerno mjesto***

Korišten je mjerni lanac koji se sastojao od dinamometra *KISTLER* 9257 A za mjerno područje $F_{xo>f}$ = 5-10 kN povezanog s adapterom, koji je dalje slao signal na SPIDER 8, koji je povezan na laptop gdje postoji zapis vrijednosti sile i vremenskog intervala u kome se događa mjerenje. Snimanje i obradu dobivenih mjernih rezultata u digitalnom obliku obavljeno je na računalu. Snimanje vrijednosti sila dobiveno je na osnovu obrade 120 epruveta sa 2400 mjerenja u jednoj sekundi.

Spider 8

Slika 4. Mjerna instrumentacija

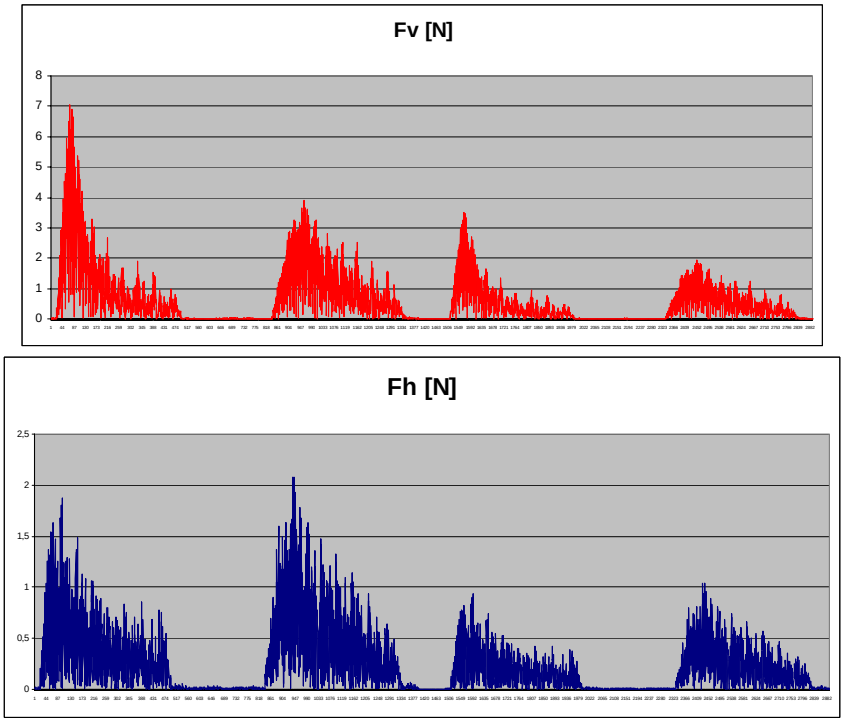
✓ ***Rezultati mjerenja***

Tablica 2 . Rezultati mjerenja vertikalne i horizontalne komponente otpora brušenja

	posmak stola s [mm/o]	dubina rezanja t [μm]	Brzina stola v [m/min]	X_0	X_1	X_2	X_3	F_v [N]	ln F_v	F_h [N]	ln F_h
10	4	0,015	7	1	1	1	1	8,26	2,11	2,79	1,03
2	1	0,015	7	1	-1	1	1	8,17	2,10	3,38	1,22
14	4	0,005	7	1	1	-1	1	7,52	2,02	1,99	0,69
17	1	0,005	7	1	-1	-1	1	8,68	2,16	2,66	0,98
29	4	0,015	3	1	1	1	-1	8,79	2,17	3,59	1,28
6	1	0,015	3	1	-1	1	-1	7,20	1,97	1,87	0,63
7	4	0,005	3	1	1	-1	-1	6,59	1,89	2,52	0,92
4	2	0,0087	4,5826	1	0	0	0	6,61	1,89	2,63	0,97
16	1	0,005	3	1	-1	-1	-1	6,59	1,89	2,01	0,70
22	2	0,0087	4,5826	1	0	0	0	6,50	1,87	2,48	0,91
23	2	0,0087	4,5826	1	0	0	0	6,48	1,87	2,53	0,93
25	2	0,0087	4,5826	1	0	0	0	6,28	1,84	2,76	1,02

Matematičkom obradom dobivenih podataka dolazimo do izraza:

$$F_v = 8{,}65 \cdot s^{0{,}01206} \cdot t^{0{,}08304} \cdot v^{0{,}13899} \, [N] \qquad F_h = 4{,}68 \cdot s^{0{,}07111} \cdot t^{0{,}17419} \cdot v^{0{,}11386} \, [N]$$



Slika 5. Isječak trake zapisa sila F_v i F_h

ZAKLJUČAK

1. Obrada titanove legure je veoma otežana te se problemima koji se javljaju pri tome mora posvetiti veća pozornost nego pri obradi konvencionalnih materijala. Naročito su potrebni obradni sustavi s povećanom krutosti.
2. obrada titanove legure brušenjem je otežana zbog loše toplinske vodljivosti, kao i zbog relativno velike duktilnosti (titan je mekan, lijepi se na radnoj površini brusa), te zbog tvrdog oksidnog sloja (800-900 HV) koji nastaje dužim stajanjem na zraku,
3. pri brušenju titana većim dubinama, a relativno niskim brzinama predmeta obrade primjećena su spaljena mjesta (što se objašnjava lošom toplinskom vodljivošću titana). Primjena mekših bruseva od upotrebljenih bi vjerojatno dala bolje rezultate.
4. primjenjivanim režimima obrade može se postići kvalitet obrade IT6 i IT7, a u nekim slučajevima i IT5, (birati bruseve veće zrnatosti u usporedbi s konvencionalnim materijalima),

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UTJECAJ HRAPAVOSTI POVRŠINE NA MEHANIČKA SVOJSTVA SiC KERAMIKE

INFLUENCE OF SURFACE ROUGHNESS ON MECHANICAL PROPERTIES OF SiC CERAMICS

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Izvorni znanstveni rad / Original scientific paper

Sažetak: U radu je određen utjecaj hrapavosti površine na tvrdoću i lomnu žilavost CVD SiC keramike. Pri određivanju lomne žilavosti i tvrdoće po Vickersu primijenjena su različita opterećenja. Lomna žilavost (K_{IC}) određena je mjerenjem duljina pukotina koje nastaju iz vrhova otisaka kada se četverostrana dijamantna piramida utiskuje na ispoliranu površinu uzorka CVD silicij karbida. Za određivanje lomne žilavosti (K_{IC}) korišten je matematički model po Anstisu. Tvrdoće i lomne žilavosti utvrđivale su se na tri različite hrapavosti površina. Rezultati su pokazali da hrapavost površine neznatno utječe na promjenu tvrdoće, ali znatno utječe na promjenu lomne žilavosti. Također je utvrđeno da porastom sile utiskivanja vrijednosti tvrdoće padaju, a smanjuje se i lomna žilavost.

Ključne riječi: CVD SiC keramika, tvrdoća, lomna žilavost, hrapavost površine.

Abstract: In this paper the influence of surface roughness on hardness and fracture toughness of CVD SiC ceramics is determined. For determination of fracture toughness and Vickers hardness different loads were applied. Fracture toughness (K_{IC}) is determined measuring the crack lenghts associate with a Vickers indentation. For determination the fracture toughness (K_{IC}) the Anstis method was applied. Hardness as well as fracture toughness were determined for three different surface roughness. Results indicate that surface roughness have negligible influence on hardness, while for fracture toughness have significat influence. Also, it was found that with increasing applied indentation load values of hardness as well as fracture toughness are decrease.

Keywords: CVD SiC ceramics, hardness, fracture toughness, surface roughness.

1. Uvod

Lomna žilavost silicij karbidne keramike izračunava se iz vrijednosti duljina pukotina koje su nastale utiskivanjem penetratora pri određivanju tvrdoće. Za određivanje tvrdoće keramičkih materijala koristi se najčešće metoda po Vickersu ili Knoopu. Određivanje tvrdoće metodom po Vickersu temelji se na mjerenju veličine otiska koji je nastao nakon utiskivanja dijamantnog penetratora određenim opterećenjem na ispoliranu površinu uzorka. Penetrator je istostrana četverostrana piramida s kutom između stranica od 136°.

Tvrdoća se određuje iz jednadžbe:

$$HV = \frac{0{,}1891 \cdot F}{d^2} \qquad (1)$$

Gdje je:

HV – tvrdoća po Vickersu,
F – primijenjena sila u njutnima (N),
d – aritmetička sredina dviju duljina dijagonala u mm, $d = \frac{d_1 + d_2}{2}$

Za izračun lomne žilavosti uzimaju se vrijednosti pukotina koje izlaze iz vrhova otiska. Duljine pukotina su obrnuto proporcionalne s vrijednostima žilavosti materijala. Nakon što se izmjere duljine pukotina, lomnu žilavost (K_{IC}) moguće je utvrditi računskim putem. Metoda za određivanje lomne žilavosti ima mnogo, ali se uobičajeno koriste metoda po Anstisu, metoda po Casellasu i metoda po Niihari, [1]. U ovom radu korištena je metoda po Anstisu. Prema Anstisu, lomna žilavost ovisi o modulu elastičnosti materijala, tvrdoći, duljini pukotina te primijenjenom opterećenju [2,3]. Anstis je predložio sljedeći izraz za određivanje lomne žilavosti::

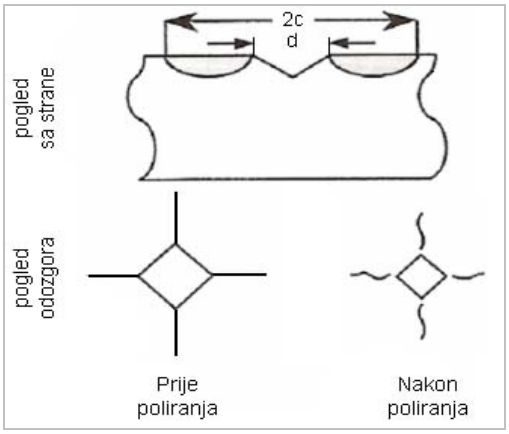
$$K_{Ic} = 0.016 \left(\frac{E}{H}\right)^{1/2} \times \frac{F}{c^{3/2}} \qquad (2)$$

Gdje je:

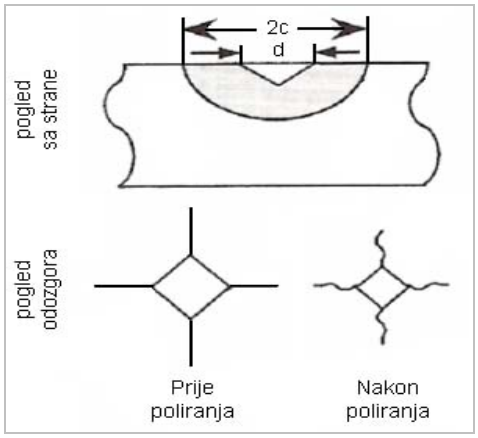
K_{IC} - lomna žilavost u $MPa \cdot \sqrt{m}$,

F - opterećenje u njutnima (N),
c - duljina pukotine od centra otiska do vrha pukotine mjerena u metrima,
E - je Youngov modul elastičnosti u GPa,
H - tvrdoća po Vickersu mjerena u GPa. (*H=0,0098067 HV*) .

Utiskivanjem penetratora pri mjerenju tvrdoće mogu nastati dvije vrste pukotina: Palmqvist pukotine i Medijan pukotine (slika 1). Jednostavan način na koji možemo razlikovati ta dva tipa širenja pukotina je uklanjanje površinskih slojeva poliranjem, pri čemu će Medijan pukotina uvijek ostati povezana sa vrhom otiska, dok će se Palmquist pukotina odvojiti, [4,5]. Vrsta dominantne pukotine (Palmquist pukotina ili Medijan pukotina) može se odrediti iz omjera duljine pukotine od centra otiska do vrha pukotine i duljine dijagonala baze piramide (c/d). Ako je omjer c/d manji od 2,5 dominantna je Palmquist pukotina, a ako je veći od 2,5 dominantna je Medijan pukotina [6].



Palmqvist pukotine



Medijan pukotine

Slika 1. Prikaz izgleda Palmqvist i Medijan pukotine [4,5].

U ovom radu ispitan je utjecaj promjene hrapovosti na tvrdoću i lomnu žilavost CVD SiC keramike. Iz omjera c/d određena je i dominantna pukotina.

1. Eksperimentalni dio

Sva ispitivanja su provedena na uzorku CVD silicij karbidne keramike (SiC) iz tvrtke Applied Ceramics, Inc., Fremont, Kalifornija, SAD. Prema deklaraciji tvrtke Applied Ceramics ispitivana keramika ima svojstva prikazana u tablici 1.

Tablica 1. Svojstva ispitivane CVD SiC keramike [7]

Svojstva	CVD SiC	Mjerne jedinice
Gustoća	3.21	g/cm^3
Veličina zrna	5-10	μm
Čistoća	> 99,9995 %	%
Apsorpcija vode	0	%
Propusnost plina	0	%
Temperatura sublimacije	~ 2700	°C
Boja	Crna	-
Savojna čvrstoća	460	MPa
Modul Elastičnosti	450	GPa
Poissonov faktor	0,21	-
Tvrdoća, HV 0,5	2500	kg/mm^2
Lomna žilavost	3,3	MPa $m^{1/2}$
Toplinska provodnost	200	W/mK
Koef. topl. širenja 25-1000°C	665	J/kgK
Specifični toplinski kapacitet	665	J/kgK

Mjerenje tvrdoće Vikersovom metodom provedeno je u Laboratoriju za ispitivanje mehaničkih svojstava u Zavodu za materijale Fakulteta strojarstva i brodogradnje na uređaju

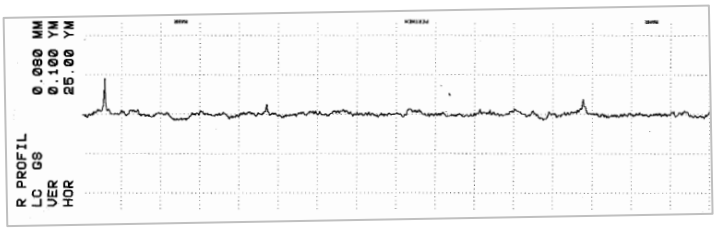
marke Zwick. U okviru planiranog istraživanja provedeno je ispitivanje tvrdoće opterećenjima od 9,81 N; 29,43 N i 49,05 N (HV1, HV3 i HV5). Za svaku kvalitetu površine napravljeno je po 30 mjerenja.

Na svjetlosnom mikroskopu su izmjerene dijagonale otisaka i pukotine koje su se širile iz vrhova otisaka. Na temelju njihove duljine određena je žilavost keramike metodom po Anstisu.

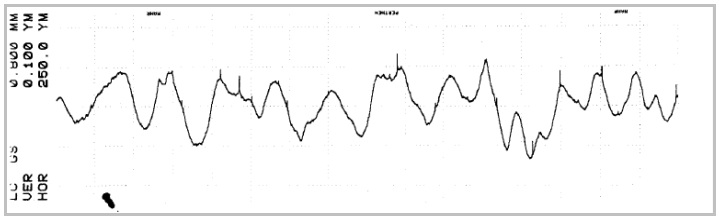
Potrebna ispitivanja su provedena na površini uzorka s tri različite vrijednosti hrapavosti. Različita hrapavost postignuta je završnim poliranjem dijamantnim pastama s česticama od 6, 3 i 0,25 μm. Prema kvaliteti paste za završno poliranje uzorci su označeni kao I (0,25 μm), II (3 μm) i III (6 μm). U Laboratoriju za precizna mjerenja dužina izmjerena je hrapavost površine na uzorcima prije ispitivanja tvrdoće.

3. Rezultati i diskusija

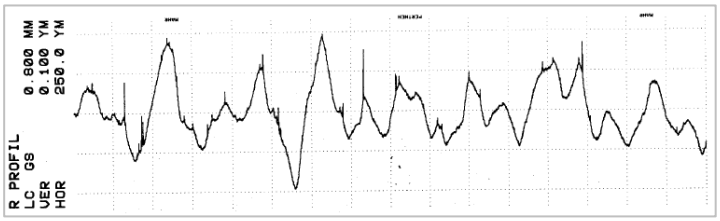
Na slici 2 prikazani su rezultati mjerenja hrapavosti površine silicij karbidne keramike za sve uzorke.



a) Uzorak I -dijamantne čestice od 0.25 μm



b) Uzorak II - dijamantne čestice od 3 μm

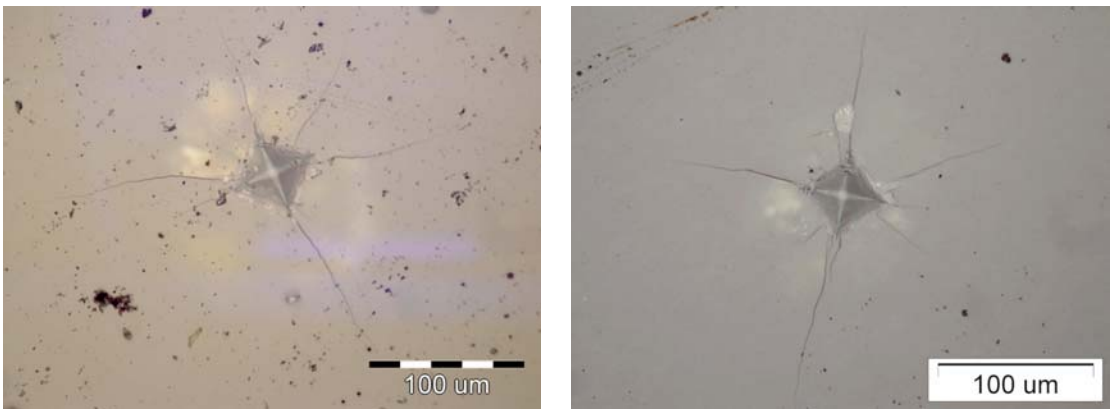


c) Uzorak III - dijamantne čestice od 6 μm

Slika 2. Hrapavost površine nakon poliranja različitim veličinama čestica

Nakon mjerenja hrapavosti provedeno je ispitivanje tvrdoće pod opterećenjem od 9,81 N (HV1), potom od 29,43 N (HV3) i na kraju od 49,05 N (HV5).

Na slici 3 prikazani su otisci nastali prodiranjem penetratora u materijal. Na slici se vide i pukotine koje izlaze iz vrhova otiska, a koje su izmjerene u svrhu izračunavanja lomne žilavosti.

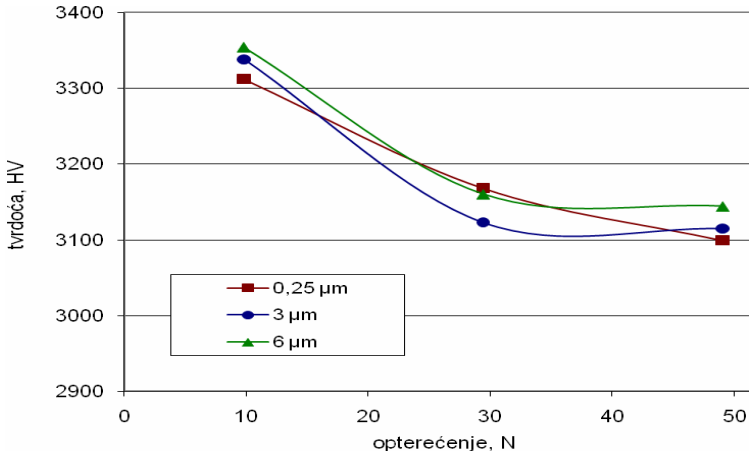


Slika 3. Prikaz otiska i pukotina nakon ispitivanja tvrdoće.

U tablici 2, prikazane su srednje vrijednosti za tvrdoće i lomne žilavosti koje su dobivene ispitivanjem na površini s različitom hrapavošću. Na slici 4, prikazana je ovisnost tvrdoće o hrapavosti i sili utisnuća.

Tablica 2. Prosječne vrijednosti tvrdoća i lomnih žilavosti

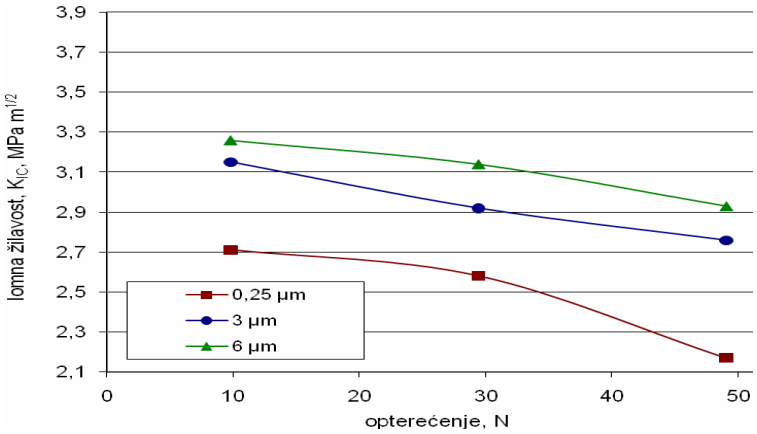
Sila, F [N]	Tvrdoća, HV			Lomna žilavost, K_{IC} $[MPa \cdot \sqrt{m}]$		
	I	II	III	I	II	III
9,81	3312	3338	3354	2,71	3,15	3,26
29,43	3168	3123	3160	2,58	2,92	3,14
49,05	3099	3115	3144	2,17	2,76	2,93



Slika 4. Ovisnost tvrdoće o sili utisnuća i hrapavosti

Očito je da hrapavost nema značajniji utjecaj na izmjerenu tvrdoću. Također se vidi da tvrdoća pada ako se sila utisnuća povećava. Ovo je osobito izraženo povećanjem sile od 9,81 na 29,43 N. Pri svim opterećenjima omjer c/d je veći od 2,5 što ukazuje da su dominantne Medijan pukotine.

Na slici 5 predočena je promjena žilavosti u ovisnosti o hrapavosti i sili utisnuća.



Slika 5. Ovisnost lomne žilavosti K_{IC} u o sili utisnuća i hrapavosti

Vidljivo je da porastom hrapavosti raste i žilavost. Također je vidljivo da porastom sile utisnuća lomna žilavost pada.

4. Zaključak

Cilj ovoga rada bio je utvrditi da li promjena površinske hrapavosti CVD SiC keramike utječe na promjenu lomne žilavosti. Na temelju provedenih istraživanja i dobivenih rezultata, može se zaključiti sljedeće:

- Promjena hrapavosti površine ne utječe značajno na promjenu tvrdoće,
- Tvrdoća pada ako se sila utisnuća povećava, što je osobito izraženo povećanjem sile od 9,81 na 29,43 N,
- Porastom hrapavosti raste žilavost,
- Porastom sile utisnuća lomna žilavost pada,
- Omjer c/d veći od 2,5 ukazuje na Medijan pukotine.

Pretpostavka je da je s povećanjem hrapavosti površine došlo do porasta žilavosti zbog toga što je veća hrapavost uvjetovala bolje akumuliranje energije koju je stvorila sila prilikom utiskivanja tvrdoće. Veće akumuliranje energije smanjilo je intenzitet širenja sile u ravnini paralelnoj sa površinom uzorka što je izazvalo manje duljine pukotina

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DAMPING PROPERTIES OF INTERPENETRATING POLYMER NETWORKS BASED ON POLY(METHYL METHACRYLATE) AND SILSESQUIOXANES

PRIGUŠNA SVOJSTVA INTERPENETRIRANIH POLIMERNIH MREŽA NA TEMELJU POLI(METIL-METAKRILATA) I SILSESKVIOKSANA

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Izvorni znanstveni rad / Original scientific paper

Abstract: New interpenetrating polymer networks based on poly(methyl methacrylate) (PMMA) and silsesquioxane-containing, organic-inorganic (hybrid) network were prepared by bulk polymerization. The inorganic (silsesquioxane) phase was generated from an organically modified silicon alkoxyde, 3-glycidyloxypropyltrimethoxysilane (GLYMO) via sol-gel chemistry. Poly(oxypropylene)diamine was used as an epoxy opening agent, as basic catalyst for GLYMO condensation and as PMMA crosslinking agent. The structure of prepared materials were studied by differential scanning calorimetry (DSC), scanning electron microscopy (SEM) and by dynamic mechanical analysis (DMA). Based on the results of dynamic mechanical analysis (DMA) the damping ability of prepared materials was estimated. The tangent of the loss angle (tan δ) at the glass transition temperature and the temperature interval of effective damping (where tan δ >0.3) were used as the criteria of damping ability.
Key words: interpenetrating polymer networks, PMMA, silsesquioxanes, sol-gel, damping

Sažetak: Polimerizacijom u masi pripravljene su nove interpenetrirane polimerne mreže na temelju poli(metil-metakrilata), PMMA, i organsko-anorganskog hibrida koji sadrži silseskvioksanske strukture. Anorganska (silseskvioksanska) faza dobivena je sol-gel polimerizacijom organski modificiranog Si-alkoksida, 3-glicidiloksipropiltrimetoksisilana (GLYMO). Poli(oksipropilen)diamin upotrijebljen je za otvaranje epoksidnog prstena, kao bazni katalizator kondenzacije GLYMO-a te kao umreživalo PMMA. Struktura pripravljenih materijala istraživana je diferencijalnom pretražnom kalorimetrijom (DSC), pretražnom elektronskom mikroskopijom (SEM) i dinamičko-mehaničkom analizom (DMA). Na temelju rezultata DMA analize procijenjena su prigušna svojstva materijala. Kriteriji procjene sposobnosti prigušenja bili su tangens kuta gubitka (tan δ) i temperaturno područje u kojem je tan δ > 0,3.
Ključne riječi: interpenetrirane polimerne mreže, PMMA, sol-gel, silseskvioksani, prigušenje

1. Introduction

Reducing the noise and vibration of structures is vital for many branches of industry (aircraft and automobile industry, instrument engineering, etc.). Due to their viscoelastic nature, polymers possess damping properties, i.e. the ability to absorb the mechanical energy and transform it into heat, especially near the glass-transition temperature, T_g, where the rate (frequency) of coordinated movement of segments of polymer chains is the same as the rate (frequency) of the mechanical action [1]. Near the T_g, polymers have maximum values of the tangent of mechanical loss angle, tan δ, and of the mechanical loss modulus E", which is the measure of dissipated energy [2].

Usually, homopolymers possess efficient damping properties in a narrow temperature range of 20–30°C around their T_g [3]. However, for outdoor materials or machinery applications, good damping materials should exhibit a high loss factor (tan δ>0.3) over a temperature range of at least 60–80°C [4]. The temperature range of damping can be expanded by blending, grafting, copolymerization or formation of interpenetrating networks (IPNs) [5].

An interpenetrating polymer network (IPN), belonging to a unique class of polymer blends, consists of two or more distinct crosslinked polymer networks held together by permanent interpenetration [6] . The level of compatibility in IPNs depends not only on the chemical nature of IPN components or on the change in their proportion in the system, but also on the nature and composition of the fillers or compatibilizers introduced into the system.

In the present study the IPN type materials based on poly(methyl-metacrylate), (PMMA) and silsesquioxane-containing hybrid networks, formed in situ by sol-gel process, were prepared and their damping properties were estimated.

2. Experimental

2.1. Materials

Methyl methacrylate,MMA, (Rohm and Haas Co., Germany) monomer was purified by distillation under reduced pressure. Azobisisobutyronitrile , AIBN, (AKZO Chemie, The Netherlands) was recrystallized repeatedly from cold methanol and dried in a vacuum oven. 3-glycidyloxypropyltrimethoxysilane, GLYMO, (98%) was supplied by Aldrich Chemicals and poly(oxypropylene)diamine, with an average molecular weight of about 230, was provided under the trade name Jeffamine D230 (in further text D230) by Fluka (Buchs, Switzerland). The latter materials were used as received.

2.2. Preparation of the IPNs

An aqueous solution of acetic acid, AA, was added to GLYMO employing a molar ratio GLYMO:H2O:AA=1:1.5: 0.01. This solution was stirred at room temperature for 1h then mixed with D230 (molar ratio GLYMO: D230=1:1) and stirred for another 30 min. Various amounts of MMA were then added to the solution and stirred for 1 h. Molar ratio MMA: GLYMO was 15:1 (sample H3); 7:1 (sample H5) ; 3.6:1 (sample H7) and 1.7:1 (sample H9). Numbers in the sample designations represent approximate weight percent of inorganic phase (silsesquioxane structures) calculated as $SiO_{1.5}$. AIBN was used as initiator of MMA polymerization. The mixtures were left for 24 h at room temperature in the flat-bottom flask equipped with a reflux condenser and a nitrogen inlet. The viscous liquids were placed

between two glass plates with a rubber spacer what allowed to prepare polymer sheets approximately 2 mm thick. The samples were then cured at 65°C for 24 h and post-cured at 140°C for 12 h.

2.3.Characterization

Glass transition temperature of PMMA and hybrids was determined by differential scanning calorimetry (DSC) using a Netzsch DSC 200 equipped with a liquid nitrogen cooling accessory. The heating rate was 10 °C/min.

Fracture surface of cured specimens after tensile tests at room temperature was studied by scanning electron microscope JEOL T300 operated at 25 kV. The samples were gold-coated.

The DMA measurements were carried out on a DuPont TA Instruments DMA 983 using rectangular samples (60 x 10 x 2 ± 0,5 mm^3) at a constant oscillation frequency of 1 Hz and heating rate of 2°C/min. The range of temperature was −120°C to 180°C and the displacement amplitude was 0.2 mm.

3. Results and Discussion

DSC thermograms showing the glass transition temperatures, T_g, of investigated systems are shown in Fig. 1. For comparison, the DSC curves of pure PMMA and GLYMO-D230 are given as well.

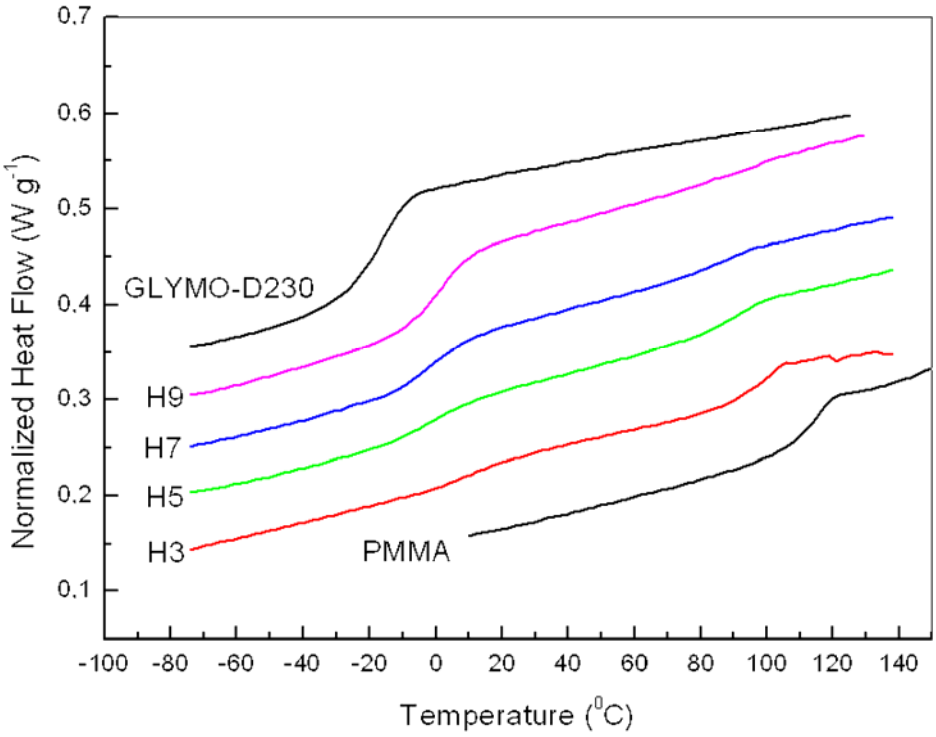

Fig.1. DSC thermograms of investigated systems

The glass transition temperatures of the GLYMO -D230 hybrid (organic-inorganic) network and PMMA were -17 and 114°C, respectively. The systems H3, H5, H7 and H9 showed two T_g values suggesting heterophase morphology (phase separated systems). An inward shift in T_g values indicated that some extent of interpenetration and/or phase mixing has occurred between GLYMO-D230 structures and PMMA. Several factors could influence T_g values of the GLYMO-D230 and PMMA reach phase. Silsesquioxane structures (Fig.2) formed by sol-gel process could reduce the dipole-dipole interactions between PMMA chains (reducing the T_g of PMMA reach phase). If inorganic structures are too big to infiltrate into the free volumes of PMMA, the free volumes of the system increase, the chain segments move more easily and the T_g decrease. On the other side crosslinks hinder the chain-segment motion making the T_g to increase. Intermolecular interactions between silsesquioxane structures and PMMA could also have a positive contribution to the T_g of GLYMO-D230 hybrid network.

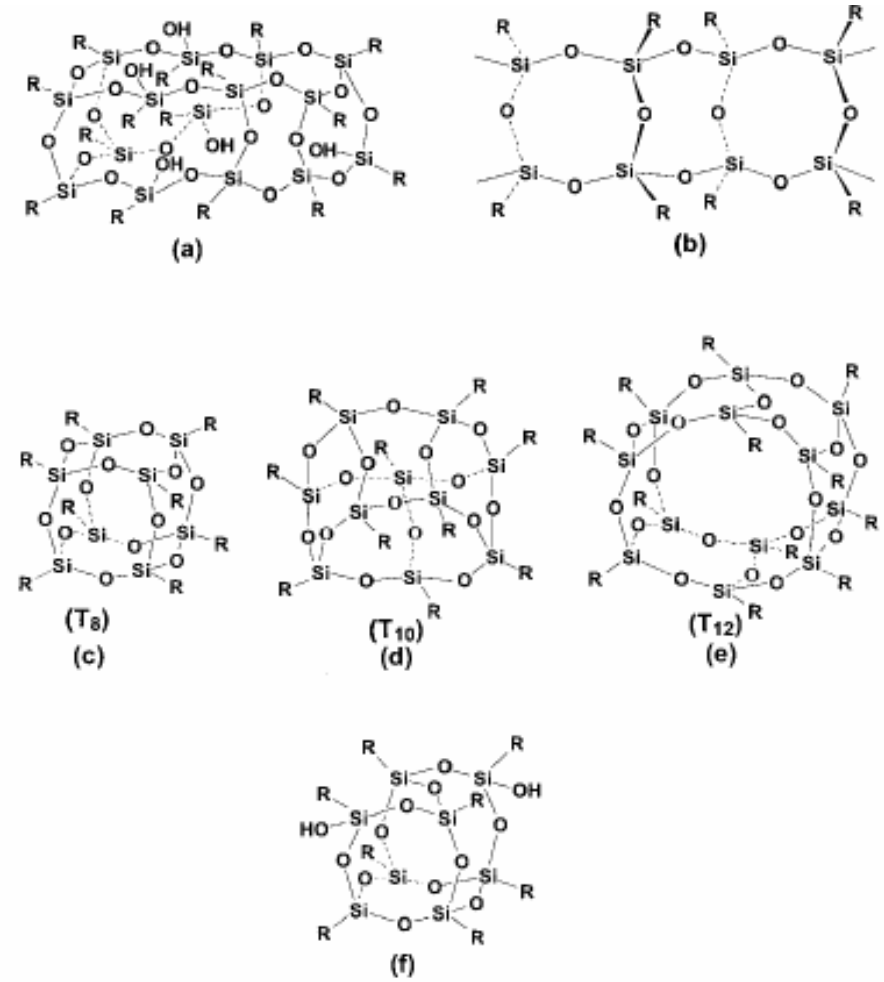

Fig.2. Structures of silsesquioxanes : (a) random structure(b) ladder structure (c),(d),(e) cage structures (f) partial cage structure [7]

The SEM images of fracture surfaces (following uniaxial tensile testing) of prepared systems. are shown in Fig. 3.

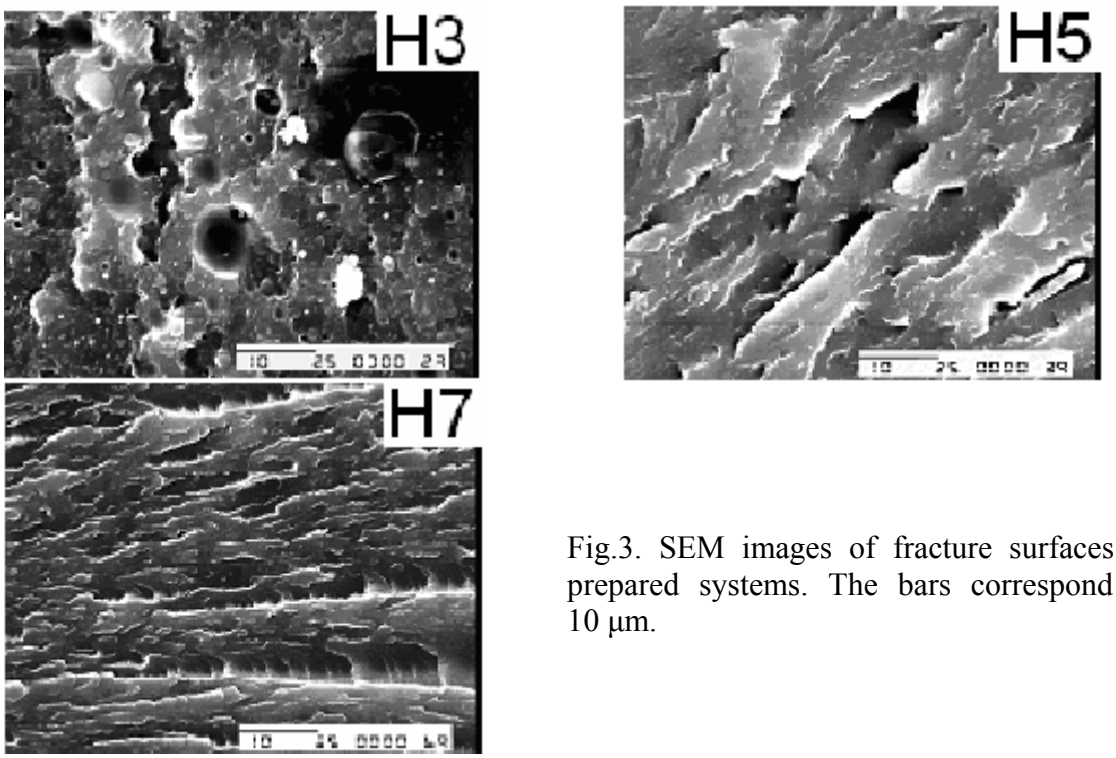

Fig.3. SEM images of fracture surfaces of prepared systems. The bars correspond to 10 μm.

The system H3 exhibits a heterogeneous morphology in which the minor phase (micrometric phase-separated inorganic domains) forms particles and agglomerates distributed in the polymer matrix. High concentration of voids across the sample surface is the evidence of particle-matrix debonding during deformation. Crack deflection (as in ceramics) is also observed. Systems H5 and H7 have more homogeneous bi-continuous morphology in the micrometric scale indicating better miscibility and interpenetration of networks.

Fig. 4 shows the loss modulus (E″) and the tangent of the loss angle (tan δ) as functions of temperature.

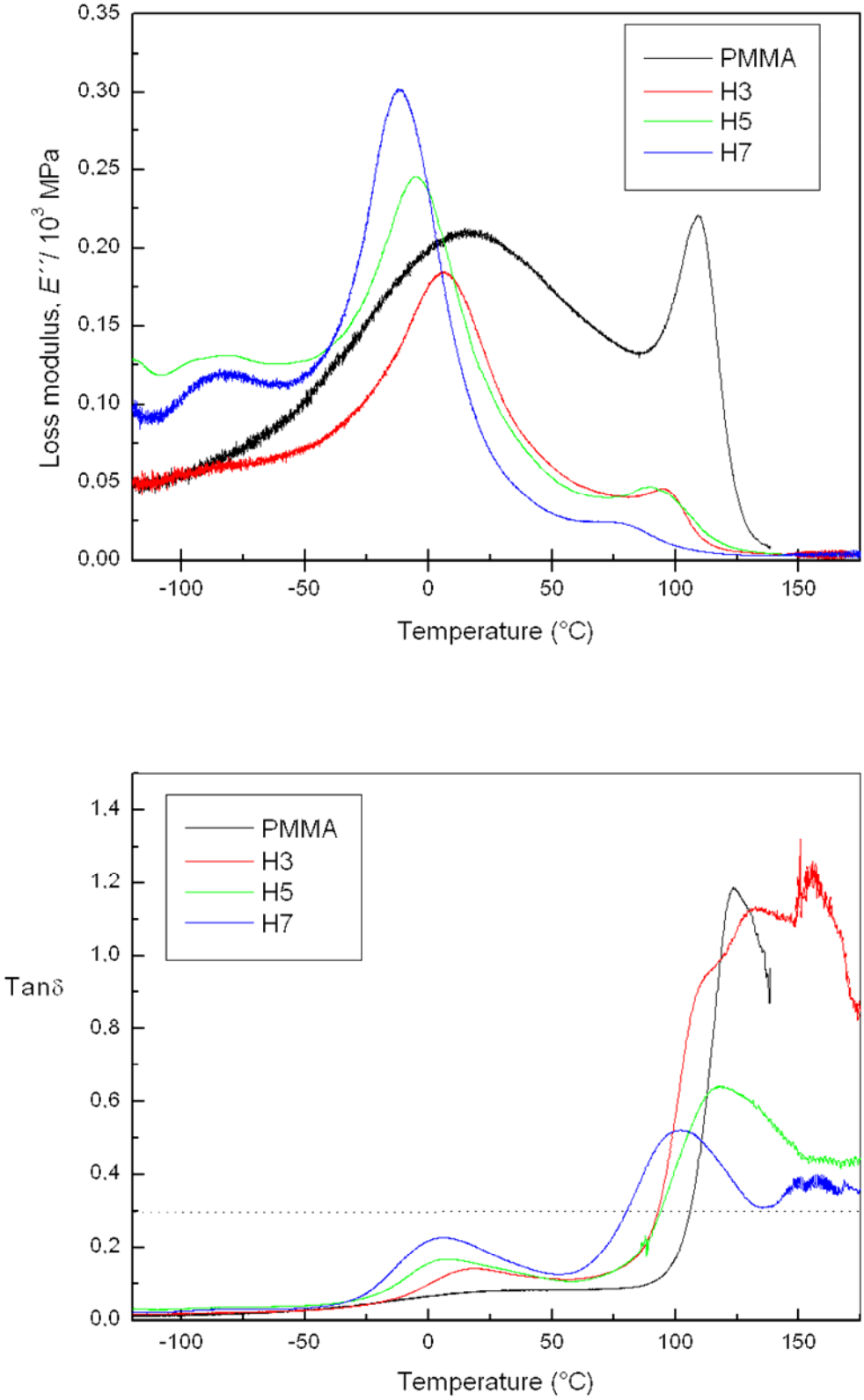

Fig.4. Dynamic mechanical properties of investigated systems

The systems H3, H5 and H7 have the low-temperature E'' maximum or a shoulder at ca. -80 °C that corresponds to the relaxation of the polyoxypropylene chain of the Jeffamine D230. Another two E'' and tan δ maxima are related to the relaxations of the GLYMO-D230 and PMMA in their glass temperature domains. Values of glass transition temperatures, obtained from the maxima of loss modulus (E″), for the GLYMO-D230 and PMMA enriched phase, T_{g1} and T_{g2}, are given in Table 1.

Table 1. Glass transition temperatures and damping ability of investigated systems

System	Wt % of PMMA	GLYMO-D230 phase	PMMA phase		
		T_{g1}/°C	T_{g2}/°C	Tan δ_{max}	$\Delta T_{tan\delta>0.3}$ /°C
PMMA	100		109	1.19	106 to 134
H3	75	6	94	1.13	94 to 180
H5	58	-5	89	0.65	93 to 180
H7	42	-12	79	0.52	81 to 180

Parameters of the damping ability of investigated systems (tan δ_{max} and the temperature range for tan δ >0.3, $\Delta T_{tan\delta>0.3}$) are given in Table 1 as well. For pure PMMA, as for the majority of homopolymers, the temperature range of effective damping is rather narrow and corresponds to an interval of 30°C in the neighborhood of its glass-transition temperature. With increasing content of GLYMO-D230 in systems the relaxation peaks of PMMA enriched phase become wider and lower. Tan δ values of IPNs exceed the value 0.3 and, consequently, can show good damping properties, at temperatures higher than 80-90°C (see Table 1).

4. Conclusion

New IPN type materials were prepared by polymerizations of methyl methacrylate (MMA) and sol-gel polymerization of an organically modified silicon alkoxide, 3-glycidyloxypropyltrimethoxysilane (GLYMO). Poly(oxypropylene)diamine was used as an epoxy opening agent, as basic catalyst for GLYMO condensation and as poly(methyl methacrylate) (PMMA) crosslinking agent. The structure of prepared hybrids were studied by means of differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA) and by scanning electron microscopy (SEM).The results of dynamic mechanical analysis (DMA) indicated that the prepared materials may have potential as damping materials.

Acknowledgments

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THERMAL STABILITY OF HIPS AND HIPS/EVA BLENDS COMPOSITES

TOPLINSKA POSTOJANOST HIPS I HIPS/EVA KOMPOZITNIH MJEŠAVINA

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Izvorni znanstveni rad / Original scientific paper

Abstract

The thermal stability of polymeric materials is studied by thermogravimetric analysis (TGA). The weight loss due to the formation of volatile products after degradation at high temperature is monitored as a function of temperature. When the heating occurs under an inert gas flow, a non-oxidative degradation of the samples occurs. Generally, the incorporation of filler into the polymer matrix was found to enhance thermal stability by acting as a superior insulator and mass transport barrier to the volatile products generated during decomposition. There is no universally accepted filler that can be used with all, or even with several polymers, one must discover the appropriate system for each polymer.

Typical fire retardant additives that may give a microcomposite are aluminum hydroxide, ($Al(OH)_3$), magnesium hydroxide ($Mg(OH)_2$) and diphenyl-2-ethylhexyl phosphate (DPO). These materials remove a good deal of the heat evolved in degradation and thus can prevent further degradation during the fire. To be effective, they must be used at high loadings, which lead in some instances to the loss of mechanical properties of interest. Further, due to poor adhesion between the filler surface and the matrix particles tend to agglomerate during melt compounding and thus affect the properties of composites. For this purpose mechanical properties (tensile strength and elongation at break) of the studied samples were followed.

Nanocomposites are formed when a small amount of nanofiller like anhydrophobic fumed silica Aerosil, SiO_2 is added to a polymer. The presence of only a small amount of nanofiller can give a significant reduction in the peak heat release rate. The difference between the microcomposite and the nanocomposite is the dispersion of the fillers in the polymer. In a nanocomposite, the filler, or the nano-filler/additive, is well dispersed throughout the polymer. Dispersion of the filler in the nanometer scale generally gives interesting insulation properties to a polymer, like enhancing thermal stability of the polymer.

The preparation of high-impact polystyrene (HIPS) and high-impact polystyrene/ethylene vinyl acetate (HIPS/EVA) blend composites was accomplished with melt blending process and aluminium hydroxide $Al(OH)_3$, diphenyl-2-ethylhexyl phosphate (DPO) and anhydrophobic fumed silica Aerosil, SiO_2 was used as fillers. From the results higher thermal stability is obtained for the HIPS/EVA composites due to higher concentration of aluminium hydroxide.

Key words: thermal stability, polymer composites, polymer blends, TGA analysis

Introduction

In recent years, research work on polymers was focused on development of new materials that can meet specific needs by adding mineral additives, especially those that form either micro- or nano-composites. There are currently believed to be four areas in which nanocomposite formation may be important: permeability, heat distortion temperature, flexural modulus and fire retardancy.

Modern fire retardants include the use of compounds of phosphorus, boron, aluminium, magnesium, sulphur and others. At this moment in time the halogens and phosphorus compounds appear to find the most use, but this is certain to change. The use of halogen is diminishing all the time but it is not yet complete. [1]

Recent work deals with the association of microsized additives with other additives and/or fillers to decrease needed loadings and obtain synergistic effects resulting from the association of nanosized additives with other additives to reach optimized fire retardancy performance. The difference between the microcomposite and the nanocomposite is the dispersion of the material in the polymer. In a nanocomposite, the clay, or the nano-filler/additive, is well dispersed throughout the polymer. Dispersion of the filler in the nanometer scale generally gives interesting insulation properties to a polymer, the fire retardancy being generally poor. [2-5]

Fire retardants have been applied to all types of materials, ranging from fabrics to hard plastics. The many applications, such as housing materials, transport and electrical engineering brings problems of low thermal stability and flammability of polymer materials resulting in reduction of usage. Polystyrene (PS) is one of the most mass-productive and commercialized polymers in the world due to its valuable properties, chemical resistance, wide application range and low costs. On the other hand thermal stability of PS is inferior compared with other common polymers; polyethylene, polypropylene, polyamide.

In this work effect of fillers on thermal stability of high-impact polystyrene (HIPS) and high-impact polystyrene/ ethylene vinyl acetate (HIPS/EVA) blend composites was studied where aluminium hydroxide $Al(OH)_3$, diphenyl-2-ethylhexyl phosphate (DPO) and anhydrophobic fumed silica Aerosil, SiO_2 was used as fillers.

Experimental

Materials

Studied samples were prepared with high-impact polystyrene (HIPS, Doki 472, Dioki, Croatia, density 1,05g/cm^3, butadiene content 8,5 %) and ethylene vinyl acetate (EVA, Elvax 265, DuPont, 28 mass % vinyl acetate, density 0,951 g/cm^3). As a microfiller $Al(OH)_3$ (Martinal OL107, Albemarle corporation, $Al(OH)_3$ content 99,6 mass %, BET 6-8 m^2/g) was used and SiO_2 (Aerosil R7200, Degussa, SiO_2 content 99,8 mass %, structure modified with a methacrylsilane) was used as nanofiller. As a plasticizer and flame retardant diphenyl-2-ethylhexyl phosphate (Disflamoll DPO, Lanxess, phosphorus content 8,6 %, viscosity 21-23 mPas) was used.

Composites preparation

Extrusion process was carried out on a Rondol Bench Top 21mm twin-screw extruder, a co-rotating extruder with standard, non-intensive screw characteristics. Temperature profile in extruder was set to T = 170/190/200/210/220/220 °C (from hopper to die) and screws rotation speed was set to 60 rpm. Extruded composites were injection moulded at 230°C according to ISO 294 and dumbbell specimens were formed according to ISO 3167 for further characterization. Compositions of studied composites are listed in Table 1.

Characterization

Thermogravimetric analyses (TGA) were carried out on ca. 10 mg samples using a TA Instruments SDT-2960 thermogravimetric analyzer under a flowing N_2 atmosphere from 25°C to 550°C at a heating rate of 5°C/ min.

The mechanical properties of composites were tested using an Instron Universal Testing Machine 1185 at a constant temperature of 23°C and the humidity of 50% RH. The gauge length of 25 mm, crosshead speed of 50 mm/min and sample size (70x4x2) mm were used to determine tensile

strength and elongation at break (according to ISO 527-1 and ISO 527-2). The results are the average of at least five samples

Table 1 - Composition of HIPS and HIPS/EVA composites, mass %

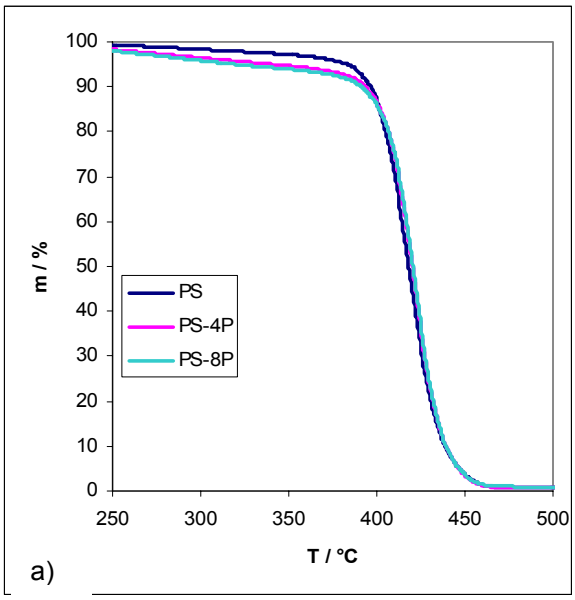
	PS	EVA	$Al(OH)_3$	SiO_2	DPO
PS	100	-	-	-	-
PS-4P	96	-	-	-	4
PS-8P	92	-	-	-	8
PS-4A-4P	92	-	-	4	4
PS-8A-8P	84	-	-	8	8
PS-E-Al	60	20	20	-	-
PS-E-Al-4P	58	19	19	-	4
PS-E-Al-8P	55	18	18	-	8

PS = high-impact polystyrene, E = ethylene vinyl acetate, Al = $Al(OH)_3$, A = Aerosil, SiO_2 ,
P =diphenyl-2-ethylhexyl phosphate, DPO

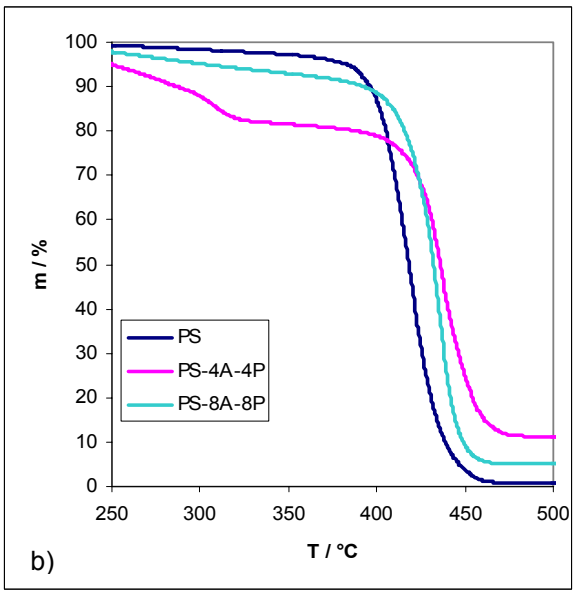
Results and Discussion

TGA Analysis

The thermal stability of the high-impact polystyrene (HIPS) and HIPS/EVA micro and nanocomposites were evaluated by TGA and the results are shown in Table 2 and Fig. 1 a) – c). The data includes the temperature at which 5%, 10%, 20%, 40%, and 60 % degradation occurs (T_{95} – T_{40}), a measure of the temperature of the degradation. Results obtained by thermal analysis show that the decomposition process is not significantly altered by incorporation of phosphate into polystyrene polymers, Fig. 1a). The mass losses between 250°C and 400 °C differ between the samples and the maximum mass loss rate for PS-8P and PS-4P were 2 - 3% higher, respectively than that of high-impact polystyrene. The mass loss between 400°C - 450°C was approximately the same; slight difference can be seen from the table 2.



On the Fig 1 b) can be seen the results for the samples prepared with diphenyl-2-ethylhexyl phosphate (DPO) and with Aerosil nanofiller (SiO_2) that is additionally modified with a methacrylsilane to sustain thermally stability where altered decomposition is observed. It is clearly observed that the degradation mechanism of phosphate nanocomposites is somehow different for PS-4A-4P sample from the homopolymer and PS-8A-8P samples; there is two-stage decomposition. The first step of the degradation of the phosphate HIPS nanocomposite, is attributed to some interaction between the Aerosil filler and the HIPS that serves to stabilize the nanocomposite forming the char. In the second-stage the PS-4A-4P sample shows the highest thermal stability. The maximum mass loss rates, determined via differentiation of the TGA data, were observed for the PS-4A-4P sample from 300 °C - 320 °C due to well incorporation of the phosphate. Both samples containing SiO_2 filler left substantial TG residues at 490°C, in nitrogen, with



residues of 11% PS-4A-4P and 4% PS-8A-8P of initial masses, respectively.

Considering the samples prepared with microfiller $Al(OH)_3$ of 20 mass% loading and DPO (the same loading as in other studied samples) it can be seen that samples show significant higher thermal stability then homopolymer HIPS (Fig. 1 c)). For these samples two-stage decompositions is evident due to presence of ethylene vinyl acetate (EVA) copolymer. It is found that the deacylation of EVA due to elimination of acetic acid in composites is accelerated, and may occur at temperatures lower than those for the pure homopolymer due to catalyst created by thermal decomposition. From the TG curves it can be observed that homopolymer and samples with fillers formed substantial residues at 450°C retaining 1% and 25% of its initial mass, respectively, while at 470°C the residue is 15% for the samples with fillers. The thermal stability of these studied samples is enhanced and temperatures are increased more than 30 °C. From the literature it is known that in air, the same composite exhibits a significant delay in weight loss that may derive from the barrier effect caused by diffusion of both the volatile thermo oxidation products to the gas and oxygen from the gas phase to the polymer [6-7].

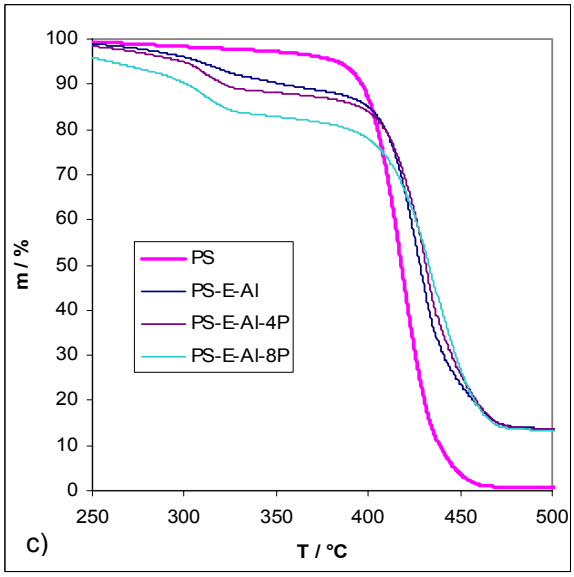


Fig 1. TG curves obtained at 5°C/min for
a) PS/phosphate
b) PS/SiO_2/phosphate
c) PS/EVA/$Al(OH)_3$/phosphate

Table 2 – TGA data for the HIPS and HIPS/EVA blend composites with various fillers

Samples	T_{95}	T_{90}	T_{80}	T_{60}	T_{40}	T_{20}
PS	383	397	405	414	422	431
PS-4P	342	394	407	417	424	432
PS-8P	320	392	407	417	424	432
PS-4A-4P	250	287	389	431	441	454
PS-8A-8P	304	393	416	429	435	442
PS-E-Al	309	354	410	423	433	457
PS-E-Al-4P	299	322	409	426	437	459
PS-E-Al-8P	259	302	390	426	440	458

Mechanical Properties

On the Figs. 2 and 3 the results of mechanical properties of the studied HIPS and HIPS/EVA composite samples are presented. From the results of the tensile strength it can be seen that the addition of the fillers and additives reduce the tensile strength. For example, the lower tensile strengths is observed for the samples prepared with ethylene vinyl acetate and it is decreased for 24 MPa to 15 MPa due to increase of elasticity. Increase of elasticity for the considered samples is seen on the Fig.3 and is approximately

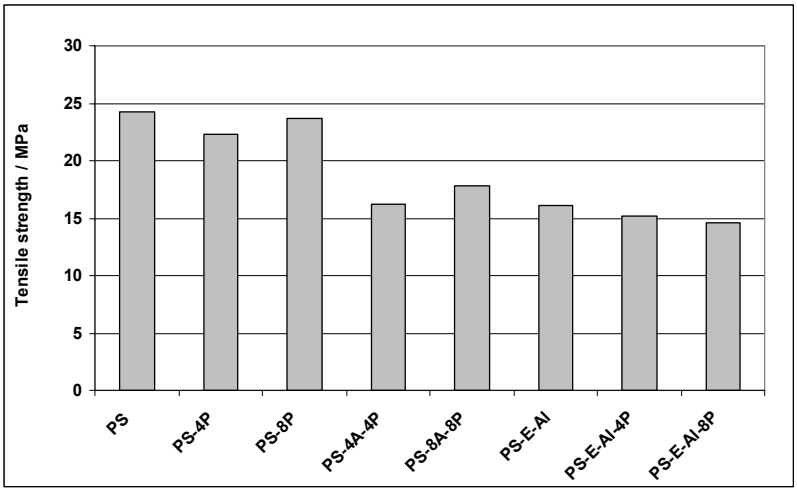


Fig. 2 –Tensile strength of HIPS and HIPS/EVA blends composites

20% for PS-E-Al-8P sample. Decrease of tensile strength does not necessary mean deterioration of properties, because tensile strength and elongation are inversely proportional. It is supposed that the main reason is good dispersion of the filler and EVA copolymer in the HIPS matrix due to higher phosphate concentration. Well dispersed filler is incorporated into the HIPS matrix and enhance thermal stability by acting as a superior insulator and mass transport barrier to the volatile products generated during decomposition. For the same sample the highest increase of decomposition temperature is observed, Table 2. The decreases of mechanical properties of HIPS nanocomposite are not expected. They show decrease of both tensile strengths and elasticity although they show significant improvement in thermal stability in comparison to homopolymer HIPS. It is assumed that SiO_2 is not uniformly dispersed due to poor interaction between the components in these multiphase systems.

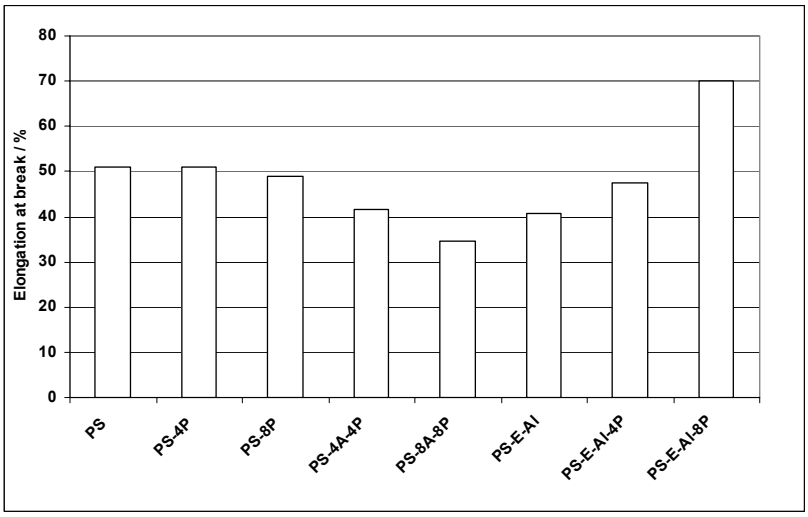


Fig. 3 –Elongation at break of HIPS and HIPS/EVA blends composites

Conclusions

HIPS and HIPS/EVA polymer blend composites were prepared with addition of phosphate DPO fire retardant to study the thermal stability and its synergistic effect with $Al(OH)_3$ and SiO_2 micro and nano fillers. It is known that clays alone are not used as fire retardants but they may be a component of the solution to the problem of fire retardancy. Synergy has been demonstrated between conventional fire retardants and nanocomposite in samples PS-4A-4P where can be seen increase of decomposition temperature for 23°C regarding homopolymer HIPS. There will need to be done additional investigations of this type to confirm the observations that have been made and to evaluate the different conventional fire retardants that could be used. Thermal stability of PS-4A-4P sample is almost as high as for samples prepared with much higher $Al(OH)_3$ loadings while their mechanical properties show no significant difference.

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ALTERNATIVE SOURCES OF ENERGY

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Abstract
Ireland relies on imports of fossil fuels for up to 83% of its energy needs and this statistic is relatively common in other European countries. Apart from the high import costs and pollutions associated with fossil fuels and the need to meet new targets in terms of CO_2 emissions, energy security is essential. This paper provides an overview and outline of the different alternative energy sources available for use either at domestic or on large scale production, some of which are established and others less likely to succeed in our climate. Some of the alternative energy sources such as wind and wave are gaining acceptance for Irish Climatic conditions and their growth rate and associated costs are outlined. The development from petrol to Liquid Petroleum Gas (LPG) to Hydrogen as a green fuel is presented. The paper will also outline how other countries are dealing with their energy needs through renewable and natural energy sources.

Keywords: Renewable Energy, Solar, Photovoltaic, Natural Light pipes

1. Introduction

With or without a shortage of traditional energy fuels such as oil, coal or gas, there is a major need to develop secure and sustainable sources of energy. The most basic ingredient in economic growth is energy and very little happens without it. Global demand for energy is set to double over the next 25 years and since it took the world economies 125 years to use the first trillion barrels of oil, we'll use the next trillion in 30 years. We are a power-hungry society, using largely fossil fuels, to move cars and trains, heat and cool buildings and provide electricity for equipment of all types. We pay for this through the price per barrel, smog, pollution and greenhouse gasses. 35 years ago it was thought that almost every energy source was about to run out

After the oil crisis of 1973, Energy industries looked to renewable energies which in theory could never run out. However after 1973 oil did not run out, huge reserves of Natural gas were discovered. Coal reserves in the UK for instance were 1,000 times the annual consumption in UK. Nuclear expansion proceeded (a six fold increase) until Chernobyl disaster.

Car sales in Russia grew 60% in 2007 and in China and Brazil, car sales grew by 20% and 30% respectively while the sales of small vehicles on growth in Europe

86 million barrels of oil are consumed each day worldwide while the UK consumes 1.7 million barrels of oil a day and The United States consumes 170 billion gallons of gasoline and diesel fuel annually. In light of all this development, OPEC presidents predict that oil prices will rise to $200 per barrel [1]. 86 million barrels of oil are consumed each day worldwide, while the UK consumes 1.7 million barrels of oil a day. The United States consumes 170 billion gallons of gasoline and diesel fuel annually. The main concern for the environment is that world global temperatures are rising, ice caps are melting and sea levels will rise as a result. The Greenhouse effect is primarily blamed for this and the emission of CO_2 is seen as main culprit. Other experts however have reported that global temperatures have not increased significantly since the Kyoto agreements (1997) and over the last 5 years global temperatures have not changed. It has been reported that the average global temperature rose by 0.6^{o}C during the last century and is forecast to rise by 3°C this century European annual mean temperatures increased by 0.3 – 0.6˚C since 1900, with 1998 the warmest on record. The primary reason for countries having their own sustainable energy supply is that it is predictable, there is less pollution, it can create employment locally, it is sensible economics, it generates savings on imports, prevents manmade disasters, makes use of environmentally friendly natural resource and areas such as wave and wind energy to Ireland are as good as Oil and Gas to the OPEC countries. CO_2 and CH4 are responsible for 70% and 24% of "greenhouse effect". CO_2 contributes to Ocean acidity through formation of Carbonic acid as outlined in tests consisting of 24,000 pH readings over an 8 year period. Chlorofluorocarbons (CFCs) used in the built environment contribute some 15% to greenhouse effect. Hydro chlorofluorocarbons (HCFCs) that replaced CFCs can have as much as 4038 times the global warming potential of CO_2, depending on their Ozone Depletion Potential. From a construction point of view, the concrete used in an average 3 bed semi-detached house produces approximately 20 tons of $C0_2$ in construction.

In the US, the annual business losses stemming from power interruption are estimated to be $70bn.

2. Developments in Renewable and sustainable energy

2.1 Renewable and Sustainable Energy Supplies

Renewable and sustainable energy supplies can be defined as environmentally desirable unlike fossil & fission fuels. Typical examples include the following:

i	Wind power	iv	Solar power
ii	Wave and Tidal power	v	Biofuels
iii	Heat pumps	vi	Fuel Cells

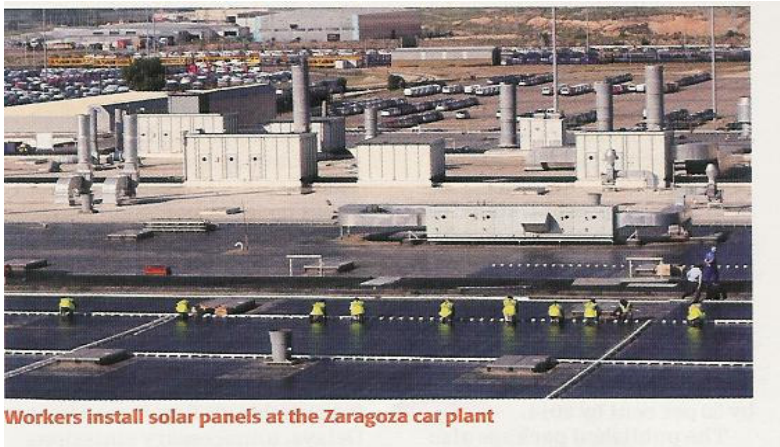
Renewable energies are theoretically carbon free and should be economically viable, not just because of global warming.

2.2 Worldwide developments

In 2007, the USA became world's second largest generator of electricity by wind power after Germany. The combined capacity of the five largest wind power states in America is over 10,000MW. At end of 2007, the US had 3,400MW of solar power including 750MW of PV, Including Alaska, the USA ranks first for Solar resources followed by Germany, Japan and Spain. Up to 5,000MW of Solar is planned for the USA by 2014(1.3M homes by 2014) and the state of California is heading for 20% Solar generated power by 2010.

General Motors (GM) is installing the world's largest rooftop solar power station at a car assembly plant in Spain (Zaragoza). This consists of 85,000 panels covering an area of 183,000 m^2. This will produce a peak output of 12MW and generate 15 M kWh annually for the local grid. This is equivalent to 4,575 households with an average annual consumption of 3,300kWh. Figure 1. shows an example of this development.

Switzerland's most powerful PV system has been installed on the river Rhone in Geneva. This provides a nominal power of 1MW. Up to 6,000 monocrystalline solar modules covering an area of 16,000 sq metres and capable of generating 1GWh of solar electricity each year is the potential output at a capital cost of €4.8M. In support of this development, four Swiss soccer clubs have installed solar systems on stadium roofs to generate 1,000,000 kWh of energy per year. Ireland with its temperate climate, lack of heavy industry and green energy potential is well positioned to capitalise on sustainable energy sources such as wind and wave. In the In UK for instance, 80% of energy comes from Fossil Fuels generating a high CO_2 footprint. In France on the other hand, 20% of the energy needs come from fossil fuels, generating a low CO_2 footprint.



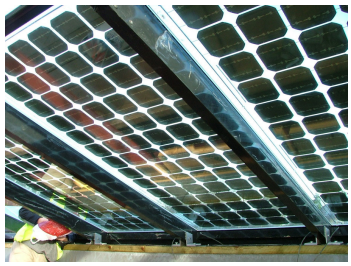


Figure 1. General Motors Photo-Voltaic plant in Zaragoza, Spain.

2.3 Solar Energy developments

In 212 b.c. it was reported that Archimedes Ignited Roman ships by reflecting sunlight through the use of mirrors. During 1695 and 1774 Diamond and Platinium was melted using focused sunlight and Solar furnaces respectively. During 1950, Felix Trombe designed a solar array to match the suns temperature (5,538^{o}C) and in 1954 the development of the first successful silicon solar cell was achieved, followed in 1980 by the development of thin film solar cells. Photovoltaics (PVs') generate electricity without emissions, no moving parts, highly reliable and need no external fuel. They are typically used to charge batteries, power circuits directly, detect sunlight, detect light from LED, lamps etc. and power satellites, remote devices, sea buoys and parking meters. Their main disadvantages are costs (30 to 40 c per kWh versus 10c standard.) and their efficiency is less than 30% with silicon units less than 15% efficient. The total radiated power from the sun is 3.83x1023 kW. However only a small fraction of this energy is radiated to earth. The Solar constant at the top of the earth's atmosphere is 1368 W/m2 and due to cloud, and local atmosphere etc. less energy is absorbed

at ground level. Figure 2. shows an example of a simple Solar system for generating hot water while Figure 3. shows the free availability of geothermal energy in Iceland. Figure 4. shows a typical wind farm in Ireland using 1MW generators. Other examples of renewable and sustainable energy sources are given in Table 1.

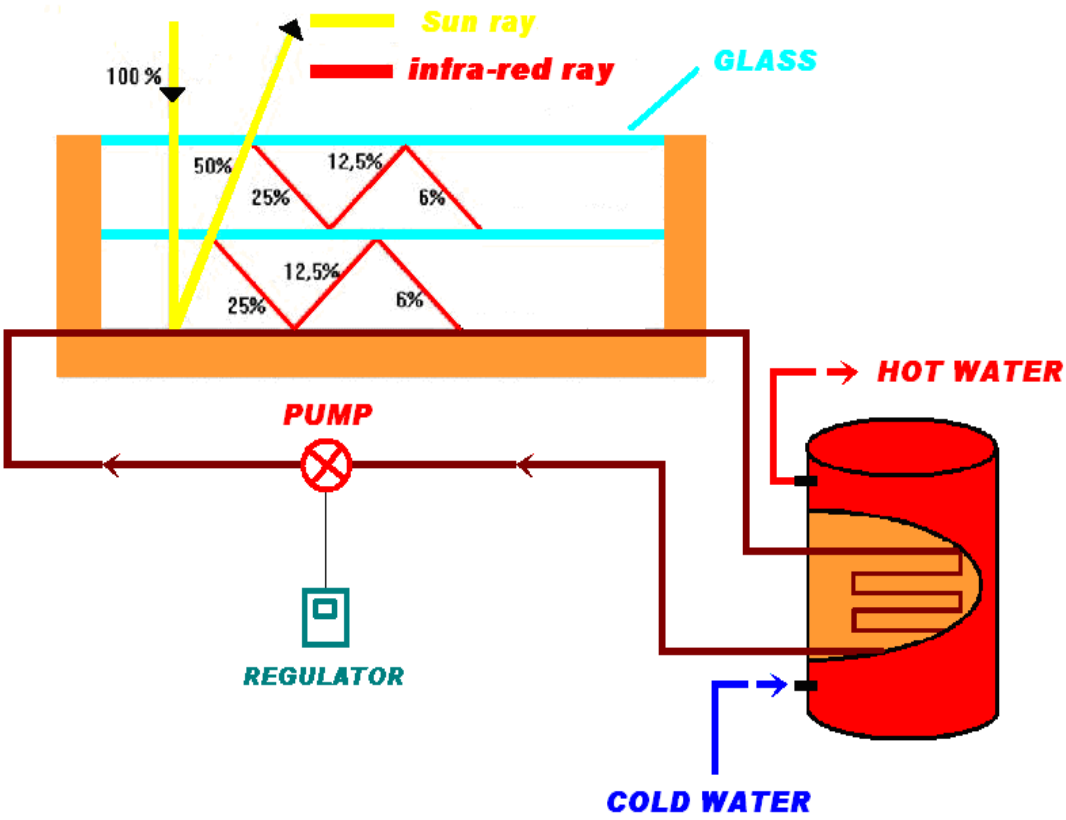


Figure 2. Basic Solar energy system.

Figure 3. Geothermal: surface and subsurface

Figure 4. Wind power generation

Wind power: Constructing windmills and wind farms to harness the wind on both land and at sea.
Waste conversion. Landfill gas, Production of Methane, Typical house hold waste, agricultural waste and industrial waste conversion.
Solar power: Solar, PV and mirrors to harness the sun's radiation. Solar ponds.
Thermal insulations: Sustainable methods
Wave power: Generating electricity from the natural energy of the oceans, Tidal power, wave and current generators, Tidal Barrages,
Fuel Cell Technology; CHP; Various types
Tidal power: Harnessing regular motion of the tides by barrages or tidal water wheels
Natural Lighting for buildings, tunnels, factories and homes.
Biofuels: converting plants(sugar cane & beet, corn, soya beans, flax, rape, camilina etc) to fuel for transport, aircraft and power stations
Hydrogen production and applications for motor transport
Heat pumps: Transferring heat from the ground to a building etc.

Table 1. Common types of renewable energy

2.4 Pressure Retarded Osmosis

If a solvent is separated from its solution by a semi permeable membrane, the solvent has a tendency to pass through the membrane, diluting the solution, caused by osmosis. This flow through a membrane against an opposing pressure across the membrane is called pressure retarded osmosis. An example f this is shown in Figure 5. The osmotic power depends on the rate at which the solution is diluted.
The power is given as follows:

Power = $k(\Pi - P)P$ and the maximum power is equal to $k*\Pi^2/4$

Where; Π = Osmotic pressure and
k= membrane permeability (10-250 $m3/m^2$-bar sec)

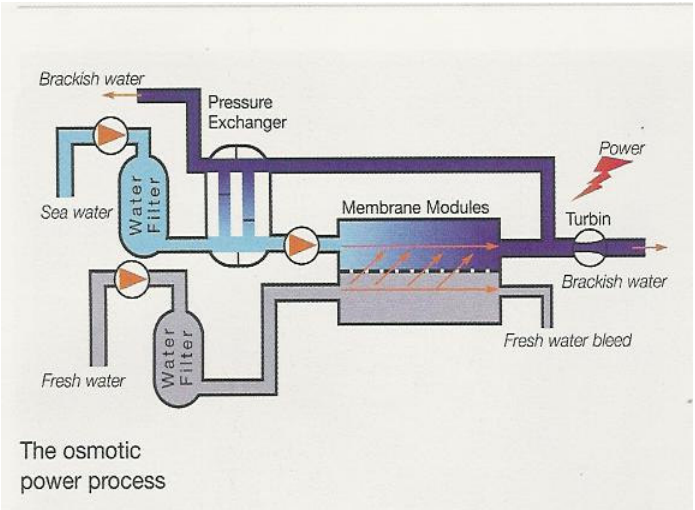


Figure 5. Pressure Retarded Osmosis System

2.5 Hydrogen adoption and Electric vehicles

To date Compressed Natural Gas (CNG) Kits have operated successfully in motor transport. This has followed the successful application of Liquid Petroleum Gas (LPG0 powered vehicles. More recent developments has led to the conversion to Hydrogen fuelled engines. By replacing the CNG tank with a Hydrogen tank, this is feasible and tests have been undertaken on a number of vehicles to date including a conventional Nissan Almera.
The key advantage of this is that a new car for this to work is not required. The main expense is the hydrogen tank. Other developments include the Ford 4X4 Edge and Ford Fusion Hydrogen 999, giving a power of 250 bhp and torque of 340 lb ft. This vehicle uses 4.5kg of hydrogen @ 350 Bar and has a range of 225 miles or 300 miles with 700bar storage, with a top speed: 88mph. Making Hydrogen from Natural Gas is no cleaner than a conventional car. However hydrogen can be produced from Nuclear Energy, Electrolysers via Photovoltaics and in Countries such as Iceland, Norway and Denmark, is produced from electricity generated from wind and wave technology. Hydrogen as a fuel is safer than petrol because it rapidly dissipates if it leaks. The British Prime Minister, Gordon Browne has pledged £90M to make Britain the European Capital for Electric Cars for the next generation of vehicles, while Toyota are preparing a petrol-electric (lithium–ion batteries) hybrid for the Japanese, US and European market for 2010. The standard Toyota Prius uses a conventional nickel-metal-hydride battery and the new technology is an advance on this. The Dyson corporation is also currently investigating the development of electrical vehicles fuelled by PV panels. Three examples of such developments are shown in Figure 6.

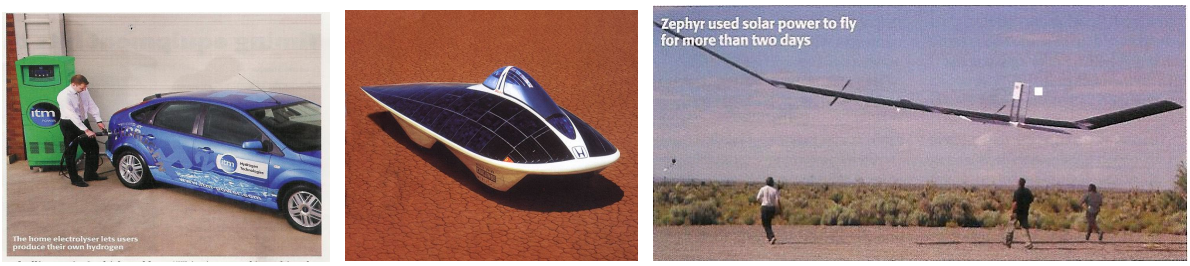


Figure 6. Electrolyser fuelled Hydrogen Car. PV Care and PV solar powered flight.

2.6 Bio fuels and LPG

Ethanol is the most widely used biofuel and over 1.5 Billion gallons are added to gasoline in the U.S. each year. It increases octane and improves emissions as a blended fuel with gasoline. The USA plan to generate 25% of its fuel from Bio materials by 2025 while Europe has targeted 10% of fuels from bio by the year 2020. Currently however up to 25% of America's corn harvest is converted to ethanol (2008) assisted by 51cent subsidy on each gallon. This subsidy has made the production of ethanol very attractive to farmers but may have a negative impact on food production. Other raw materials include Methanol, Waste Cooking oil, Camelina Sativa, Rapeseed, and Beef Tallow.
Camelina Sativa has a similar yield to rapeseed, grows well on poor soil and is cheaper to produce than rapeseed oil. One of the drawbacks of biodiesel include solidification at low temperatures and it is normally blended with petroleum diesel to operate in vehicles, taking account of engine modification requirements. Figure 7. shows a typical process for converting seed to biodiesel. The glycerol produced can be used for pharmaceutical applications provided there is enough supply.
For Liquid Petroleum Gas, gases such as Propane and Butane are a minority of transport fuels to date. The CO_2 emissions with LPG are estimated to produce 12% less than a gasoline vehicle based on Tank-To-Wheel, or tailpipes, emissions. For example, an originally gasoline-fuelled car emitting 148 g/km would emit 130 g/km at the tailpipe on LPG when running on LPG and therefore the 4.6 million LPG vehicles, supported by 22,500 stations, in Europe equates to ~ 1.4 million tons of CO_2 savings each year. Although the market for LPG vehicles reduced considerably in Ireland, other EU countries have a thriving market. In

Germany for instance, LPG vehicles numbered 65,000 in 2005, 125,000 in 2006 and 190,000 in 2007. Projections are for 430,000 by 2010 and 1,000,000 by 2015. LPG has substantial reserves due to its dual origins: 66% from gas field extraction and 34% from crude oil refining

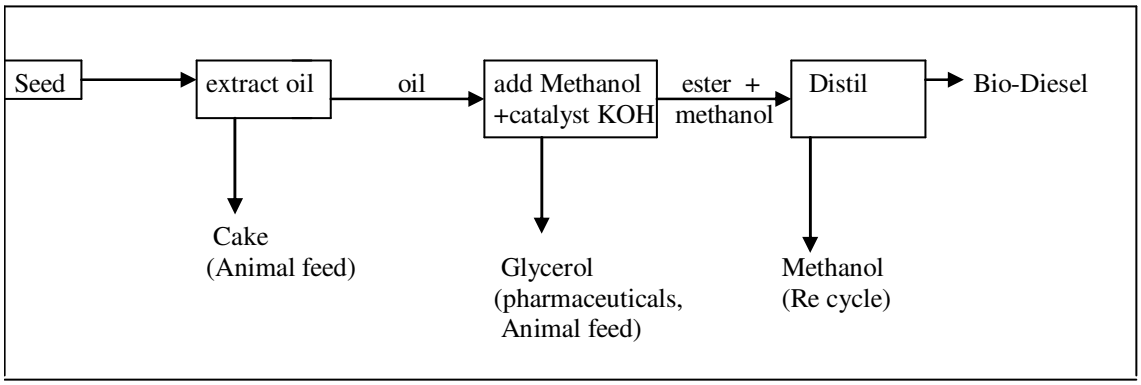


Figure 7. Biodiesel production from vegetable oil seed such as Rape Seed or Camelina Sativa.

2.7 Fuel Cells

Fuel Cells convert Hydrogen to a viable and sustainable electrical energy. Hydrogen Fuel Cells generate a current by passing hydrogen and Oxygen over either side of a membrane. This allows an exchange of protons and causes electrons to flow. The by products are water and heat energy which can be used for heating purposes. Approximately 50%of the hydrogen energy is converted to electricity in the process. The main types of Fuel Cells include:

Proton Exchange Membrane (PEM)
Phosphoric Acid Fuel Cells (PAFC)
Molten Carbonate Fuel Cells (MCFC)
Zinc-Air Fuel Cells (ZAFC)
Regenerative Fuel Cells (RFC)
Alkaline Fuel Cells (AFC)
Direct Methanol Fuel Cells (DMFC)
Solid Oxide Fuel Cells (SOFC)
Protonic Ceramic Fuel Cell (PCFC)

Recent developments in fuel cells include signage, lighthouses, and transport applications in motor bikes, cars and busses for urban use.

2.8 Bio Gas

Landfill gas contributes the largest proportion of renewable energy in the UK. One such application includes Heathfield landfill which opened in 1998 and due to close in 2016, burying 9M tonnes of refuse and currently potential to generate up to 6MW of electricity. Organic matter breaks down in the absence of oxygen, anaerobic digestion occurs, producing methane, CH_4. However CH_4 is 21 times more potent than Carbon as a greenhouse gas. The main energy of biogas comes from methane (37.78 MJ/m^3). Following scrubbing the methane content can be brought to 97% and with an energy value of 36.6MJ/m^3 is equivalent to 1 litre of petrol. In the Linkoping Biogas plant in Sweden, up to 99,000tpa of waste is treated and the produced CH_4 is used to fuel 56 buses and 360 other vehicles. The Biogas replaces 2,000000 litres of diesel fuel. By using Biogas systems efficiently, the waste products of a city may typically fuel the bus fleet of the city. In Ireland, aagricultural wastes are the main source of biomass as shown in Figure 8.

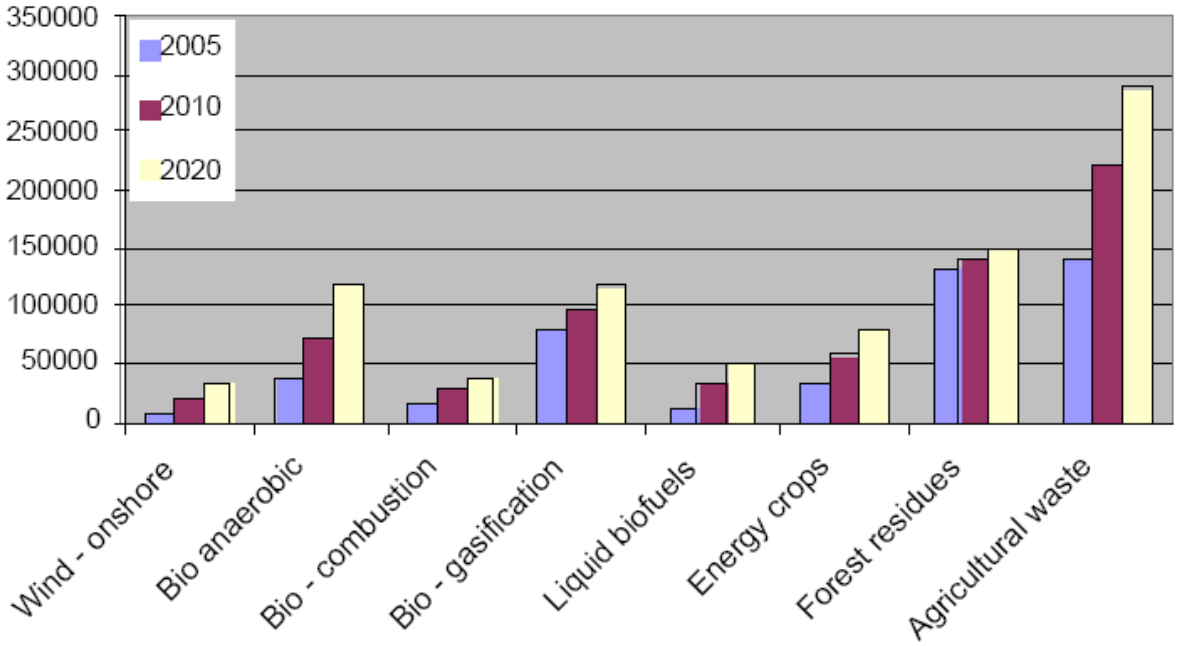
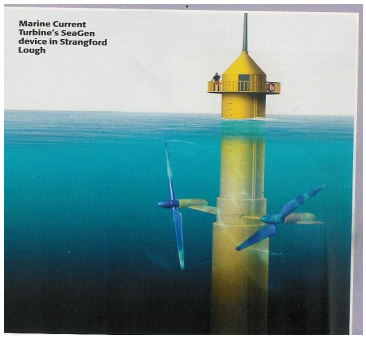


Figure 8. Sources of Bio gas production in Ireland 2005 to 2020.

2.9 Tidal, wave energy and solar ponds

In May 2008, the worlds first commercial tidal turbine was installed in Strangford Lough, in Northern Ireland by Marine Current Turbines. This is designed to produce 1.2 MW of electricity and when connected to the National Grid, will provide power to 1,000 homes. Also in May 2008, Open Hydro connected a demonstration tidal power rig to the UK grid of 250kW in Orkney. Wave power is predictable and Ireland is well positioned to harness this energy. Other applications include Tidal Barrages which are very rare and require a 5m head of water for worthwhile electricity. Examples of these are shown in Figure 9. and Figure 10.



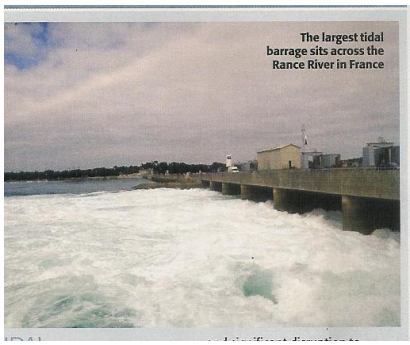


Figure 9. Tidal Turbine In Ireland **Figure 10. Tidal Barrage in France**

Solar pond technology inhibits convection by dissolving salt into the base layer of a pond. The salt concentration increases with depth, forming a salinity gradient. Solar ponds generally utilize a 1- 2 m salinity gradient and operate at moderately high temperatures. The salinity gradient prevents dense hot water rising from the bottom. The sunlight which reaches the bottom of the pond remains entrapped there and the useful thermal energy is then withdrawn from the solar pond in the form of hot brine. Even when covered with a sheet of ice and surrounded by drifts of snow, the El Paso (Mexico) Solar Pond's lower zones produce temperatures of 154°F which is hot enough to generate electricity. Application include

generating heat and electricity, water desalination, space heating thermal energy storage, heating for greenhouses and livestock buildings

3.0 Conclusions

Climate change could cost the world at least 5% of GDP each year and if more dramatic predictions come to pass, the cost could be more than 20%. Natural cycles and sinks are not absorbing atmospheric carbon as fast as we are releasing it as GHGs and atmospheric CO_2 concentrations have increased by almost 100 ppm since their pre-industrial level, reaching 379 ppm in 2005. The benefits of strong, early action considerably outweigh the costs.

It is estimated that each tonne of CO_2 emitted causes damages worth at least $85, but emissions can be cut at a cost of less than $25 per tonne. The annual emissions of Ireland for 2007 are 70.1 Million tonnes CO_2 while the Kyoto Targets for Ireland are 62.8 Mt for the years 2008-2012. This is 13% above the 1990 base. The EU Targets for Ireland under the 20-20 strategy include emissions reduction of 20% (on 2005 base), increase renewables from 3.1% to 16% and use energy in a smarter way in all applications. The Introduction of Low energy Buildings, combined-cycle power plants, efficient lighting should enhance this.

Renewables are not load following like traditional power generation. They are intermittent, variable in production, often distant from loads, and not dispatchable.

In light of the development in renewable and sustainable energy, the energy storage sector is central to the full integration of wind energy generation and Carbon Capture is crucial to reduce CO_2 emissions by 60%-80% by 2050. The EU envisages wide scale deployment of CCS from 2020 onwards. In the Transport sector, improvements in Engine efficiency is required coupled with a move to hybrid & electric vehicles with a market for Biofuels and Hydrogen powered machinery.

References

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USING FERROGRAPHY TO TEST ENGINE CONDITION

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Stručni članak / Professional paper

Abstract: Oils extracted from the engines of two vehicles, using petrol and LPG as an alternative fuel, respectively, were tested in order to check applicability of ferrography as a method for assessing material wear and to show intensity of the engine material wear. The condition of the two engines was monitored by analyzing of the oil samples from the two vehicles. Based on the testing results, the changes of the indexes of wear intensity in relation to the vehicle mileages were compared. After the testing results had been processed, the conclusions about applicability of the method for the material wear monitoring were made.

Key words: ferrography, ferrogram, index of wear particles content, wear

Sažetak: Provedena su ispitivanja ulja izvađenih iz motora dvaju vozila pogonjenih benzinom UNP-om kao alternativnim gorivom kako bi se provjerila primjenljivost ferografije kao metode za procjenu trošenja materijala, te pokazao intenzitet trošenja materijala motora. Praćenje stanja oba motora izvršeno je analizom ulja na uzorcima iz oba vozila. Na osnovi dobivenih rezultata ispitivanja uspoređene su promjene indeksa intenziteta trošenja u odnosu na broj prijeđenih kilometara. Nakon obrade rezultata ispitivanja izvedeni su zaključci o primjenjivosti metode za praćenje trošenja materijala.

Ključne riječi: ferografija, ferogram, indeks sadržaja čestica trošenja, trošenje

1. INTRODUCTION

Due to the recent sharp fluctuations in prices of petrol and diesel fuels, concerns about dependency on oil products have been revived. One of the strategies for a reduction of the dependency is a production of vehicles that are fueled by alternative fuels, which replace both petrol and diesel. The development of the alternative fuels has also been prompted by the environmental concerns, since the alternative fuels reduce noxious emissions.

Several fuels are considered to be alternative fuels: electric energy, natural gas, liquid petrol gas - LPG, ethanol, methanol, bio-diesel and hydrogen. Some of them are similar to the conventional fuels and can be used in conventional vehicles with minor or no modifications, while some are considerably different from the conventional fuels and require employment of a completely different engine and the vehicle steering system.

For the petrol vehicles the most acceptable alternative is the LPG use. In order to use this alternative fuel, minor modifications on the engine are necessary, and this fuel can be used without restrictions in both older and new vehicles. Nowadays it is possible to get some vehicles which are already factory-adjusted for the LPG use, and consequently the engine can work with both fuel types – petrol and LPG.

Since ever more vehicle owners decide to modify their vehicles for the LPG use, a question needs to be asked about the engine behavior during the utilization of this fuel, i.e. whether the engine parts wear is bigger with the LPG changeover or similar to the wear when the fuel is petrol.

In order to answer this question the time-consuming tests of a larger sample material are necessary, and this paper aims at demonstrating whether in such tests Ferrography can be applied as the method for assessing the material wear.

2. FERROGRAPHY

Ferrography is an analytical method of precipitating the ferrous particles and determining their content, which was developed in the 1970s. Determining the quantity and size of the metal particles in the used engine oil has answered numerous questions and stimulated further research and development of respective analytical techniques. Thus, the Ferrography has enabled:

- precipitation of metal ferrous particles and their classification by size
- providing of basic information about four key features of the particles – quantity, size, morphology and composition
- introduction of new morphological description of particles created through the metal wear and better knowledge of the types and causes of the material wear.

A ferrographic process comprises the pumping of the lubricating oil, which is then tested, at a slow speed (normally around 0.25 ml/second) in vicinity of a very strong magnetic field that affects the metal particles and makes them concentrate on a movable transparent carrier. This method has also enabled a separation of metal particles not only from the lubricating oils, but also from lubricating grease, exhaust gasses of the internal combustion engines, and even from biological materials. Due to the influence of the magnetic field the precipitated particles can be further analyzed in different ways, employing various technical processes. The optical techniques are used for this, as well as the spectrophotometry for the quantification of the particles.

The spectrometry methods have provided insight into the content of other metals in the particles, primarily copper, which would allow conclusions as to which engine parts are in particular cases most subjected to the material wear. In medical sciences the advanced ferrographic methods have enabled insights into the behavior of viruses in the human body, and even into the monitoring of specific diseases such as AIDS. The development of ferrography as an analytical method, particularly advanced due to the employment of computers, has been an important contribution to the technique of lubrication as well as many other segments of modern science.

3.1 WEAR PARTICLE CONTENT (WPC)

In determining the index of Wear Particle Content the Direct Reading Ferrograph is used.

A sample of the used oil with wear particles flows above a strong magnet which attracts the metal particles and consequently they are deposited onto the bottom of a glass tube. Large particles are precipitated first, while the small particles are deposited later because the force in the magnetic field is proportional to its volume, and resistance to movement through the medium is proportional to the surface of the particle cross section transversal to the movement through the medium. Research has demonstrated that the ration between the small and the large particles, which remains relatively constant for as long as the wear process is unchangeable, is an interesting feature of the wear process.

The index of Wear Particle Content is read directly on the device, and it is calculated by the following formula:

$$\mathbf{WPC = D_L + D_S, \%}$$

where:

- WPC is – Index of Wear Particle Content, %
- D_L is – surface covered with large particles, %
- D_s is – surface covered with small particles, %

A sudden increase of the wear particles content indicates irregularities of the wear process itself. It is in this way that irregularities can be determined prior to a serious damage within the observed tribosystem. The first warning occurs at ¾ of the total duration of the test, which leaves enough time to intervene, prevent failures and serious damages.

3.2 FERROGRAM ANALYSIS

Direct Reading Ferrograph is used for a routine control of the wear process condition. Once the Ferrograph registers an undesirable change, further information is obtained through a Ferrogram analysis. The Ferrogram is obtained by the passage of the medium sample onto the glass tube under which a strong magnet is placed.

The particles are deposited onto the tube selectively, depending on their size. This phenomenon is more distinct whit magnetic materials, so that large but magnetically weak particles can be found precipitated along the whole of the Ferrogram. The particles of nonferrous materials or nonmetals become magnetic in a limited manner through the conveyance of ferrous materials if there is a contact between them. The carrier can precipitate even the completely nonmagnetic particles.

After the precipitation of the particles has been completed, the rest of the medium is washed with a solvent, and the particles are fixed with a fixation agent on the stand. The plate with the particles deposited by size is called Ferrogram.

Ferrogram can be analyzed using:

- a bichromatic microscope or ferroscope
- a scanning microscope

4. TESTING

The testing was aimed at checking the applicability of Ferrography as a method for assessing of the material wear, as well as to show the wear material intensity in a petrol fueled engine and in an engine fueled with LPG as an alternative fuel. The condition of the two engines was monitored by analyzing the oil samples from both of the vehicles.

The testing was conducted on two VW Golf V vehicles with 1.6 l petrol engines of 75 kW, of which one was fueled with LPG and the other with petrol.

From both vehicles the samples were taken 9 times, and this covered the mileage range of 0 to 30.000 kilometers.

It was very important that the sample of the lubricating agent which was subjected to the testing was as representative as possible. The sampling itself was given much attention because the errors are possible due to which a real insight into the condition of the monitored tribosystem would not be possible.

While storing the samples it is desirable that the sample vessel be of at least 15ml capacity and that it be made of transparent glass with flat side walls. The advantage of the transparent glass and the flat walls lies in the possibility of a visual control of the samples. With the visual control it is possible to control:

- color – oxidation as a consequence of over-heating or degradation of lubricant agent in general make the oil darker
- degree of sludge creation after the samples' storage
- very serious wear cases – very large single wear particles are visible
- presence of alien fluids in the oil

Vessels of polymeric materials are not used because the polymeric materials in contact with the oil could pollute the sample with polymeric particles, various gels and corrosive fluids. The polymeric vessels can get sticky, thus keeping the wear particles on their inner surface. Consequently, the sample can become unrepresentative.

4.3 TESTING EQUIPMENT

The testing was conducted on a PMA 90 S Direct Reading Ferrograph (Illustration 1) in the Laboratory for Tribology, Institute for Materials, Faculty of Machine Engineering and Naval Engineering in Zagreb.

Illustration 1 – PMA 90 S Direct Reading Ferrograph

5. TEST RESULTS

5.1 RESULTS OF THE OIL ANALYSIS FROM THE LPG FUELED VEHICLE

Table 1 shows the results of the analysis of the oil from the LPG fueled vehicle.

Table 1: Results of the oil analysis from the LPG fueled vehicle

OIL SAMPLES (FUEL - LPG)				
Sample	D_L	D_S	WPC	km
1	1,05	0,48	1,53	673
2	0	0,75	0,75	4.212
3	0,03	0,14	0,17	14.386
4	0	1,66	1,66	18.877
5	0,06	0,41	0,47	20.165
6	0,18	0,24	0,42	22.050
7	0,48	0,50	0,98	24.780
8	0,51	0,52	1,03	27.511
9	0,09	0,99	1,08	20.257

The data from the Table 1, obtained through a ferrographic analysis of the sample, can be presented in a chart, which makes it possible to monitor potential tendency of the wear particles content, depending on the mileage. The chart is shown in Illustration 2.

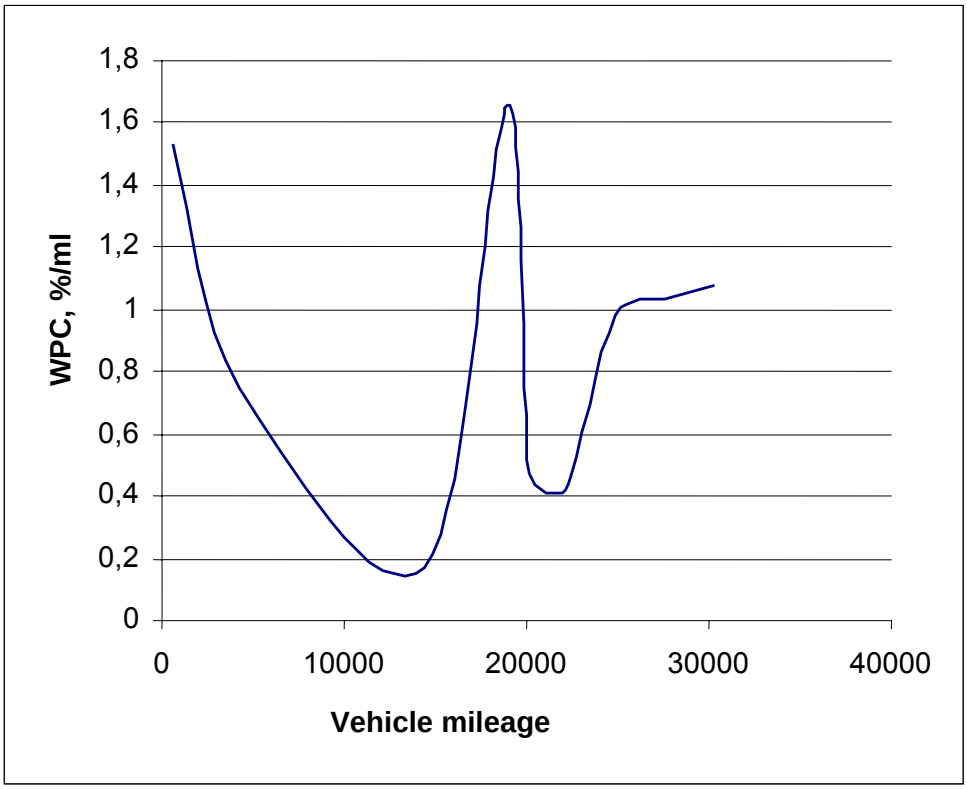

Illustration 2 – Wear Particle Content Curve for the LPG fueled vehicle

The curve allows us to conclude that after the initial running-in of the engine, a considerable decrease in the wear particles content will occur until around 20000 km when a sudden increase in the wear particles content will occur, and that after additional 5000 km the wear will stabilize around the value of about 1 %/ml.

5.2 RESULTS OF THE OIL ANALYSIS FROM THE PETROL FUELED VEHICLE

Table 2 shows the results of the analysis of the oil from the petrol fueled vehicle.

Table 2: Results of the oil analysis from the petrol fueled vehicle

OIL SAMPLES (FUEL - PTEROL)				
Sample	D_L	D_S	WPC	km
1	1,04	0,47	1,51	1.069
2	0,05	0,44	0,49	4.600
3	0,11	0,46	0,57	12.794
4	0,04	0,65	0,69	17.348
5	0	1,28	1,28	19.300
6	0	0,03	0,03	22.571
7	0,16	0,45	0,61	26.087
8	0,21	0,36	0,57	28.104
9	0,10	0,58	0,68	30.150

The date from the Table 2, obtained through a ferrographic analysis of the sample, can be presented in a chart, which makes it possible to monitor potential tendency of the wear particles content, depending on the mileage. The chart is shown in Illustration 3.

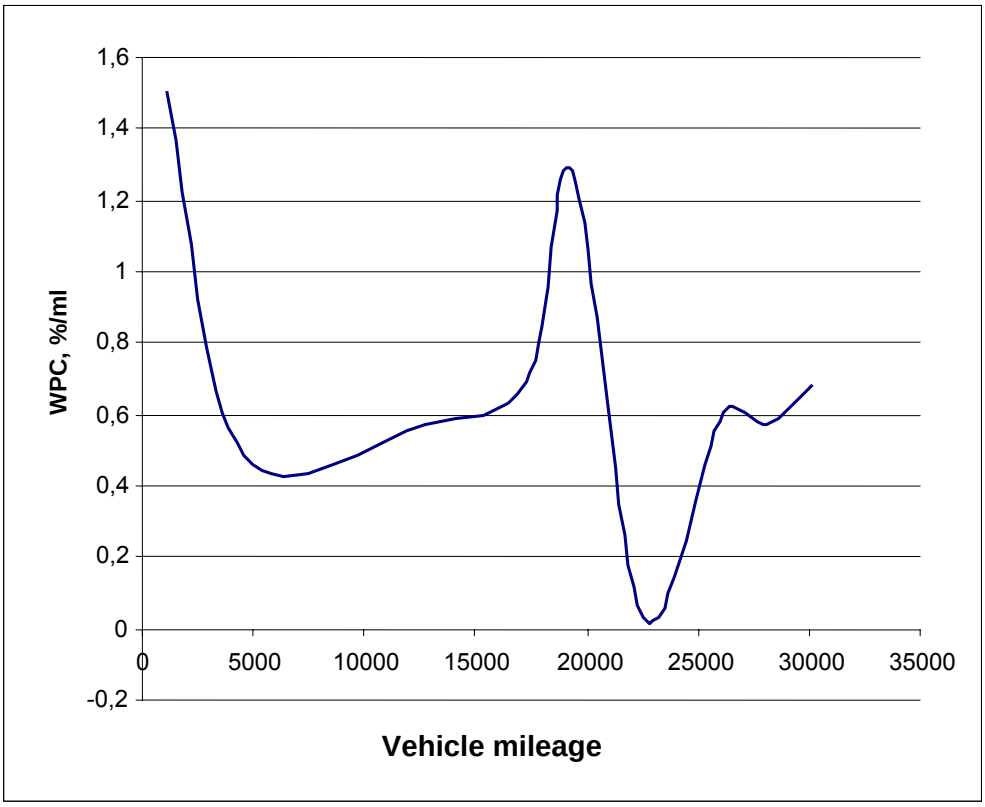

Illustration 3 - Wear Particle Content Curve for the petrol fueled vehicle

The curve allows us to conclude that after the initial running-in of the engine, a considerable decrease in the wear particles content will occur until around 20000 km when a sudden increase in the wear particles content will occur, and that after additional 5000 km the wear will stabilize around the value of about 0.6 %/ml.

6. ANALYSIS OF THE TESTING RESULTS

Based on the obtained results of the testing, we can compare the changes of the indexes of wear intensity in relation to the vehicle mileages. Illustrations 4 and 5 show the changes of the indexes of wear intensity in relation to the vehicle mileage for the LPG and the petrol fueled vehicle, respectively.

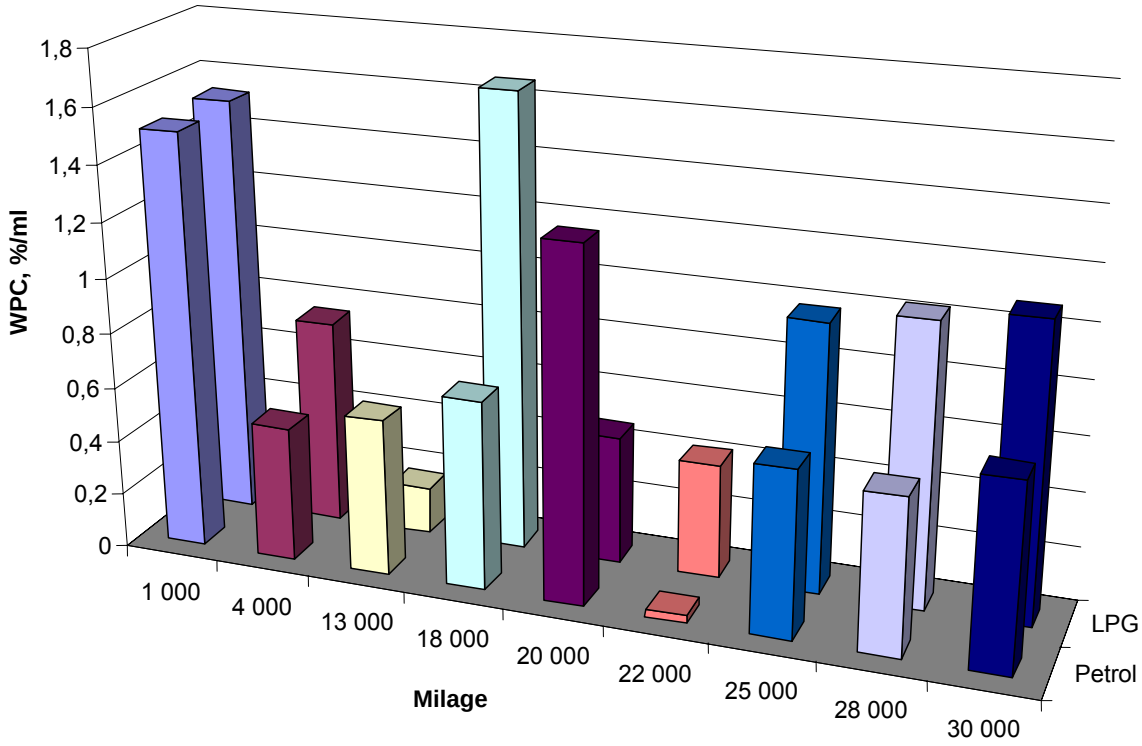

Illustration 4 – Comparison of the changes of WPC indexes in relation to the mileage

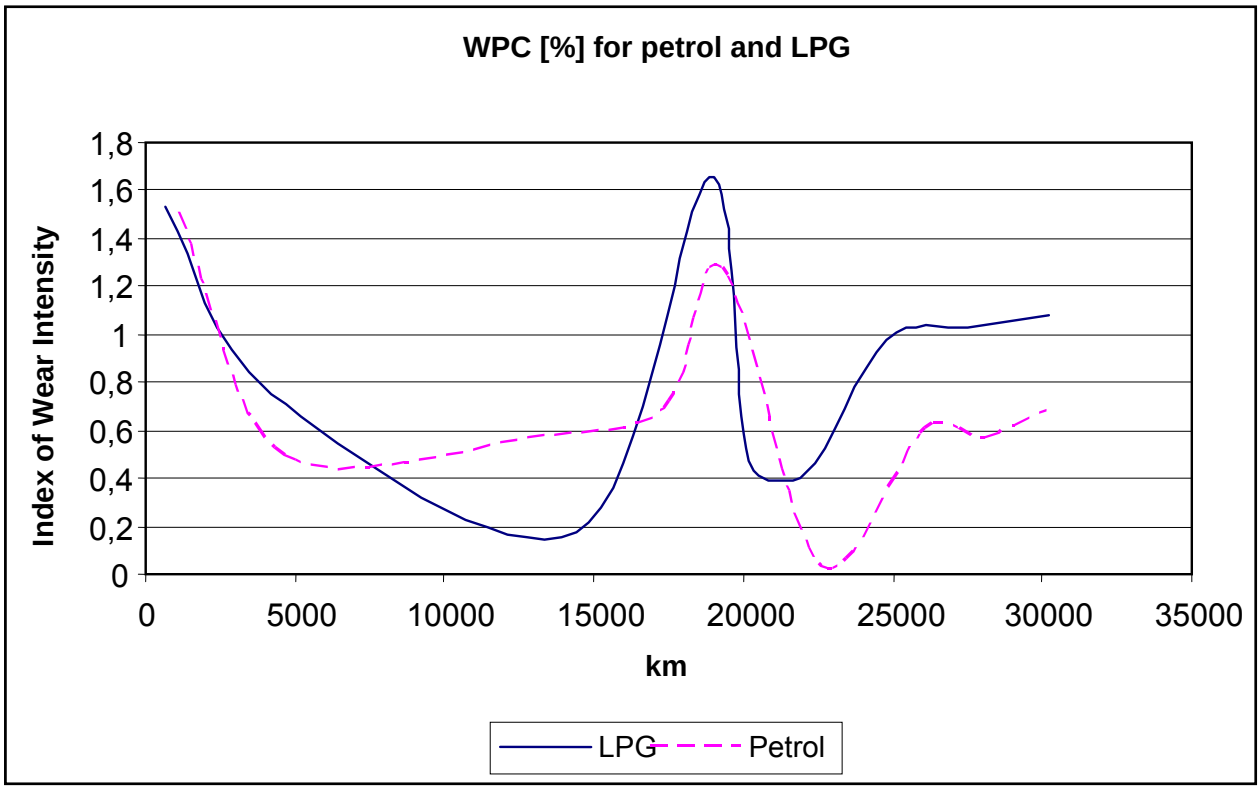

Illustration 5 – Index of Wear Particle Intensity in relation to the mileage

After the testing and the results analysis, the changes of the indexes of wear intensity were noticed, with no significant differences between the LPG fueled vehicle and the petrol fueled vehicle. After 20000 km, sudden changes occur, i.e. the WPC increases, and after additional 5000 km the wear process stabilizes.

This can be concluded by observing the changes of values of the measured surfaces covered with large (Illustration 6) and small (Illustration 7) particles for the two tested engines.

After the running-in of the engine (up to 5000 km) the number of large particles decreases significantly, only to increase after a total of 20000 km. With 27000 km, the number of large particles reaches its maximum and decreases afterwards.

The change of the number of small particles (Illustration 7) does not correspond entirely to the change of the large particles. At first there are less small particles than the large ones, and from their number it could be concluded that the running-in ends with 13000 km, when their number is at the lowest point. After that, their number suddenly grows, and at 18000 km it reaches the maximum. At the same time, the number of large particles is almost 0. After 22000 km the number of small particles grows again.

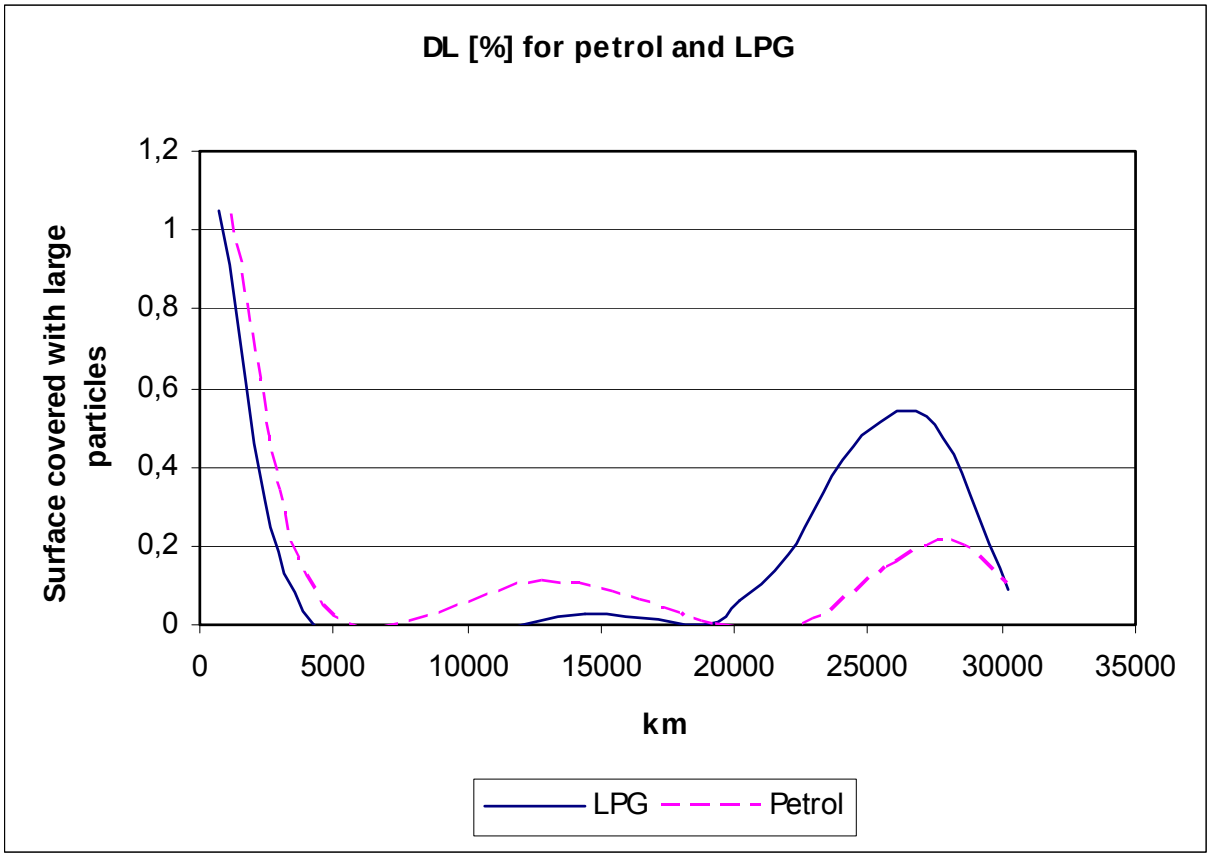

Illustration 6 – Surface covered with large particles in relation to mileage

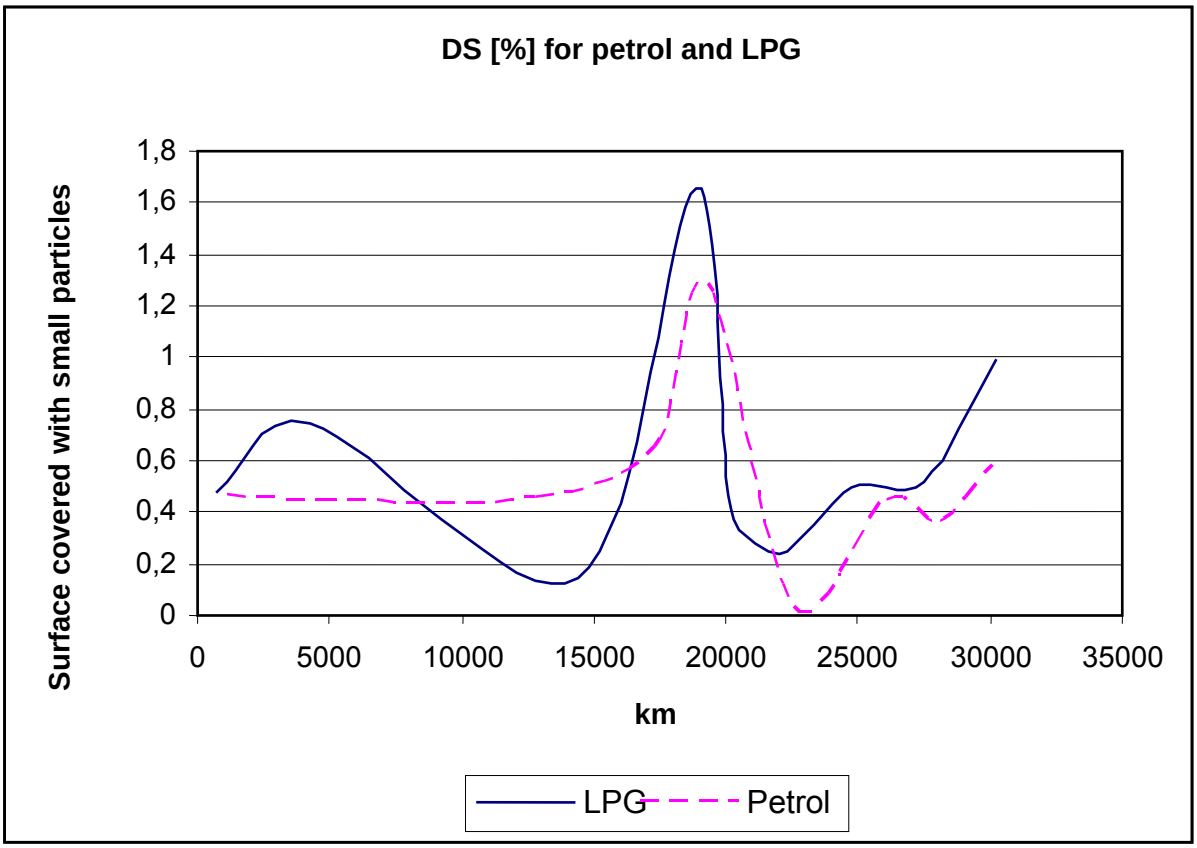

Illustration 7 – Surface covered with small particles in relation to mileage

We can find an explanation of this most probably in the process of the running-in of the engine, but it is possible that an error occurred during the sampling (a short waiting time between the putting out of the engine and the sampling can cause a deposition of particles and a collection of non-representative samples; taking the samples from too close to the bottom of the oil container can also result in an unrepresentative sample). Also, errors are possible in measurements during the sample preparation and the ferrograph use.

In order to establish the precise cause of such testing results, it would be necessary to dismantle the two engines after they reach the mileage at which the mentioned changes occur, but such an opportunity has not arisen and thus it is not possible to determine with certainty the precise cause of such changes.

Since the Wear Particle Content increased at the same mileage for both vehicles, it can be concluded that an operation failure in the engine occurred, which was not caused by the fuel type.

7. CONCLUSION

Based on the data obtained in an oil analysis this paper attempted to compare the condition of an engine fueled by LPG with the condition of an engine fueled by petrol.

The obtained results show that it is not possible to determine unambiguously that one of the two types of fuel is better in terms of engine wear, because during the mileage of 30000 km the periods when one or the other fuel type causes smaller engine wear alternate.

The vehicles tested in this research are of the same make, but during the testing period they were steered by various drivers, and the driving regimes were not equal. In addition to it, errors can easily be made during the sampling. Furthermore, based on the WPC increase there is a possibility of a failure occurring in the engine that is not related to the fuel type.

Considering all this, and the fact that the testing was conducted on a small number of samples, monitoring the wear over a relatively short period of time, it is not possible to evaluate which of these two fuel types causes less engine wear.

However, the testing has revealed that Ferrography can be used to monitor the material wear, and consequently get insight into the engine condition, i.e. its wear. Thus, it can considerably contribute to an improvement of the vehicle maintenance system and prevent failures in a timely manner.

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DESIGN OF SMALL DIVERTOR SEGMENTS FOR FUSION REACTOR APPLICATIONS

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Izvorni znanstveni rad / Original scientific paper

Abstract

The coefficient of thermal expansion (CTE) of Cu/W composite tubes (copper matrix reinforced with the continuous tungsten fibres) with outer diameter of 10 mm, inner diameter of 6 mm and length of 5 or 2 mm was characterised. Tube samples served as demonstrators for cooling system of the divertor, which is a part of the fusion reactor machine. Cu/W samples were made by liquid metal infiltration technology and contained different volume fractions of continuous tungsten fibres in the copper matrix (10 vol. % and 76 vol. %). The W-fibre had circumferential orientation or it was arranged in the plane normal to the tube axis as a woven mesh. Tubes with fibre fraction of 10 vol. % showed at 300 ^{o}C lower CTE (14.8 ppm.K^{-1}) if the reinforcing mesh was lying in the plane normal to the tube axis and in the case when the mesh orientation was circumferential the CTE was 22.0 ppm.K^{-1}. Tubes with higher fibre fraction (76 vol. %, circumferential winding) showed much lower values (CTE = 5 - 7 ppm/K) at the same temperature.

Introduction

In fusion reactors isotopes of hydrogen (tritium and deuterium) are used as fuel for power production. Both components weight less after the reaction than those before the reaction and the mass difference is released as energy. According to Albert Einstein's equation: $E = m.c^2$ (energy = mass × speed of light^2) it is seen that very small changes of mass in nuclear fuel can release a great deal of usable energy.

Most fusion reactors use deuterium and tritium, which have a single proton but, while hydrogen has no neutrons, deuterium has one and tritium has two. For preparation of fusion, these isotopes are heated and become plasma - an ionised gas consisting of free electrons and nuclei not bound into atoms.

Deuterium and tritium ions are positively charged and repel each other strongly with an electrostatic force. To overcome this repulsion and to bring these lighter nuclei into collision it is necessary to confine the plasma at very high temperatures. The fusion plasma must be confined and kept clean for the longest possible sustained fusion reaction – ideally for several hours [1].

Fusion reaction occurs inside the Sun at 15 million°C, however in experimental reactors it needs be at about more than 100 million °C. It is due to the fact that the pressure inside a fusion reactor will be similar to atmospheric pressure. It is much lower than the one in Sun [2].

Neutrons as an electrically neutral particles are unaffected by any magnetic fields and during fusion these fast neutrons are emitted in all directions. They slow down in the blanket walls that become heated. This heat can be transferred to a medium such as high-pressure helium or steam. This hot, high-pressure gas can be used for driving of an electricity-generating turbine.

The ITER divertor consists of a cassette body, which holds three plasma-facing components, namely the inner and outer vertical targets and the dome. The heat from plasma is removed in the inner and outer targets. The design of targets can foresee different types of armour: tungsten monoblocks and carbon-fibre monoblocks. As a result of contact with the vacuum vessel the tiles of the divertor will be exposed to very high temperature and need to withstand cyclic thermal load in a large temperature interval (up to 550 ^{o}C).

For the reactor cooling system it is proposed to use the same materials as for other divertor parts – except tungsten and CuCrZr also the copper matrix reinforced with continuous tungsten fibre composite (Cu/W MMC) is in the focus.

In the paper some thermophysical properties of the Cu/W composite are presented. From the composite small tubes were prepared and their thermal expansion tested. Results would serve for designing and preparation of small mock-ups for cooling system of the divertor body.

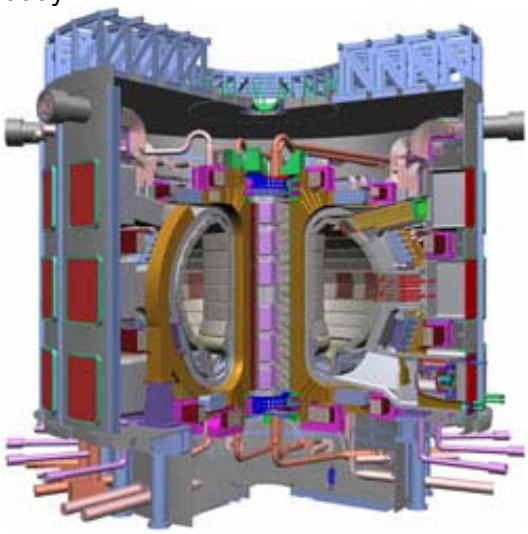

Figure 1 The ITER machine – the divertor is situated to its lower part

Figure 2 Divertor - situated in the bottom of the ITER vessel

Experimental

Sample preparation

The Cu/W MMC samples were produced by the liquid metal infiltration technology, where tungsten fibre preforms were immersed to the molten copper that penetrated to the porous body. Suitable wetting angle between copper and tungsten enables that infiltration of fibrous tungsten body is spontaneous. However, in this case very little gas pressure (up to 1 MPa) was used to achieve higher infiltration quality. The infiltration was performed at temperature Ti = 1200 °C during the period of 180 s.

Continuous tungsten fibres that were used for preform production had diameter of 100 μm. The first type of reinforcing fibre was delivered on coils and the second one in the form of a mesh. The tungsten wire mesh contained 12 wires per centimetre (Fig.5) i.e. the maximum volume fraction of fibres in the preform made from a mesh could be very low (about 10 vol. %).

Three types of Cu/W MMC samples were prepared. First two types were reinforced either with the mesh or with the wire from the coil. Reinforcement was wound around the graphite rod with a diameter of 6 mm until it formed the 2 mm thick layer.

For the W-mesh the graphite rod had length of 60 mm. After copper infiltration the MMC tube with outer diameter of 10 mm and fibre content of 10 vol. % of was obtained (Fig.3).

The W-fibre from the coil was wound around the shorter graphite rod (length of 35 mm). The outer diameter of the tube was the same as in the first case. However, the fibre content in the composite was much higher (76 vol. % - Fig.4).

The third type of the tube presented completely different fibre orientation. W-fibres that were lying in the plane normal to the tube axis had woven orientation. During sample production several layers of the reinforcing W-mesh were stacked to the graphite die with dimensions 50 x 80 x 2 mm and closed. After infiltration the Cu/W MMC plate was obtained. From the plate a tube sample with outer diameter of 10 mm, inner diameter of 6 mm and length 2 mm were cut-out.

Coefficient of thermal expansion measurement

Thermal expansion tests were performed in a classical push-rod dilatometer. Characterised were the relative dilatation and the coefficient of thermal expansion. Measurements were performed in radial direction for tubes made from both the Cu/W composite and pure copper. Tube samples had outer diameters of 10 mm, inner diameter of 6 mm and length l = 5 mm or 2 mm. During each measurement three heating and cooling cycles in temperature range from 20 °C up to 550 °C were performed in argon atmosphere. Obtained CTE results are presented in Table 1.

Results

Microstructure

Microstructure of the Cu/W composite with different fibre content and orientation is presented in Figures 3 – 5. It is visible that the MMC reinforced with the tungsten mesh contained very low fibre fraction (Fig.3 and 5). On the other hand the sample reinforced with the W-fibre from the coil had very high fibre content (Fig.4).

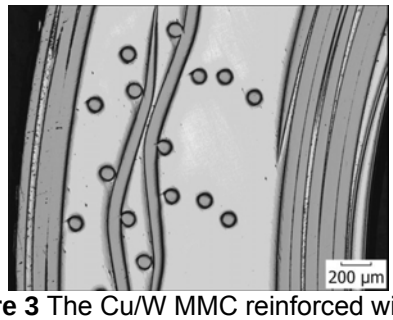

Figure 3 The Cu/W MMC reinforced with W-mesh wound on graphite rod: cross section in the plane normal to the tube axis

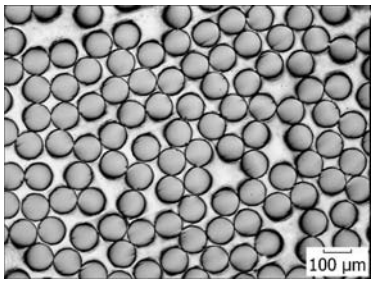

Figure 4 The Cu/W MMC reinforced with the W-fibre from a coil wound on the graphite rod. Volume fraction of fibres was of about 76 %

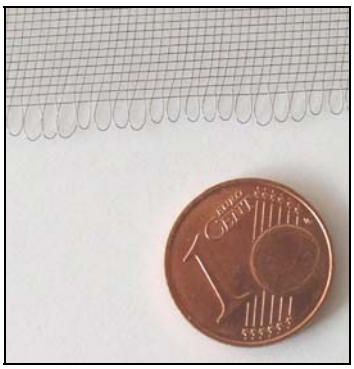

Figure 5 Tungsten wire mesh used for MMC tube production

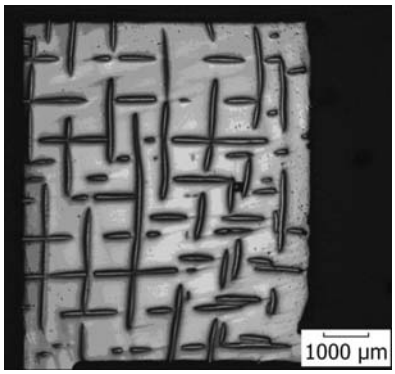

Figure 6 Microstructure of the Cu/W composite reinforced with the W-mesh: view on he plane normal to the tube axis

Thermal expansion

The tube reinforced with the circumferentially wound W-mesh (fibre content: 10 vol. %) showed in the temperature range 100 ^{o}C - 300 ^{o}C the CTE between 10 ppm.K^{-1} and 22 ppm.K^{-1}. Then it decreased to 14 ppm.K^{-1} at 500 ^{o}C. This behaviour was typical for the second and the third thermal cycle. The tube reinforced with the W-mesh lying in the plane normal to the tube axis showed lower CTE – especially above 300 ^{o}C (Table 1).

In comparison to previous samples the one with high fibre content (76 vol. %) showed much lower CTE values (5 – 7 ppm.K^{-1}). This is due to much higher fibre content. However properties of the tube with this type of reinforcement can not be adjusted according to requirements because it would be difficult to lower the fibre content.

The CTE of the copper ring was higher than those made from the composite material. Only at 200 ^{o}C the tube with circumferential reinforcement and low fibre content presented very similar CTE.

Table 1 CTE values of different tube samples

		Coefficient of thermal expansion ($x10^{-6}.K^{-1}$)				
MMC description	Tube cross - section	100 (°C)	200 (°C)	300 (°C)	400 (°C)	500 (°C)
tube reinforced with the W-mesh circumferentially wound, (fibre content -10 vol.%)		10.4	15.4	22.0	17	14
tube reinforced with the W-mesh lying in the plane normal to the tube axis		10.6	14.4	14.8	10.2	7.1
tube reinforced with the W-fibre circumferentially wound (fibre content - 76 vol.%)		5	6	7	6.5	6.2
pure copper		14	18	22	19	18.5

Conclusions

- For tubes with low fibre fraction (10 vol. %) one can see that the reinforcement with a mesh lying in the plane normal to the tube axis is more effective than the reinforcement with circumferential orientation. It is obvious especially at temperatures above 300 °C.
- Tubes with higher fibre fraction showed much lower CTE in radial direction – it was nearly at the level of that of pure tungsten (4.2 ppm.K^{-1}).
- Based on the CTE results a divertor segment for cooling system with dimensions of 27 x 27 x 41 mm^3 was produced by liquid metal infiltration method. The sample MMC tube composed of several layers of: W mesh, thin Cu foils (thickness of 0,02 mm) and wound W wire, was prepared (Fig. 7 and 8) and tested at another partner of the project consortium.

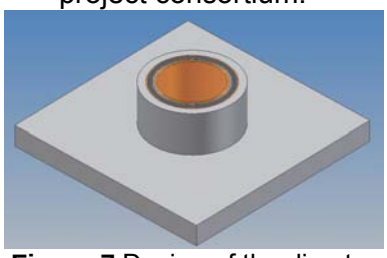

Figure 7 Design of the divertor segment – Cu/W MMC tube and W-rectangle (in lower part)

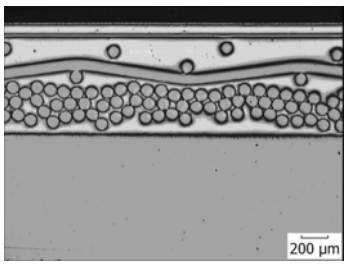

Figure 8 Microstructure of the divertor tube segment made from the Cu/W MMC

Acknowledgement

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SYNTHESIS AND CHARACTERIZATION OF POROUS GELATIN/HYDROXYAPATITE COMPOSITE

SINTEZA I KARAKTERIZACIJA POROZNOG KOMPOZITA ŽELATINA/HIDROKSIAPATIT

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Izlaganje sa znanstvenog skupa / Conference paper

Abstract: The composition of human bone is well-known inorganic/organic hybrid consisting of ~70 wt.% hydroxyapatite (HAp, $Ca_{10}(PO_4)_6(OH)_2$) and 30 wt.% organic (largely collagen) constituents. In this work a two-stage route to prepare porous composite scaffold, suitable for bone graft application, has been involved. In the first stage, complete conversion of aragonite originated cuttlefish bone *(Sepia officinalis L.)* to pure HAp, maintaining the original porous micro-architecture of bone, was achieved. In the second stage, 5 wt. % gelatin solution (GEL), derived from the organic constituent of bone (collagen), was impregnated into the HAp scaffolds and cross-linked with glutaraldehyde.

Morphology of the prepared porous HAp/GEL composite scaffold has been examined by SEM. The phase composition of the composites has been investigated by XRD, FTIR and TG analysis.

The FTIR spectra of HAp/GEL composites contain only the characteristic peaks of HAp and GEL. There is no evidence of formation new chemical bonds between HAp and GEL. Different content of organic phase obtained by TG analysis, after heat treatment of the samples up to 1000°C, corresponds to the different procedure of impregnation. The TGA curves showed two main weight losses centered approximately at 350°C and at 520 °C that are attributed to the elimination of proline and to the oxidation of all content of glyicine, respectively. Morphological investigations of the prepared composite scaffold performed by SEM revealed the appearance of much more regular sponge-like microspheres deposited on the original microstructure of HAp converted cuttlefish bone. The EDX spectra of sponge-like microspheres indicated the presence of C (~18.8 wt.%), P (~14.8 wt.%) and Ca (~20.2 wt.%).
Keywords: hydroxyapatite scaffold, gelatin, composite, bone tissue engineering

Sažetak: Koštano tkivo je građeno od prirodnog kompozitnog materijala kojeg čine anorganska komponenta hidroksiapatit ~70 mas.% (HAp, $Ca_{10}(PO_4)_6(OH)_2$) i organska komponenta 30 mas.% (uglavnom kolagen). U ovom istraživanju pripravljen je porozni kompozitni kostur pogodan za implantaciju u koštano tkivo. HAp je sintetiziran konverzijom aragonita iz sipine kosti *(Sepia officinalis L.)* pri čemu je zadržana porozna mikrostruktura kosti. HAp uzorci su zatim impregnirani 5% otopinom želatine (GEL) izvedene iz kolagena te umreženi glutaradlehidom.

Morfologija pripravljenih poroznih kompozitnih uzoraka određena je SEM mikroskopijom. Fazni sastav uzoraka utvrđen je XRD, FTIR i TG analizom.

Vrpce FTIR spektra kompozitnih uzoraka su karakteristične za HAp odnosno GEL te ne ukazuju na formiranje novih kemijskih veza. Promjena sadržaja organske faze određene TG analizom odgovara različitim načinima impregnacije GEL-om. TG krivulje ukazuju na dva značajna gubitka mase oko 350°C i 520°C koji odgovaraju raspadu prolina odnosno glicina. SEM mikrografi ukazuju na spužvastu strukturu kompozitnih čestica sferičnog oblika nastalih na površini sintetiziranog HAp. EDX spektar spužvastih kompozitnih čestica pokazuje prisutnost C (~18.8 mas.%), P (~14.8 mas.%) i Ca (~20.2 mas.%).
Ključne riječi: hidroksiapatit, želatina, kompozit, tkivno inženjerstvo

MOGUĆNOST USPOREDBE METODA ZA MJERENJE DEBLJINA PREVLAKA

COMPARABILITY OF COATING THICKNESS MEASUREMENT METHODS

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Izvorni znanstveni rad / Original scientific paper

Sažetak: Mjerenje debljina prevlaka provodi se u svrhu kontrole nanošenja prevlaka te praćenja kvalitete prevlaka tijekom vijeka uporabe. U cilju što točnije i preciznije karakterizacije komponenata sa zaštitnim prevlakama, čiji je integritet neophodan za pouzdanu uporabu konstrukcija i postrojenja, potrebno je osigurati određeno povjerenje u rezultate mjerenja debljina prevlaka. U tu svrhu uobičajeno se provode usporedbena mjerenja. Za potrebe ovog rada provedeno je istraživanje mogućnosti usporedbe dviju nerazornih metoda za mjerenje debljina prevlaka na metalnim podlogama - magnetske metode i metode vrtložnih struja. Mjerenja su provela tri mjeritelja na dva uzorka različitih osnovnih podloga - feromagnetska podloga (čelični lim) te nemagnetska podloga (aluminijski lim) na koje su naneseni organski premazi u tri različite debljine slojeva. Dobiveni rezultati analizirani su i komentirani s obzirom na ponovljivost i obnovljivost. Usporedba rezultata mjerenja dviju metoda dana je u odnosu na referentne vrijednosti utvrđene mjerenjem pomoću programa za analizu slike uzetih metalografskih uzoraka.
Ključne riječi: mjerenje debljine prevlaka, magnetska metoda, elektromagnetska metoda, usporedbena mjerenja

Abstract: Coating thickness measurement is applied as a standard pre-service quality control procedure or as a condition monitoring in-service procedure. To ensure the integrity and reliable exploitation of components, structures and plants, the accurate and precise characterisation of components with protective coatings is necessary. In order to provide certain level of confidence in coating thickness measurement results, measurement comparisons are usually carried out.
Purpose of the paper is to examine the possibility of peer comparison of two measurement methods that could be applied for coating thickness measurement on different metal substrates: magnetic method for measurements on magnetic substrates and eddy current method for measurements on non-magnetic electrically conductive materials. The measurements were performed by three persons on two samples for each method respectfully. Each sample has three different organic coating thicknesses. Obtained results are analysed and commented regarding repeatability and reproducibility. Measurement comparisons of two methods is based on reference values of coating thicknesses that are determined by means of image analysis software for metalographic specimens.
Keywords: coating thickness measurement, magnetic method, electromagnetic method, measurement comparisons

1. Uvod

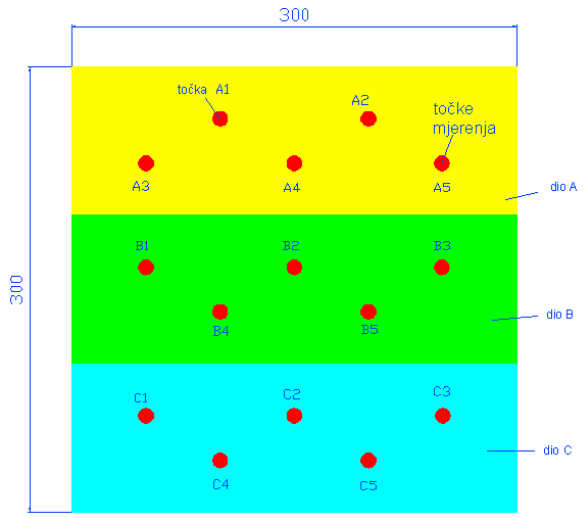
Kontrola kvalitete prevlaka redovito se temelji na zapažanjima prilikom vizualnog pregleda kao i na rezultatima mjerenja debljine prevlake. Osnovna zadaća prevlaka i premaza je zaštita konstrukcijskih dijelova u eksploataciji kako bi se omogućio siguran rad u danim uvjetima tijekom projektiranog vijeka uporabe.
Uređaji za mjerenje debljine prevlaka koriste različita fizikalna načela ovisno o svojstvima prevlaka i podloga na koju je prevlaka nanešena. Cilj rada je provjeriti mogućnost usporedbe mjerenja debljine prevlaka za dvije različite metode. Pomoću magnetske metode (MT) mjere se debljine nemagnetskih prevlaka na magnetskim podlogama, a pomoću metode vrtložnih struja (EC) mjere se debljine nevodljivih prevlaka na nemagnetskim, električki vodljivim metalnim podlogama. U tu svrhu izrađeni su odgovarajući uzorci kako je opisano u drugom poglavlju.
Usporedna analiza rezultata mjerenja dviju metoda, prikazana je u trećem poglavlju, a temelji se na analizi odstupanja mjernih rezultata od referentnih vrijednosti debljina prevlaka koje su određene na poprečnim presjecima metalografskih uzoraka, mjerenjima pomoću programa za analizu slike.

2. Priprema uzoraka i plan mjerenja

Za svaku od dvije mjerne metode pripremljen je odgovarajući uzorak:

- ***uzorak M1*** za mjerenja magnetskom metodom organska je prevlaka nanesena na magnetsku podlogu (čelični lim dimenzija 300 x 300 x 5 mm),
- ***uzorak E2*** za mjerenja metodom vrtložnih struja organska je prevlaka nanesena na nemagnetsku, električki vodljivu metalnu podlogu (aluminijski lim dimenzija 300 x 300 x 10 mm).

Organske prevlake nanesene na oba uzorka ispunjavaju kriterije za provedbu mjerenja pomoću obje metode jer su nemagnetske i električki nevodljive, za MT odnosno za EC metodu respektivno.
Na svakom su uzorku prevlake nanešene u tri sloja različitih debljina (dio A, B i C), a na tim je površinama odabrano i označeno pet mjernih točaka kako je prikazano slikom 1.

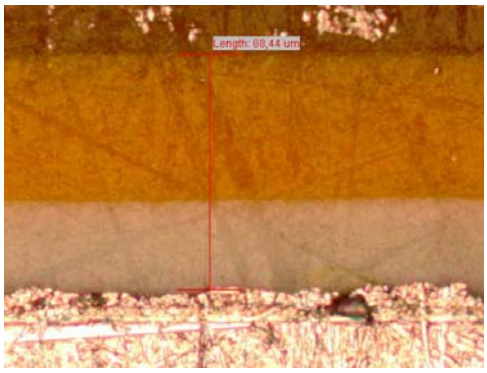


Slika 1. Prikaz uzorka s tri debljine prevlaka i pet mjernih točaka

Točke mjerenja označene su ručno i obilježavaju nešto veću površinu od kontaktne površine mjerne sonde. Postoji realna mogućnost da neravnomjernost debljine nanešenih prevlaka doprinese rasipanju rezultata mjerenja.
Prije svakog mjerenja, odnosno planiranog niza mjerenja na pojedinoj debljini prevlake na uzorku, provedeno je odgovarajuće podešavanje (kalibriranje) mjernog instrumenta korištenjem etalonskih listića.
Mjerenja su provela tri mjeritelja s pet ponavljanja u pojedinoj mjernoj točki.

2.1 Određivanje referentnih vrijednosti debljina prevlaka

Iz odgovarajućih dijelova ploča izrezani su i pripremljeni uzorci, a na poprečnim su presjecima na tri mjesta izmjerene debljine prevlake mikroskopom (slika 2.). Procijenjene referentne vrijednosti pojedinih debljina prevlaka na uzorcima prikazane su u tablici 1 u retku $\overline{x}$ (aritmetička sredina za tri mjerenja) pri čemu je ***s*** procijenjena standardna devijacija.



Slika 2.Određivanje referentne vrijednosti debljine prevlake

Tablica 1. Referentne vrijednosti debljina prevlaka

µm	uzorak M1			uzorak E2		
	dio A	**dio B**	**dio C**	**dio A**	**dio B**	**dio C**
1.	65,13	126,57	188,92	34,90	84,71	168,92
2.	57,27	138,91	194,14	41,17	88,44	153,18
3.	71,88	152,12	202,17	43,23	90,13	141,93
$\overline{x}$	**64,76**	**139,2**	**195,07**	**39,77**	**87,99**	**154,67**
s	7,3	12,7	6,67	4,34	2,38	13,56

3. Analiza rezultata mjerenja

Provedene su sljedeće analize rezultata mjerenja korištenjem programa Statgraphics plus 5.1:

1. analiza ponovljivosti i obnovljivosti (R&R) rezultata na uzorku M1,
2. analiza ponovljivosti i obnovljivosti (R&R) rezultata na uzorku E2,
3. usporedba metoda s obzirom na ponovljivost i obnovljivost razlika rezultata mjerenja.

3.1. R&R analiza za magnetsku metodu

Podaci su za R&R analizu organizirani na sljedeći način: tri mjeritelja (*operators*), pet mjernih točaka na tri dijela uzorka (*parts*) uz pet ponavljanja (*trials*), a rezultati analize prikazani su u tablici 2.

Tablica 2. Statistički parametri R&R analize za magnetsku metodu - uzorak M1

	µm	dio A	dio B	dio C
1.	s_r	3,45	3,77	2,97
2.	s_R	1,34	3,31	0,91
3.	$s_{R\&R}$	3,70	5,01	3,11
4.	s_{tm}	8,32	9,99	9,31
5.	$R_{\bar{x}}$	2,88	6,48	2,08
6.	$4 \cdot s_{R\&R}$	±7,41	±10,03	±6,21
7.	T	±6,5	±13,9	±19,5

gdje je:

s_r - procijenjena standardna devijacija ponovljivosti

s_R - procijenjena standardna devijacija obnovljivosti

$s_{R\&R}$ - kombinirana procijenjena standardna devijacija ponovljivosti i obnovljivosti

s_{tm} - procijenjena standardna devijacija rezultata koja proizlazi iz različitosti predmeta mjerenja tj. različitosti debljina prevlaka u točkama mjerenja (*parts*)

$R_{\bar{x}}$ - raspon aritmetičkih sredina rezultata mjerenja

$4 \cdot s_{R\&R}$ - intervalna procjena preciznosti uz razinu povjerenja P = 95,45% (±2 $s_{R\&R}$)

T - tolerancija zahtijevana normom [1] - 10% stvarne (referentne) vrijednosti (vidi tablicu 1)

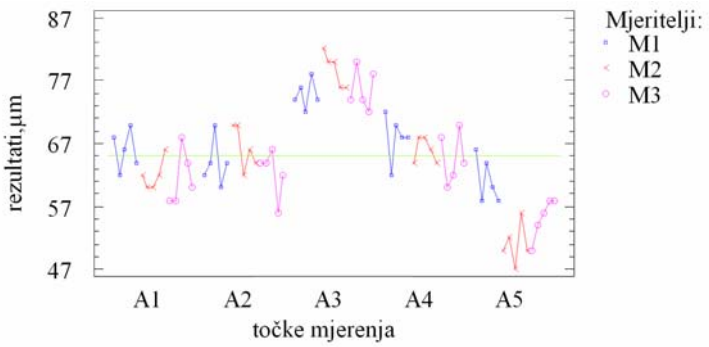
Ostvarena preciznost mjerenja na dijelu A na uzorku M1 iznosi ±7,41µm što je veće od dopuštene točnosti T=±6,5 µm (*10% referentne vrijednosti*) zahtijevane normom [1]. Preciznost mjerenja na dijelovima B i C unutar je granica tolerancije i korišteni MT postupak za te debljine prevlaka ispunjava zahtjev norme.

Na slikama 3, 4 i 5 grafički su prikazani rezultati mjerenja debljina prevlaka na uzorku M1:

- za tri mjeritelja (M1, M2 i M3),
- na dijelovima uzorka A, B i C,
- u pet točaka mjerenja "x1, x2, x3, x4 i x5" pri čemu "x" označava dio uzorka A, B ili C respektivno.

Grafički prikazi rezultata popraćeni su odgovarajućim komentarima. Općenito, u odnosu na vrijednosti standardnih devijacija ponovljivosti i obnovljivosti, uzrok najveće varijabilnosti rezultata na sva tri dijela uzorka proizlazi iz različitosti vrijednosti u točkama mjerenja (s_{tm}) što upućuje na neravnomjernost debljine nanešenih premaza.
Također, ponovljivosti rezultata mjerenja s_r, približno su jednake na sva tri dijela uzorka M1, a ponovljivost na dijelu B tek je neznatno veća, s_r=3,77µm.

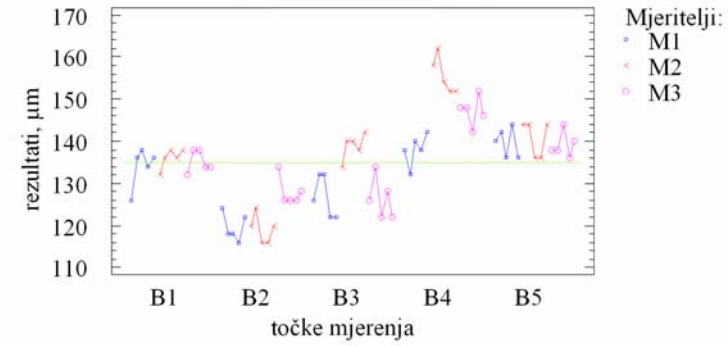
<u>Uzorak M1 – dio A</u>



Slika 3. Grafički prikaz rezultata mjerenja na uzorku M1 – dio A

Može se uočiti da su u pojedinim točkama mjerenja rezultati relativno ujednačeni, kako u pogledu ponovljivosti tako i u pogledu obnovljivosti. U točki mjerenja A5 ponovljena mjerenja mjeritelja M1 značajnije se razlikuju od rezultata druge dvojice mjeritelja. Promatrajući sveukupne rezultate mjerenja u pojedinim točkama uočljivo je da rezultati u točkama A3 i A5 u nešto većoj mjeri odstupaju od rezultata u ostale tri točke mjerenja. Temeljem toga može se pretpostaviti da se u tim točkama (A3 i A5) debljine prevlake značajnije razlikuju od vrijednosti debljine prevlake u ostalim točkama (A1, A2 i A4) i od referentne vrijednosti debljine utvrđene u poglavlju 2.1.

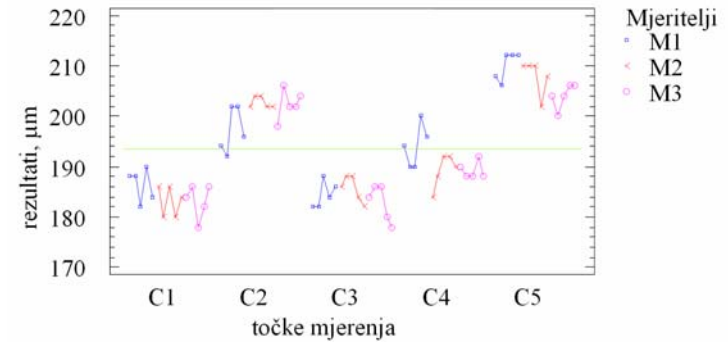
Uzorak M1 – dio B



Slika 4. Grafički prikaz rezultata mjerenja na uzorku M1 – dio B

Za razliku od rezultata na dijelu ploče A, na dijelu B su izraženije razlike u rezultatima između pojedinih mjeritelja u točkama B2, B3 i B4 što se očituje i u iznosu obnovljivosti rezultata na dijelu ploče B, s_R=3,31µm (tablica 2), koji je značajno veći od obnovljivosti na dijelovima A i C - s_R je 2,5 puta veća od standardne devijacije obnovljivosti na dijelu A i 3,5 puta veća od iste na dijelu C uzorka M1.
Raspon aritmetičkih sredina rezultata mjerenja na ovom dijelu uzorka ($R_{\bar{x}}$ =6,48µm) značajno je veći od istog raspona na preostalim dijelovima ploče.

Uzorak M1 – dio C



Slika 5. Grafički prikaz rezultata mjerenja na uzorku M1 – dio C

U svim točkama mjerenja, zasebno promatrano, rezultati između mjeritelja ujednačeni su u pogledu obnovljivosti, a u usporedbi s dijelovima A i B, na ovom su dijelu uzorka mjeritelji ostvarili najbolju obnovljivost (s_R=0,91µm).

3.2. R&R analiza za metodu vrtložnih struja

Podaci su organizirani identično kao i za R&R analizu za MT metodu u poglavlju 3.1. Rezultati analize prikazani su u tablici 3, a na slikama 6, 7 i 8 grafički su prikazani rezultati mjerenja debljina prevlaka na uzorku E2.

Tablica 3. Statistički parametri R&R analize za metodu vrtložnih struja - uzorak E2

	µm	dio A	dio B	dio C
1.	s_r	0,51	0,86	1,08
2.	s_R	1,62	2,0	1,32
3.	$s_{R\&R}$	1,69	2,18	1,71
4.	s_{tm}	1,52	2,15	13,13
5.	$R_{\bar{x}}$	3,08	3,84	2,56
6.	$4 \cdot s_{R\&R}$	±3,38	±4,36	±3,42
7.	T	±4,0	±8,8	±15,5

gdje je:

s_r - procijenjena standardna devijacija ponovljivosti

s_R - procijenjena standardna devijacija obnovljivosti

$s_{R\&R}$ - kombinirana procijenjena standardna devijacija ponovljivosti i obnovljivosti

s_{tm} - procijenjena standardna devijacija rezultata koja proizlazi iz različitosti predmeta mjerenja tj. različitosti debljina prevlaka u točkama mjerenja (*parts*)

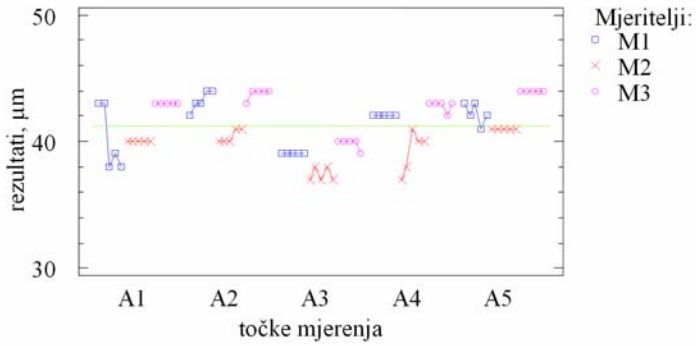
$R_{\bar{x}}$ - raspon aritmetičkih sredina rezultata mjerenja

$4 \cdot s_{R\&R}$ - intervalna procjena preciznosti uz razinu povjerenja P = 95,45% (±2 $s_{R\&R}$)

T - tolerancija zahtijevana normom [2] - 10% stvarne (referentne) vrijednosti (vidi tablicu 1)

Zahtjev norme [2] za točnost mjerenja metodom vrtložnih struja također iznosi 10% stvarne, odnosno referentne vrijednosti. Procijenjena preciznost mjerenja (*T*) na svim dijelovima uzorka E2, odnosno na tri različite debljine premaza ispunjava zahtjev norme.

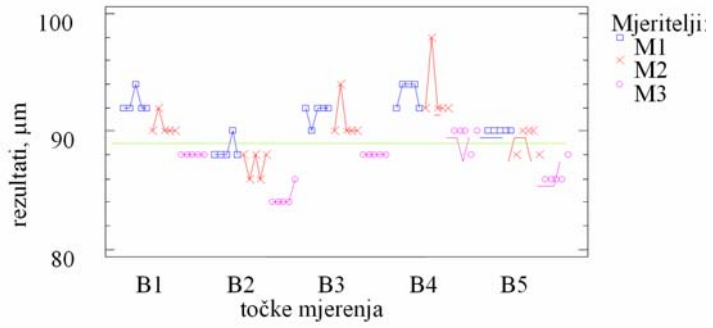
<u>Uzorak E2 – dio A</u>



Slika 6. Grafički prikaz rezultata mjerenja na uzorku E2 – dio A

Može se uočiti da su u svim točkama mjerenja rezultati relativno ujednačeni, posebice u pogledu ponovljivosti (s_r=0,51µm). Iznos standardne devijacije obnovljivosti (s_R=1,62µm) istog je reda veličine kao i kod magnetske metode.

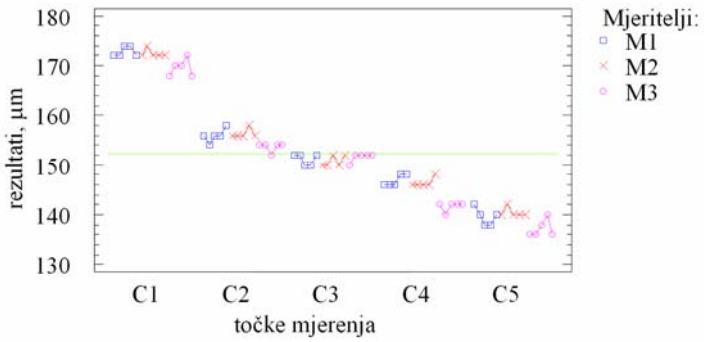
Uzorak E2 – dio B



Slika 7. Grafički prikaz rezultata mjerenja na uzorku E2 – dio B

Rezultati mjerenja trećeg mjeritelja (M3) neznatno se razlikuju od preostala dva mjeritelja u pojedinim točkama mjerenja, a po iznosu su redovito manjih izmjerenih vrijednosti. To izravno utječe na obnovljivost rezultata (s_R=2,0µm) koja je nešto veća od obnovljivosti rezultata na dijelovima A i C.

Uzorak E2 – dio C

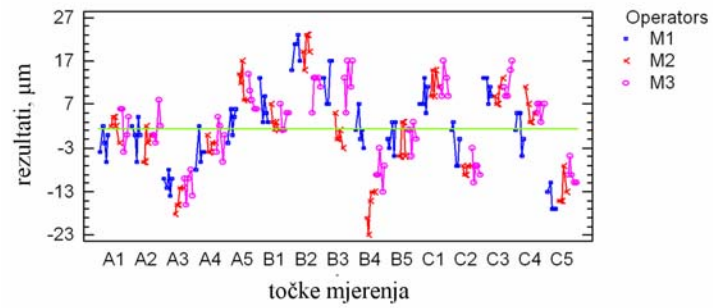


Slika 8. Grafički prikaz rezultata mjerenja na uzorku E2 – dio C

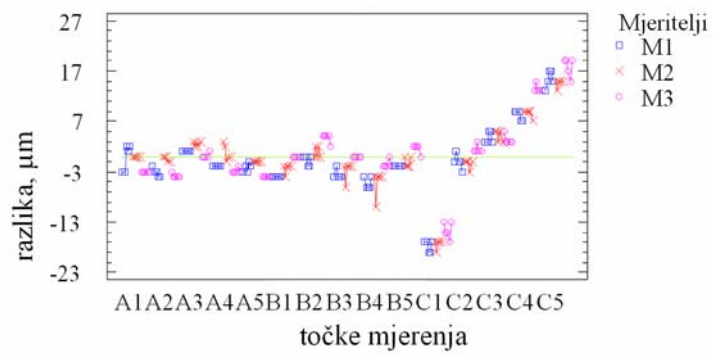
U svim su mjernim točkama rezultati ujednačeni kako u pogledu ponovljivosti tako i u pogledu obnovljivosti, osim u točki C4, gdje se niz mjerenja mjeritelja M3 ponovo u neznatno većoj mjeri razlikuje od rezultata druge dvojice mjeritelja. Standardna devijacija ponovljivosti (s_r=1,08µm) neznatno je veća od iste standardne devijacije na dijelovima A i B ovog uzorka, dok je standardna devijacija obnovljivosti (s_R=1,32µm) najmanja upravo na ovom dijelu uzorka (tablica 3).
Nizovi mjernih rezultata značajnije se razlikuju između pojedinih točaka mjerenja, posebno u točkama C1 i C5, što proizlazi i iz standardne devijacije točaka mjerenja (s_{tm}=13,13µm) na ovome dijelu C, koja je 6 puta veća od iste standardne devijacije na dijelu B i 8 puta veća od iste standardne devijacije na dijelu A. Temeljem toga može se pretpostaviti da se na dijelu C uzorka E2, debljine premaza u pojedinim točkama mjerenja (posebno u točkama C1 i C5) međusobno razlikuju.

3.3. Usporedba rezultata mjerenja dviju metoda

Budući da dvije promatrane i široko primjenjivane metode mjerenja debljine prevlaka, podrazumijevaju različite vrste osnovnog materijala, te time i različite uzorke, planirana je usporedna analiza odstupanja rezultata mjerenja u odnosu na referentne vrijednosti debljine prevlaka koje su utvrđene metalografskim ispitivanjem kako je prikazano u drugom poglavlju.



Slika 9. Razlike rezultata mjerenja za magnetsku metodu



Slika 10. Razlike rezultata mjerenja za metodu vrtložnih struja

Uočava se da su rezultati dobiveni metodom vrtložnih struja točniji i precizniji od rezultata dobivenih magnetskom metodom. Procijenjene razlike rezultata, dobivenih metodom vrtložnih struja, manje se rasipaju u odnosu na magnetsku metodu, što potkrepljuju i iznosi za s_r prikazani u tablici 4 - standardna devijacija ponovljivosti (s_r) za EC je približno 4 puta manja od iste za MT metodu.

Standardne devijacije obnovljivosti (s_R) približno su jednake za obje metode temeljem čega se može zaključiti da mjeritelji i ostali čimbenici uvjeta obnovljivosti pri provedenim mjerenjima podjednako doprinose rasipanju rezultata.

Tablica 4. Procijenjene standardne devijacije razlika rezultata mjerenja

µm	MT	EC
s_r	3,39	0,80
s_R	0,89	0,88
$s_{R\&R}$	3,50	1,19
S_{tm}	8,20	9,16

Također je uočljiva izdvojenost mjernih nizova u točkama C1 i C5 na uzorku E2 u odnosu na referentnu vrijednost (slika 10) što potvrđuje prethodno iznesenu pretpostavku da se debljine prevlake u točkama C1 i C5 na uzorku E2 značajnije razlikuju od vrijednosti debljine prevlake u ostalim točkama, odnosno od referentne vrijednosti.

Varijabilnosti promatranih razlika koja proizlaze iz različitosti debljina prevlaka u pojedinim točkama mjerenja (s_{tm}) približno su jednake kod obje metode što je razumno za očekivati zbog nesavršenosti prilikom izrade uzoraka. Istovremeno su s_{tm} znatno veće od standardnih devijacija ponovljivosti i obnovljivosti ($s_{R\&R}$) kod obje metode.

4. Zaključak

Planiranjem i provođenjem usporedbenih mjerenja metodom vrtložnih struja te magnetskom metodom na odgovarajuće pripremljenim i različitim uzorcima, dobiveni statistički pokazatelji ponovljivosti i obnovljivosti (R&R) rezultata ukazuju na prikladnost mjernih postupaka u odnosu na zahtjeve utvrđene referentnim normama.

Izravna usporedna analiza obiju metoda temelji se na odstupanjima mjernih rezultata od referentnih vrijednosti debljina prevlaka koje su određene na poprečnim presjecima metalografskih uzoraka, mjerenjima pomoću programa za analizu slike. R&R analiza provedena je pomoću programskog paketa Statgraphics plus 5.1.

Procijenjena standardna devijacija ponovljivosti, odnosno preciznost rezultata dobivenih metodom vrtložnih struja (s_r=0,80μm) četiri je puta manjeg iznosa od ponovljivosti mjerenja magnetskom metodom (s_r=3,39μm). Utvrđeno je da preciznost magnetske metode na manjim debljinama (65μm) ne ispunjava zahtjev norme [1] u iznosu ±10%.

Dodatno je potrebno istaknuti da je za magnetsku metodu ponovljivost rezultata mjerenja (s_r=3,39μm) približno četiri puta veća od obnovljivosti rezultata mjerenja tom metodom (s_R=0,89μm) što je neuobičajeno.

Izravna usporedna analiza obiju metoda pokazala je da doprinos rasipanjima rezultata uslijed različitosti debljina prevlaka u pojedinim mjernim točkama uzoraka, a radi nesavršenosti tehnologije nanošenja prevlaka, nije značajno različit na dva uzorka (M1 i E2) koji su zasebno korišteni za mjerenja magnetskom metodom (s_{mt} =8,20μm) i metodom vrtložnih struja (s_{mt}=9,16μm).

Temeljem svega iznesenog može se zaključiti da je ovakvim pristupom omogućena provedba usporedbenih ispitivanja za dvije različite metode kojima su mjerenja provedena na zasebnim uzorcima različitih svojstava osnovnog materijala.

5. Zahvala

Usporedbena mjerenja i provedene analize dio su znanstveno istraživačkog rada na projektu odobrenom od MZOŠ-a pod brojem 120-1201767-1763, naziva *Pouzdanost metoda nerazornih ispitivanja*, a koji je dio znanstvenog programa br. 1201767 *Pouzdanost energetskih postrojenja i pomorskih konstrukcija*.

6. Literatura

[1] HRN EN ISO 2178: 1999 – Nemagnetske prevlake na magnetskim podlogama – Mjerenje debljine prevlake – Magnetska metoda
[2] HRN EN ISO 2360: 2003 – Nevodljive prevlake na nemagnetskim električki vodljivim metalnim podlogama – Mjerenje debljine prevlake – Metoda vrtložnih struja

KOLORIMETRIJSKA ANALIZA ELEKTROFOTOGRAFSKIH OTISAKA OTISNUTIH NA PVC-u I POLIKARBONATU

COLORIMETRIC ANALYSIS OF ELECTROPHOTOGRAPHIC PRINTS PRINTED ON PVC AND POLYCARBONATE

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Stručni članak / Professional paper

Sažetak: Cilj ovoga rada je pobliže analizirati mogućnost elektrofotografskog otiskivanja na neupojne i transparentne tiskovne podloge (PVC i polikarbonat). Njih karakterizira velika debljina, specifičani kemijski sastav i struktura, čime se postižu različita površinska svojstva (optička bjelina, površinska hrapavost, transparentnost). Dobiveni otisci komparirani su sa standardnom tiskarskom podlogom (papiri za umjetnički tisak), pri čemu se primjenjuju standardnizirane kolorimetrijske metode (CIE Lab). Na temelju CIE Lab vrijednosti konstruirani su gamuti reprodukcije, iz kojih su ekstrahirana specifična tonska područja s njihovim spektrima (ljudskom oku vidljvo područje). U rezultatima će se analizirati i utjecaj strane arka na transparentnom mediju na konačnu vrijednost obojenja (razlika u obojenju CIE LAB ΔE_{2000}). Rezultati pokazuju da će elektrofotografski tisak tekućim tonerom, na bijelom PVC-u ostvariti gamut volumena V=590,323 prostornih jedinica, što je manje od gamuta na bijelom papiru (V=677,055). Otisak na prozirnom PVC reduciranog je kolorita (V=151,638), što je slučaj i kod prozirnog polikarbonata (V=188,779). Otiskivanjem na poleđinu transparentnih medija, dodatno će se smanjiti vrijednosti kolorita (V_{PVC} =82,882; te $V_{Polikarbonat}$=88,865).
Ključne riječi: elektrofotografski tisak na PVC i polikarbonat, CIE Lab ΔE_{2000}, gamuti reprodukcije

Abstract: The aim of this work is the detailed analysis of the possibility of electro photographic printing process on non-absorbent and transparent printing substrates (PVC and polycarbonate). They are characterized by great thickness, specific chemical composition and structure which achieve different surface properties (optical whiteness, surface roughness and transparency). The obtained prints were compared with the standard printing substrate (fine art paper) with the application of the standardized colorimetric method (CIE Lab). Based on CIE Lab values the gamuts of reproduction were constructed, from which the specific extracted tone areas with their spectra were visible areas for human eye. It was analyzed in the results, how the side on the transparent medium could influence the final value of coloring (color difference CIE LAB ΔE_{2000}). The results show that the electro photographic printing process with the liquid toner on white PVC will create the gamut volume V=590,323 of space unit which is less than the gamut of the white paper (V=677,055). The print on the transparent PVC has reduced coloring (V=151,638), which is the same as with the transparent media, which additionally decreases the coloring values (V_{PVC} =82,882; and $V_{polycarbonate}$=88,865).
Key words: electro photographic printing on PVC and on polycarbonate, CIE Lab ΔE_{2000}, gamut reproduction

1. Uvod

Tehnike digitalnog elektrofotografskog tiska namijenjene su za kvalitetno ispisivanje na poroznim (papirnim) tiskovnim podlogama. Za tu potrebu konstruirana su i specijalna tiskarska bojila (toneri) koja moraju zadovoljiti mnoga tiskarska svojstva. Najvažnija su: specifična električna provodljivost tonera, mogućnost triboelektričkog nabijanja tonera, niska temperatura taljenja tonera, generiranje što ujednačenijih rasterskih tonova, postizanje što većeg bojnog opsega, dobivanje kontrastnih ilustracija i postizanje teksta sa što oštrijim konturama.

Problemi u elektrofotografskoj tehnologiji nastaju prilikom otiskivanja na krutu i neupojnu tiskovnu podlogu. Takvi materijali su PVC i polikarbonat, koji su idealni za izradu grafičkih proizvoda kao što su korice, kreditne kartice, displeji i podloške raznih namjena. Karakteristično je da ova dva materijala mogu biti u raznim oblicima (arak, folija, tuba, ploča, granula), pri čemu su najčešći transparentni i bijeli.

Cilj ovog rada je ispitati s kakvim uspjehom možemo nanašati tekuće elektrofotografsko bojilo na PVC-u i polikarbonatu, tj. izvršiti spektrofotometrijsku analizu obojenja nastalu interakcijom procesnih bojila (CMYK) s neupojnom tiskovnom podlogom. Pritom će se izvršiti i komparacija rezultata sa otisnutom standardnom tiskovnom podlogom (papir).

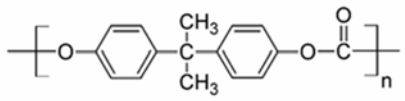
2. Teoretski dio

2.1. Polikarbonat

Bez polikarbonatnih spojeva nemoguće je zamisliti svakodnevni život. On je osnova za proizvodnju CD-a, DVD-a, Blue Ray diskova, čaša, sterilizirane laboratorijske opreme, leća, automobilskih dijelova, displeja i kućišta, polikarbonatnih araka i filmova, te cjevastih i šipkastih profila.(1)

Polikarbonati su posebna grupa termoplastičnih polimera, koja zbog svoje lagane izrade i formiranja u kalupima imaju široku primjenu u industriji. Polikarbonat posjeduje indikacijski kod 7, što znači da se svojim toplinskim i mehaničkim i optičkim svojstvima uvrštava između običnih plastika i industrijskih plastika.(2)

Naziv polikarbonati nastao je zbog polimera sa funkcionalnom grupom koja je povezana sa karboksilnom skupinom (-O-(C=O)-O-), tvoreći tako dugački molekularni lanac. Pri proizvodnji primijenjen je i ugljični monoksid (poznat pod trgovačkim nazivom C1 Synthon), koji može omogućiti izradu poliaromatskih i polialifatskih karbonata (3)



(2.1)

C1 Synthon u industrijskoj proizvodnji služi za dobivanje difenil karbonata, što se kasnije trans-esterificira sa difenolnim derivatima, dajući kasnije poliaromatske polikarbonate. Polialifatski karbonati proizvode se reakcijom ugljičnog dioksida sa epoksidima (nosioci termodinamičke stabilnoti ugljičnog dioksida) uz primjenu katalizatora (porfirinina, alkoksida, karboksilata) i metalnih centara (Al, Zn, Co, Cr).

Polialifatski karbonati (spojevi u kojima su molekule ugljika vezane u lančastu strukturu) posjeduju bolja biodegradirajuća svojstva od aromatskih karbonata, te se koriste za razvoj specijalnih tipova polimera. Čest predstavnik takvih polikarbonata je građen od bisfenola A (BPA), koji laminiranjem daje čvrst i trajan materijal (neprobojno staklo). Kako polikarbonati posjeduju veliku mehaničku otpornost na udarce i nisku otpornost na razvlačenje, dobar je materijal za izradu leća i vanjskih automobilskih dijelova.

Polikarbonati otporni na visoke temperature građeni su od polimetil-metakrilata. Takav polikarbonat posjeduje izvrsna optička svojstva (visoku propusnost vidljivog svijetla), koja su bolja od mnogih staklenih materijala. U ovu skupinu spada i polikarbonatna plastika CR 39. Svojim izvrsnim mehaničkim i optičkim svojstvima neće propuštati štetno UV zračenje, što je iskorišteno u proizvodnji leća i sunčanih naočala.

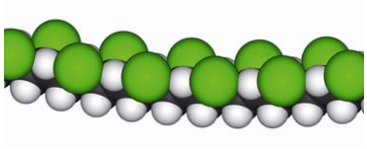
Zagrijavanjem, polikarbonat će pri temperaturi od 150°C preći u staklastu fazu, te će se daljnjim zagrijavanjem lagano omekšavati, postajući tekući pri temperaturi od 300°C. Pritom je oblikovanje mnogo teže nego kod ostalih termoplastičnih materijala. Pri proizvodnji termoplastičnih materijala općenito vrijedi pravilo da se nisko molekularne mase lakše tale, pri čemu posjeduju nižu površinsku napetost u kontaktu sa proizvodnim kalupom. Visoko molekularne mase karakterizira žilavost konačnog proizvoda, ali i teže oblikovanje. Tijekom izrade polikarbonatnog proizvoda, kalupi moraju biti zagrijavani na temperaturu od 80°C, čime će se smanjiti površinska napetost.(4)

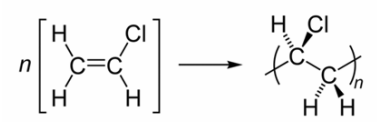
Polikarbonatne plastike možemo pronaći pod slijedećim trgovačkim nazivima: Colibre (Dow Chemical), Lexan (Sabic Inovated Plastik), Makrolit (Arlaplast), Makrolon (Bayer), Pehlite (Teijin Chemical). (5)

2.2 Polivinil-klorid (PVC)

Poslije polietilena i polipropilena, polivinil klorid (po IUPAC-u Poly(chloroethanediyl)) je treći najčešće korišteni polimer u industriji. Pritom je u 50% slučajeva korišten u građevinarstvu kao materijal za konstruiranje (prozori, vrata, krovišta….). Dodatkom plastifikatora PVC će postati mekši i fleksibilniji. Time se PVC može koristit za izradu umjetnih tkanina, fleksibilnih cijevi, instalacijskih kablova, proizvoda za napuhavanje, figurica. Pritom su ftalati najčešće korišteni plastifikatori.(6)

Polivinil klorid dobiven je polimerizacijom monomera vinil-klorida (VCM). Maseni udio klora iznosi 57%. Klor te je bitan za formiranje PVC-a osiguravajući mu gustoću, te smanjuje potrebu sa većim udjelom petroleja.





(2.2)

Najšire korišten proizvodni proces je suspenzijska polimerizacija. Pri tom procesu se VCM i voda dovode u polimerizacijski reaktor dodajući im polimerizacijski starter i druge kemijske dodatke.

Za postizanje čvrstoće, fleksibilnosti, transparentnosti i obojenja, PVC-u se dodaju dodaci u obliku pigmenata i stabilizatora. Dodatkom pigmenata ujecati će se na konačno obojenje PVC-a , dok će dodatak stabilizatora utjecati na mehanička i optička svojstva. Kao stabilizatori dodaju se slijedeći metali: Pb, Pb-Ba-Cd, Ba-Cd, Ca-Zn, Ba-Zn, Sn, K-Zn. (7)

Sadržaj u reakcijskoj posudi je pod stalnim tlakom i kontinuirano se miješa, čime se održava konzistencija supstance. Za trajanja reakcije, volumen PVC-a se smanjuje, te je potrebno povremeno dodavanje vode uz konstantno miješanje. Reakcija je egzotermna, te je tijekom cijelog proizvodnog procesa potrebno hlađenje reaktora, uz održavanje konstantne temperature od 40- 60°C i tlaka od nekoliko bara. Prekidom reakcije PVC se prosijavanjem odvaja od ostatka vinil klorida, te prolazi kroz sustav centrifuga koje otklanjaju glavninu vode. Rezultat je neutraliziran i mutan PVC čije su čestice granule veličine od 50 – 200 μm. Takvim načinom proizvodnje dobiva se S-PVC koji mora sadržavati manje od 1:1000000 VCM-a. (8)

Drugi način proizvodnje baziran je na mikrosuspenzijskoj polimerizaciji i emulzijskoj polimerizaciji. Na takav način postižu se P-PVC proizvodi čija je granulacija oko 10 μm, što daje mogućnost formiranja pločastih folija i filmova upotrebljivih za otiskivanje u grafičkoj industriji.(9)

3. Eksperimentalni dio

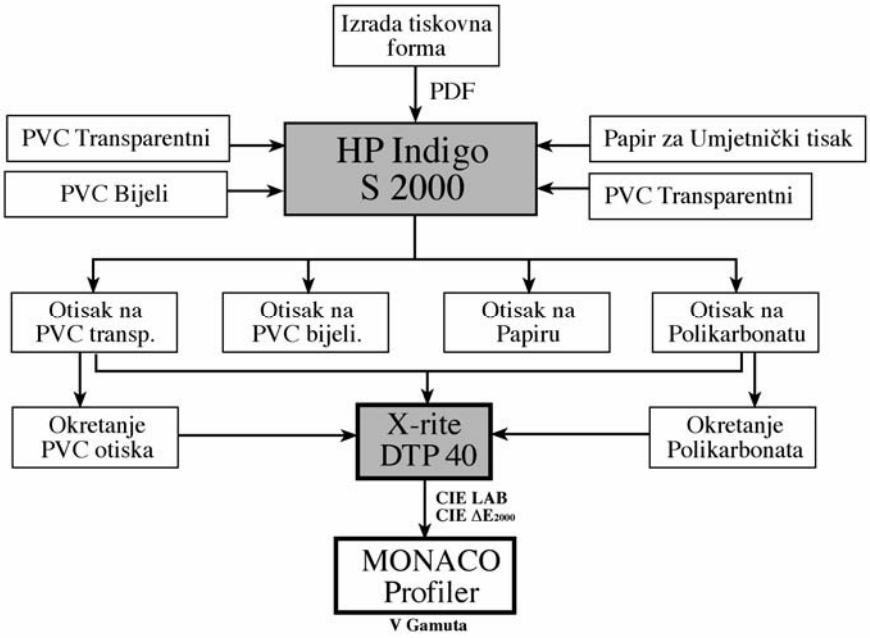
U ovom radu će se analizirati mogućnost elektrofotografskog otiskivanja na debele i neupojne tiskovne podloge, čija je građa propusna za bijelo svjetlo. Konkretno to su transparentni polikarbonat debljine 350 μm, bijeli PVC debljine 500 μm i transparentni PVC debljine 350 μm.

Za potrebe istraživanja napravljena je specijalna tiskovna forma koja sadrži standardni CMYK RGB stepenasti klin (u rasponu od 10 do 100% RTV), ISO standardne ilustracije i 378 polja (za izradu ICC profila i gamuta).

Eksperimentalni otisci napravljeni su na prethodno kalibriranom elektrofotografskom stroju HP Indigo S2000, nakon čega je nastupilo eksperimentalno otiskivanje. Kvaliteta kolornih otisaka, komparirana je sa standardnim papirnim otiskom (250 μm debeli sjajni papir za umjetnički tisak), koji je otisnut identičnom tehnologijom otiskivanja.

Za kolorimetrijsko mjerenje korišteni su spektrofotometri X-rite DTP 41 i X-rite SwatchBook, koji rade sa pripadajućim programima MONACO verzija Platinum (3D

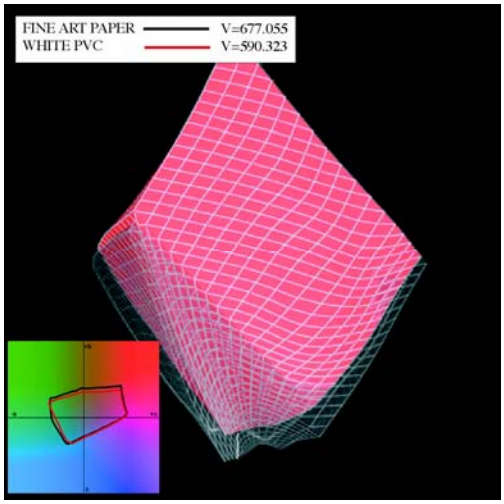
gamuti) i ColorShop X (određivanje ΔE_{2000} CIE Lab). Pritom su pobliže analizirana samo najzahtjevnija kalibracijska područja (puni tonovi cijana, magente, žute i crne). Zbog transparentnosti tiskovne podloge izvršeno je i konačno ispitivanje utjecaja same tiskovne podloge na intezitet obojenja, mjerenjem kroz rotiranu (180°) tiskovnu podlogu.

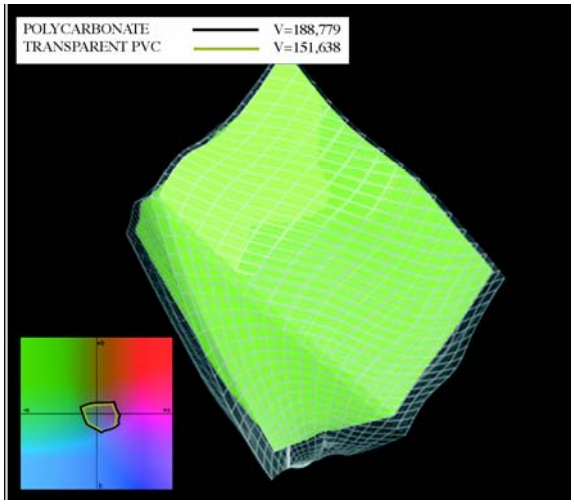


Slika 1.Shematski prikaz izvršenog eksperimenta

4. Rezultati i diskusija

Kvaliteta reproducije definira se uspješnošću reproduciranja što većeg broja tonova. Pritom se standardno koristi ECI tiskovna forma s otisnutim 378 polja. Njihovom matematičkom obradom stvoreno je 3D tijelo (gamut) koji u CIE LAB prostoru pokazuje maksimum reprodukcije tonova. Na slici 2. prikazana je razlika između neprozirnih otisaka (papir-PVC) i prozirnih otisaka (PVC-polikarbonat), dok su na slici 3. prikazane promjene u reprodukciji nastale rotiranjem i mjerenjem transparentnih otisaka (Polikarbonat-180° Polikarbonat i PVC-180° PVC).

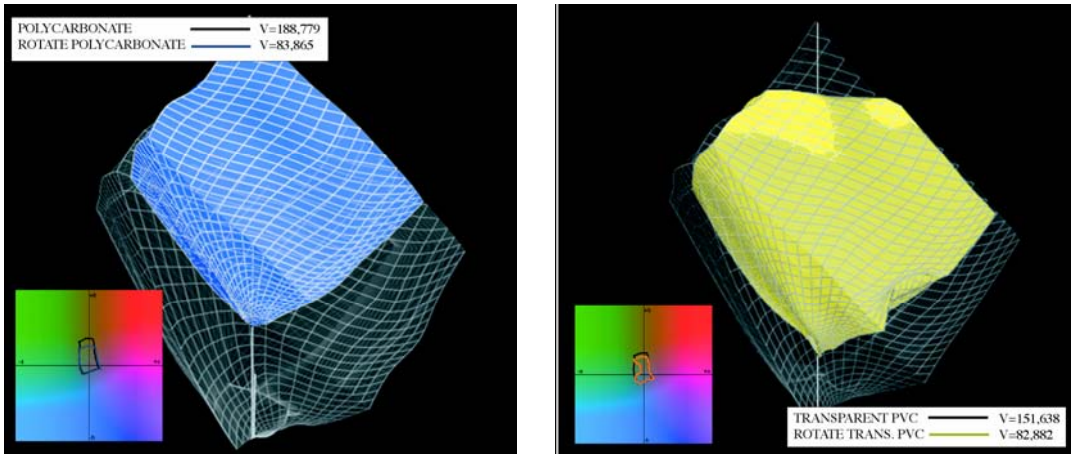




Slika 2. Prostorni gamut neprozirnih podloga i karakterističan presjek napravljen po sredini svjetloće (L=50)

Analizom gamuta reprodukcije papira i bijelog PVC-a, može se uočiti razlika od ΔV=86,732 gamutne jedinice. Pritom je došlo do redukcije kod bijelog PVC, tj. pri otiskivanju najtamnijih tonova. Po kromatičnosti došlo je do većih promjena, koje su izražene po osi +b (žuta), što je utjecalo na promjenu u crvenim i zelenim tonovima.

Različiti transparentni mediji (PVC-polikarbonat) ostvarili su razliku u volumenu ΔV=37,141 gamutnih jedinica. Pritom je došlo do redukcije raspona obojenja transparentnog PVC-a u svim područjima.

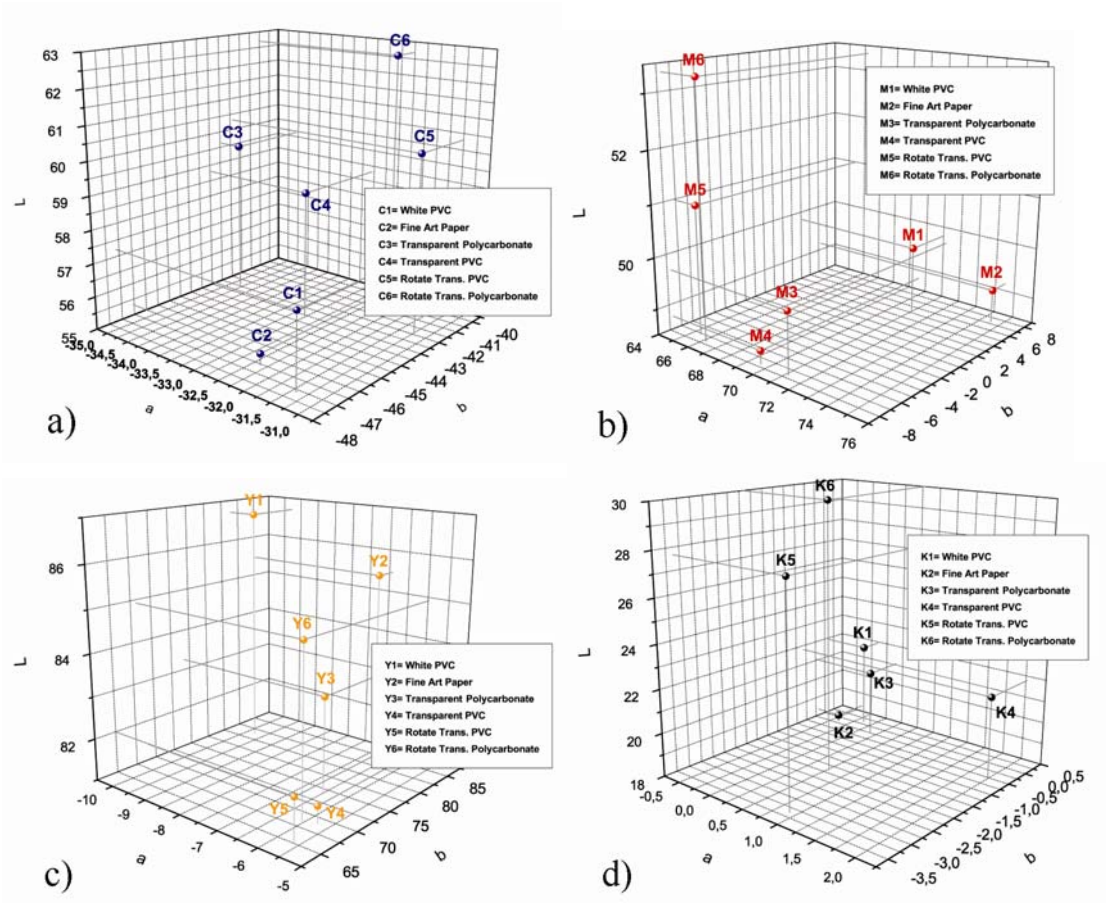


Slika 3. Prostorni gamut neprozirnih podloga i karakterističan presijek napravljen po sredini svjetloće (L=50)

Promjena strane mjerenja na transparentnom polikarbonatu generirati će promjenu u reprodukciji za ΔV=104,914 gamutne jedinice. Pritom je došlo do pada kontrasta, pri čemu je izgubljena oštrina otiska. Također je došlo i do najveće kromatske promjene u žutoj boji koja je najsvjetlija. Ipak se preokretanjem medija postiže sposobnost zaštite otiska od oštećenja prilikom uporabe proizvoda (velika mehanička otpornost otiska). To je iskorišteno za tisak prozirnih displeja, gdje je mehanička otpornost važnija od vizualne uočljivosti.

Preokretanjem PVC-a ostvariti će se puno manja promjena u prostornom gamutu (ΔV=68,756). Ovakva promjena nastala je i u svjetlijim i tamnijim tonovima. Vrlo je bitno da je promjena u tamnijim tonovima puno manja, što će omogućiti i reprodukciju puno većeg kontrasta.

Detaljna analiza reprodukcije prikazana je spektrofotometrijskim mjerenjima CMYK otisaka u području punih tonova (cijan slika 4a, magenta slika 4b, žuta slika 4c i crna slika 4d).



Slika 4. CIE LAB vrijednosti CMYK boja otisnutih na papiru, bijelom PVC-u, polikarbonatu, preokrenutom polikarbonatu, prozirnom PVC-u i preokrenutom PVC-u.

U tiskarstvu je standardna tiskovna podloga papir, te je mehanizam vezivanja bojila prilagođen vezivanju za poroznu tiskovnu podlogu. Zbog toga se pri promatranju razlike obojenja (ΔE) sve otisnute tiskovne podloge uspoređuju s otiscima na papiru za umjetnički tisak.

Pri reprodukciji cijan boje najbolji rezultati postignuti su otiskivanjem na bijeli PVC (ΔE_{PVC}=1,8188) dok su lošiji rezultati (promjena vidljiva golim okom) dobiveni kod prozirnog PVC-a (ΔE_{PVC}=3,4494) i polikarbonata (ΔE_C=4,3814). Rotacijom transparentnih medija ostvarene su promjene ΔE_{PVC}=4,7437 i ΔE_C=6,8788. Pritom je PVC ostvario promjenu od ΔE_{PVC}=1,2943 dok je polikarbonat ostvario promjenu ΔE_C=2,4974.

Pri otiskivanju magente nastale su veće razlike u obojenju. Najveća promjena dobivena je otiskivanjem na transparentni PVC i polikarbonat (ΔE_{PVC}=6,2761; ΔE_C=6,1865), dok je najmanja promjena nastala otiskivanjem na bijeli PVC (ΔE_{PVC}=1,3405). Preokretanjem transparentnih medija ostvarene su promjene ΔE_{PVC}=6,6730 i ΔE_C=7,7725. Pritom je PVC ostvario promjenu od ΔE_{PVC}=0,3969, dok je polikarbonat ostvario promjenu ΔE_C=1,586.

Pri reprodukciji žute boje ostvarene su najmanje razlike u obojenju. Najbolji rezultati postignuti su otiskivanjem na bijeli PVC i polikarbonat (ΔE_{PVC}=2,0710; ΔE_C=2,81),

dok su lošiji rezultati dobiveni kod prozirnog PVC-a (ΔE_{PVC}=4,5286). Preokretanjem transparentnih medija ostvarene su promjene ΔE_{PVC}=5,1438 i ΔE_C=3,8500. Pritom je PVC ostvario promjenu od ΔE_{PVC}=0,615 dok je polikarbonat ostvario promjenu ΔE_C=1,0377.

Nakon magente, akromatsko crno bojilo doživjelo je najveću devijaciju sa promjenom tiskovne podloge. Najveća promjena dobivena je otiskivanjem na transparentni PVC (ΔE_{PVC}=4,2387), dok je najmanja promjena nastala otiskivanjem na bijeli PVC (ΔE_{PVC}=2,5454) i polikarbonat (ΔE_C=2,0717). Preokretanjem transparentnih medija ostvarene su promjene ΔE_{PVC}=7,5503 i ΔE_C=5,6322. Pritom je PVC ostvario promjenu od ΔE_{PVC}=3,3116, dok je polikarbonat ostvario promjenu ΔE_C=3,5605.

5. Zaključak

U tehnici elektrofotografskog tiska moguće je vršiti otiskivanje na neupojnim tiskovnim podlogama (PVC-u i polikarbonatu) sa primjenom ElectroInk boje, koja se samo površinski veže za otisak.

Pri otiskivanju ispitanih neprozirnih medija, ElektroInk će se bolje vezivati na poroznu papirnu podlogu (V=677,055) nego na neupojni bijeloi PVC (V=590,323).

Od ispitanih prozirnih matrijala, polikarbonat će omogućiti širi raspon obojenja (V=188,779), u odnosu na prozirni PVC (V=151,638).

Preokretanjem i mjerenjem transparentnih medija, manja promjena će nastati kod transparentnog PVC-a (ΔV=68,756 gamutne jedinice), u odnosu na polikarbonat (ΔV=104,914 gamutne jedinice).

Za postizanje što točnijih rezutata na prozirnim tiskovnim podlogama preporuča se slijedeća tiskovna podloga: PVC_{Cijan}=3,4494; $Polikarbonat_{Magenta}$=6,1865; $Polikarbonat_{Žuta}$= 2,8123; $Polikarbonat_{Crna}$= 2,0717.

Preokretanjem i mjerenjem otiska kroz tiskovnu podlogu ostvariti će se veće razlike u obojenju kod prozirnog polikarbonata nego kod transparentnog PVC-a. Time se nameće preporuka da se za tisak zahtjevnijih višebojnih displeja koristi PVC materijal.

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UTJECAJ UGLJIKA U OTPADNOM LJEVAONIČKOM PIJESKU NA ADSORPCIJU FENOLA IZ VODENIH OTOPINA

THE INFLUENCE OF CARBON IN SPENT FOUNDRY SAND ON PHENOL ADSORPTION FROM WATER SOLUTIONS

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Sažetak: Fenol je spoj za kojega je poznato da se akumulira u tlu, podzemnim vodama i tkivima živih bića. Ugrožava zdravlje jer i u malim količinama može djelovati štetno te uzrokovati različite poremećaje. Obvezujući zakoni ograničavaju sadržaj fenola u vodenim otopinama, pa se za uklanjanje fenola koriste različiti postupci. Oni se temelje na taloženju, flotaciji, ekstrakciji otapalima, koagulaciji, osmozi, ionskoj izmjeni i adsorpciji.
Postupci koji se temelje na adsorpciji zahtijevaju upotrebu selektivnih, cijenom prihvatljivih adsorbensa visoke adsorptivnosti. Poznato je da takva svojstva posjeduju komercijalni aktivirani ugljici, ali se istraživanja sve više usmjeravaju ka uporabi otpadnih materijala koji su nusproizvod tehnoloških postupaka u različitim industrijskim postrojenjima.
Svrha ovog rada je ispitati potencijal otpadnog ljevaoničkog pijeska u smjesi s ugljikom, kao adsorbensa za uklanjanje fenola iz vodenih otopina. Pokazalo se da dodatak aktiviranog ugljika može značajno poboljšati učinkovitost kvarcnog pijeska u obradi fenolom zagađenih voda.
Ključne riječi: otpadni ljevaonički pijesak, fenol, adsorpcija

Abstract: Phenol is known as the substance accumulating in soil, underground waters and living organisms. It is harmful even at low concentration, leading to different health problems. Legislative regulations are restrictive to phenol content in water effluent so that different methods for phenol removal are used. They are based on sedimentation, flotation, solvent extraction, coagulation, osmosis, ion exchange and adsorption.
Adsorption based processes use highly selective and commercially acceptable sorbents. It is known that activated carbons posses such characteristics, but research activities are now attempted to utilize the waste materials which are by-products from different technologies in industrial plants.
Therefore, the aim of this investigation is to study the potential of spent foundry sand mixed with activated carbon in order to removal phenol from water solutions. It was shown that activated carbon added can significantly improve the efficiency of spent foundry sand in phenol removal from waste waters.
Key words: spent foundry sand, phenol, adsorption

1. UVOD

Fenoli pripadaju grupi otrovnih organskih spojeva koji nastaju u brojnim industrijskim postrojenjima i stoga predstavljaju značajan ekološki problem [1]. Maseni udjel fenola u otpadnim vodama kreće se od 50 mg/L do 2000 mg/L [2]. Obvezujući zakoni ograničavaju sadržaj fenola u vodenim otopinama, pa se za uklanjanje fenola koriste različiti postupci. Oni se temelje na taloženju, flotaciji, ekstrakciji otapalima, koagulaciji, osmozi, ionskoj izmjeni i adsorpciji [3].
Proces adsorpcije obično se primjenjuje pri obradi voda za uklanjanje malih koncentracija onečišćujućih tvari, a u posljednje vrijeme adsorpcija na aktiviranom ugljiku upotrebljava se kao primarni postupak obrade industrijskih otpadnih voda, pri čemu se posebno radi na uklanjanju topljivih organskih tvari iz vode [4]. Aktivirani ugljik je jedan od najboljih adsorbensa za uklanjanje fenola iz vodenih otopina. Zbog visoke cijene na svjetskom tržištu, nastoje se pronaći načini da se smanji potrošnja aktiviranog ugljika. Stoga se istraživanja sve više usmjeravaju ka uporabi otpadnih materijala koji su otpad i/ili nusproizvod tehnoloških procesa u različitim industrijskim postrojenjima [5].
Tako se, na primjer, kod proizvodnje odljevaka pomoću jednokratnih kalupa stvaraju velike količine otpadnih kalupnih mješavina koje sadrže kvarcni pijesak s raznim vezivima i aditivima [6]. Jedan dio pijeska se u izvjesnoj mjeri obnavlja da bi se smanjili troškovi proizvodnje odljevaka, ali preostala kalupna mješavina predstavlja otpad koji pri odlaganju treba propisno zbrinuti [7]. Otpadne kalupne mješavine su nusproizvod ljevaoničkih procesa te stoga lako dostupni kvarcni materijali koji se prije konačnog odlaganja mogu iskoristiti kao komponente u građevinskoj industriji [8,9]. Ako se prije konačnog zbrinjavanja dodatno uporabe tako da vežu na sebe fenol, pretpostavlja se da bi tada njihova iskoristivost bila daleko veća.
Stoga se u ovom radu ispituju sorpcijska svojstva otpadnog ljevaoničkog pijeska kao sredstva za uklanjanje fenola iz zagađenih voda.

2. EKSPERIMENTALNI DIO

Adsorbensi

U laboratorijskim je ispitivanjima kao adsorbens korišten kvarcni pijesak-P_{VS} (s vodenim staklom kao vezivom) koji je osnovni sastojak otpadne kalupne mješavine iz ljevaonice Felis d.o.o. Radi usporedbe, adsorpcija fenola je provedena i na aktiviranom ugljiku-AU koji se uspješno koristi [10] kao sredstvo za uklanjanje organskih tvari iz zagađenih voda.
Aktivirani ugljik koji se koristio u eksperimentima bio je komercijalni proizvod analitičke čistoće (Kemika, Carbon Activatus) u obliku praha. Poznato je da takvi ugljici imaju veliku specifičnu površinu (oko 1500 cm^2/g) i visok kapacitet sorpcije fenola [10]. Stoga su neki adsorbensi u ovom radu pripremljeni miješanjem AU i otpadnog ljevaoničkog pijeska prema tablici 1.
Adsorpcijska su ispitivanja provedena „batch“ metodom pri sobnoj temperaturi 20 ± 2 °C. Određena masa adsorbensa stavljena je u PVC posudice, dodano je 100 mL otopine fenola poznate koncentracije (10-500 mg/L) te zatvoreno da ne dođe do isparavanja fenola i prskanja prilikom miješanja. Naime, radi pospješivanja kontakta adsorbensa i fenola, otopine su bile na laboratorijskoj tresilici CHYRANA (brzina = 60 okretaja/min) u trajanju od 60 min, jer je prethodnim istraživanjima ustanovljeno da se ravnoteža uspostavlja nakon tog vremena.

Tablica 1. Uzorci adsorbensa korištenih za uklanjanje fenola

Oznaka adsorbensa	Udjel AU/ mas.% u smjesi s P_{VS}	Masa adsorbensa g
P_{VS} (kvarcni pijesak)	-	10,00
AU (aktivirani ugljik)	100	3,00
PAU_1 (smjesa AU i P_{VS})	1,3	11,44
PAU_2 (smjesa AU i P_{VS})	6	10,04
PAU_3 (smjesa AU i P_{VS})	20	8,20

Otopine fenola

Budući da je fenol kristalna tvar, otopine se priređuju iz komercijalnih uzoraka. U ovom je radu korišten fenol analitičke čistoće, Sigma-Aldrich, Riedel-de Haen®. Standardna otopina fenola koncentracije 1000 mg/L pripremljena je s demineraliziranom vodom i stabilna je oko tjedan dana. Iz nje su za adsorpcijska mjerenja priređene otopine početne koncentracije fenola u području od 10 mg/L do 500 mg/L.

Spektrofotometrijska metoda određivanja fenola

Koncentracija fenola u vodenoj otopini prije i nakon adsorpcije, određena je prema normi HRN ISO 6439 – 98 (4-amino antipirinska metoda).
Metoda se zasniva na spektrofotometrijskom određivanju promjene intenziteta svjetlosti pri prolazu kroz obojene otopine fenola. U tu svrhu potrebno je otopine fenola nakon završene adsorpcije odvojiti filtriranjem od krutog adsorbensa, a filtrat obojiti odgovarajućim reagensima (amonijev klorid, 4-amino antipirin, kalijev(III) heksacijanoferat) uz dodatak tekućeg NH_3, jer se stabilnost ružičasto obojenog kompleksa održava u lužnatom mediju (pH cca 10). Nakon 15 min stabilizacije boje, mjeri se apsorbancija, A kod valne duljine od 510 nm. Spektrofotometrijska mjerenja izvedena su na uređaju Camspec M–107.
Za izračunavanje koncentracije fenola koji je ostao u otopini nakon uspostavljanja ravnoteže (c_e), koristi se jednadžba baždarnog pravca, prethodno određenog s pomoću otopina poznate koncentracije:

$$A/\% = 0{,}15618 \cdot c\,/\mathrm{mgL^{-1}} \qquad (1)$$

Budući da ova linearna zakonitost vrijedi za područje koncentracija fenola od 0 do 5 mg/L, ravnotežna (nepoznata) koncentracija fenola c_e, računa se pomoću te jednadžbe uzimajući u obzir razrjeđenje otopine koje je prije spektrofotometrijskog mjerenja nužno da bi se jednadžba (1) mogla koristiti.
Rezultati mjerenja prikazani su u obliku tablica i dijagrama u kojima se koriste srednje vrijednosti iz dva neovisna seta mjerenja.

3. REZULTATI I RASPRAVA

Svojstva kvarcnog pijeska

Otpadna kalupna mješavina koja se koristi kao osnovni sorbens u ovom radu, sastoji od kvarcnog pijeska s vodenim staklom kao vezivom. Parametri kvalitete kvarcnog pijeska i njegov sastav navedeni su u tablici 2 i 3, a fizikalno-kemijska svojstva vodenog stakla u

tablici 4.

Tablica 2. Neka svojstva kvarcnog pijeska korištenog za pripremu kalupnih mješavina

FIZIKALNO- KEMIJSKI PARAMETRI	
Srednja veličina zrna, mm	0,25 – 0,27
Stupanj ravnomjernosti zrna, %	70-80
Broj finoće zrna	50-60
pH	6,8-7,2
Vlaga vlažnog pijeska, %	4,0-8,0
Vlaga osušenog pijeska, %	max 0,5

XRD analiza kvarcnog pijeska [11] pokazala je da u ispitanom uzorku ima najviše SiO_2 (90,0%), nakon čega slijede Fe (6,8%) i Al_2O_3 (1,6%), kako se to vidi iz tablice 3.

Tablica 3. Kemijski sastav ljevaoničkog pijeska

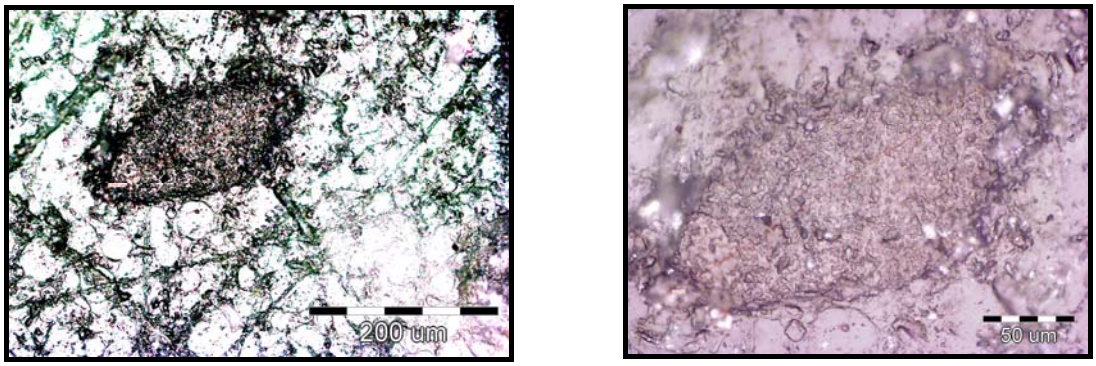
Komponenta	**Sastav /%**
SiO_2	90,0
Al_2O_3	1,6
Fe	6,8
Ca	0,55
Mg	0,08
Mn	0,04
Ni	0,004
Cr	0,01
C	0,98

Iz tog se kvarcnog pijeska priprema svježa kalupna mješavina za jednokratne kalupe, tako da se uz uvođenje CO_2 [12] miješa s vodenim staklom čija su svojstva dana u tablici 4.

Tablica 4. Fizikalno-kemijska svojstva vodenog stakla

KEMIJSKI SASTAV I pH			
Natrijeva sol silicijeve kiseline		43-46 mas. **%**	
Voda		54-57 mas. **%**	
pH		11,5-12,3	
FIZIKALNI PARAMETRI			
Vrelište, ºC	100	Talište, ºC	0
-	Relativna gustoća, g/cm^3	1,500-1,550	-

Na slici 1 je metalografski prikaz karakterističnog zrna kvarcnog pijeska iz otpadne kalupne mješavine koja je korištena u ovom radu kao sorbens za fenol.



(a) (b)

Slika 1. Zrno kvarcnog pijeska iz otpadne kalupne mješavine s vodenim staklom kao vezivom: (a) povećanje 200x; (b) povećanje 500x

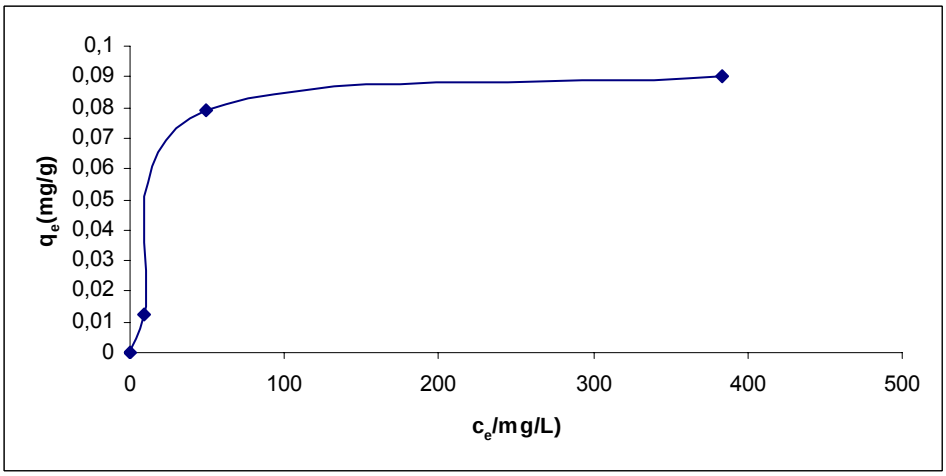
Iz slike 1a se vidi da je tipično zrno obloženo tamnijim slojem natrij-silikata, koji kod pripreme kalupne mješavine nastaje reakcijom kvarca s vodenim staklom u prisustvu CO_2. Na slici 2b pokazano je da približna duljina zrna iznosi cca 250μm. Za takve je dimenzije komercijalnog kvarcnog pijeska poznato iz literature da ima specifičnu površinu cca 5 m^2/g, što je više od 100 puta manje nego kod uspješnih, ali ekonomski zahtjevnih sorbensa kao što je AU.

Adsorpcija u sustavu kvarcni pijesak/fenol

Uobičajeno je da se sorpcijom dobiveni rezultati prikazuju kao adsorpcijske izoterme iz kojih se vidi ovisnost mase tvari adsorbirane po jedinici mase sorbensa (q_e, mg/g) i tvari preostale u otopini nakon uspostavljanja ravnoteže na granici faza krutina/otopina. Te su vrijednosti određene iz razlike početne koncentracije (c_o/mgL^{-1}) i ravnotežne koncentracije fenola (c_e/mgL^{-1}) u vodenoj otopini, te mase kvarcnog pijeska, m(g) i volumena otopine fenola V (L) prema jednadžbi:

$$q_e = \frac{c_o - c_e}{m} V \qquad (2)$$

Izračunate vrijednosti prikazane su kao adsorpcijska izoterma na slici 1.



Slika 1. Adsorpcijska izoterma konstruirana iz eksperimentalnih podataka u sistemu kvarcni pijesak/fenolna otopina

Vidi se da postoje dva stadija sorpcijskog procesa. Strmi porast vrijednosti q_e u području malih koncentracija fenola može se protumačiti činjenicom da na površini sorbensa ima dovoljno slobodnih mjesta za sve prisutne molekule fenola. Porastom koncentracije sorpcijski se doseg više ne povećava, već se asimptotski približava nekom maksimalnom iznosu. Vrijednost dobivena u ovom radu za q_e (približno 0,1 mg fenola adsorbiranog na 1 g kvarcnog pijeska), u skladu je s onima iz literature za sorbense silikatne osnove [13]. Taj iznos, prema Langemuirovoj teoriji [14], odgovara potpunoj prekrivenosti površine sorbensa s monomolekularnim slojem adsorbirane tvari.

Adsorpcija u sustavu PAU/fenol

Sposobnost adsorpcije kod sorbensa koji su dobiveni primješavanjem aktivnog ugljika otpadnom kvarcnom pijesku, izračunata je iz jednadžbe (2) na osnovi eksperimenata izvedenih s otopinom fenola početne koncentracije 392,914 mgL^{-1}. Rezultati su prikazani u tablici 5, a radi usporedbe navedene su također i vrijednosti iz literature [15].
Iz tablice se vidi da su vrijednosti za q_e sukladne s iznosima dobivenim za interakciju fenola sa sličnim sorbensima od prirodnih materijala. Međutim, kod sorbensa korištenih u ovom radu, masa adsorbiranog fenola ovisi o udjelu ugljika u kvarcnom pijesku, a maksimalni doseg adsorpcije pokazao se, prema očekivanju, na aktivnom ugljiku.
Uočljivo je da se sorpcijski potencijal smjese kojoj je osnova otpadni kvarcni pijesak značajno povećava s dodatkom čak i malog udjela AU. Tako se npr. q_e četverostruko povećava (s početnih 0,09 mg/g za P_{VS} na 3,51 mg/g za PA_2), kad je dodano 6 mas.% AU.

Tablica 5. Spektrofotometrijski određeni parametri sorpcije fenola na različitim adsorbensima

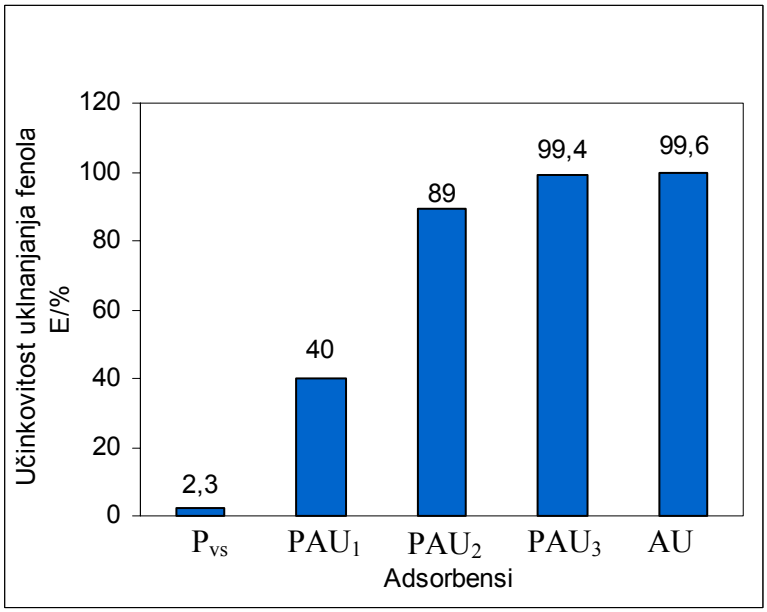
Oznaka adsorbensa	**Ravnotežni adsorpcijski doseg, q_e mg/g**	**Literatura**
P_{VS}	0,09	ovaj rad
PAU_1	1,38	"
PAU_2	3,51	"
PAU_3	4,76	"
AU	13,06	"
Bentonit	1,3	15
Klinoptilolit	0,23	15
Aktivni ugljik	13,22	15

Laboratorijska mjerenja izvedena u ovom radu pokazala su da se fenol adsorbira na lako dostupnom industrijskom otpadu kao što je to ljevaonički kvarcni pijesak s dodatkom AU.

Učinkovitost uklanjanja fenola

Iz apsorbancije otopina prije (A_0) i nakon adsorpcije (A_e), izračunata je prema jednadžbi (3) učinkovitost sorbensa primjenjenih u ovom radu. Iznosi za E omogućavaju da se bolje uoči razlika u sposobnosti uklanjanja fenola dodavanjem različitih udjela ugljika u kvarcni pijesak, a rezultati su prikazani na slici 2.

$$E = 1 - \frac{A_e}{A_o} \qquad (3)$$



Slika 2. Učinkovitost uklanjanja fenola iz vodenih otopina na različitim adsorbensima

Iz prikazanih rezultata može se zaključiti da otpadni ljevaonički pijesak uklanja fenol iz vodenih otopina, no učinkovitost je niska i iznosi svega 2,3%. Međutim, dovoljno je dodati oko 2% AU, pa da se E poveća na 40%. U sustavima kod kojih je kao adsorbens korištena mješavina P_{VS} i aktiviranog ugljika, učinkovitost uklanjanja fenola značajno se povećava u nizu $PAU_1 < PAU_2 < PAU_3$, te gotovo dostiže iznos karakterističan za komercijalni AU.

4. ZAKLJUČAK

Na osnovi ispitivanja mogućnosti korištenja otpadnog ljevaoničkog pijeska kao potencijalnog adsorbensa za uklanjanje fenola iz vodenih otopina "batch"- metodom pri sobnoj temeperaturi, zaključeno je sljedeće:

- Upotrebom otpadnog ljevaoničkog pijeska moguće je uklanjanje fenola iz vodenih otopina, u području ispitanih koncentracija (10-500 mg/L).
- Dodatkom aktiviranog ugljika povećava se adsorpcijska sposobnost otpadnog ljevaoničkog pijeska desetak puta.
- Već i mala primjesa aktiviranog ugljika (1-6 mas. %) pretvara otpadni ljevaonički pijesak u djelotvorni jeftini adsorbens za uklanjanje fenola iz vodenih otopina.

ZAHVALA
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CORROSION OF LANTHANUM DOPED, SOL-GEL DERIVED, MULLITE CERAMICS IN NITRIC ACID

KOROZIJA SOL-GEL METODOM PRIREĐENE, LANTANOM DOPIRANE MULITNE KERAMIKE U DUŠIĆNOJ KISELINI

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Abstract: Samples of monophasic mullite ($3Al_2O_3 \cdot 2SiO_2$); undoped and doped with 9.09 mol% of La_2O_3, were prepared by a sol-gel process. Prepared gels were dried, grinded, pressed into pellets and sintered at temperatures 1100 and 1600 °C for 4 h. Influence of La_2O_3 content on phase formation and corrosion behavior has been investigated. Mullite thermal evolution was analyzed by Differential Thermal and Thermogravimetric Analysis (DTA/TGA) and X-ray diffraction (XRD). The corrosion behavior of the sintered ceramics bodies was explored in HNO_3 solution by measuring the amount of eluted ions. Samples with lanthanum were found to be more susceptible to dissolution in corodent. The amount of eluted La^{3+} ions confirms the existence of glassy phase which can easier dissolute in corodent, as well as predominant incorporation of La_2O_3 in the glassy phase during the sample synthesis.
Keywords: Mullite, lanthanum, sol-gel, corrosion

Sažetak: Sol-gel metodom sintetizirani su uzorci čistog monofaznog mulita ($3Al_2O_3 \cdot 2SiO_2$), i mulita dopiranog sa 9.09 mol% La_2O_3. Priređeni gelovi su sušeni, mljeveni, te stiješnjeni u tablete koje su sinterirane na temperaturama od 1100 i 1600 °C 4 sata. Istražen je utjecaj dopiranja mulitne keramike sa La_2O_3 na koroziju, kao i na razvoj faza. Termička svojstva ispitana su simultanom diferencijalnom termalnom i termogravimetrijskom analizom (DTA/TGA) te rendgenskom difrakcijskom analizom (XRD), dok je korozija praćena mjerenjem količine izlučenih iona iz sinteriranih uzoraka u vodenu otopinu HNO_3 Uzorci s lantanom pokazali su se podložnijima otapanju u korozivnom mediju. Postojanje lakše topive staklaste faze potvrđeno je količinom izlučenih La^{3+} iona; koja ukazuje da La_2O_3 tijekom sinteze preferirano formira silicijem bogatu staklastu fazu.
Ključne riječi: mulit, lantan, sol-gel, korozija

Introduction

Mullite is a solid solution with a general formula $Al_2[Al_{2+2x}Si_{2-2x}]O_{10-x}$ where x represents the number of oxygen vacancies per unit cell ranging from 0.17 to 0.59.[1] Mullite ceramic is used widely as a structural and refractory ceramic material because of its intrinsic high strength, low thermal expansion, good chemical stability and good creep resistance at high temperatures.[2,3,4] Sol-gel synthesis is fabrication method that meet high mullite requirements and enable high purity, homogeneity and lower processing temperatures.[5]

In molecularly mixed amorphous single-phase system, mullite is formed at about 980 ºC[6], while mullitization from less homogeneous, diphasic mixtures occurs at temperatures higher than 1150 °C via metastabile spinel phase.[7]

Mullite formation is related not only to material processing but also to introduction of other compounds. Mullite is able to incorporate different foreign atoms whereas their solubility limit depends on radii and oxidation states.[8] The introduction of various oxides in gels has also been shown to be advantageous to mullitization process,[9,10] as well as mullite properties.[8] The same has been shown when La_2O_3 has been employed as dopant.[11]

Mullite ceramics usually contains small ratio of crystal α-alumina and amorphous glass phase.[12] It has been shown that La_2O_3 exhibits strong glass formation tendency with Al_2O_3 and SiO_2[11] i.e. the mullite crystal lattice incorporates only a small amount of La. Also, the increase of amount of doped La_2O_3 propagates even more the formation of a glass phase in mullite ceramics.[13] Complete interpretation of this system should include crystal phase as well as amorphous phase properties investigation.

Pure mullite chemical corrosion properties are well known and defined.[14] However researches of chemical corrosion properties of doped mullite ceramics are scarce. To the best of our knowledge, no information could be found on the corrosion of such systems. Therefore, the intention of this study is to examine the corrosion process of lanthanum-doped mullite ceramics.

The corrosion behavior of mullite sample with and without addition of lanthanum has been investigated in nitric acid aqueous solutions with various concentrations. The monitoring of corrosion in aqueous solution is usually performed by checking mass and/or amount of eluted ion from a fixed volume of corodent after immersion. The chemical stability could be determined more precisely by measurement of eluted ions concentrations rather than the measurement of the total weight loss of specimens. Therefore, the elution of elements after immersion in different concentrations of HNO_3 aqueous solution has been measured. The influence of the microstructure of the sintered samples on the corrosion susceptibility was also considered.

Experimental

Starting materials for gel synthesis were ($La(NO_3)_3{\cdot}6H_2O$, p.a., Kemika, Croatia), ($Al(NO_3)_3{\cdot}9H_2O$, p.a., Kemika, Croatia), ($Si(OC_2H_5)_4$ 98%, Merck, Germany) and (C_2H_5OH 96%, Kemika, Croatia). The appropriate amount of $La(NO_3)_3{\cdot}6H_2O$ and $Al(NO_3)_3{\cdot}9H_2O$ were mixed with C_2H_5OH in reactor. $Si(OC_2H_5)_4$ was dissolved in C_2H_5OH separately, stirred for 1 h and then added drop-wise to the reactor. The mixture was stirred in a closed reactor for 8 days at 60 °C. Two mullite samples were prepared: without addition of La_2O_3 (sample A: 40.00 mol.% SiO_2, 60.00 mol.% Al_2O_3) and with addition of La_2O_3 (sample B: 36.36 mol.% SiO_2, 54.55 mol.% Al_2O_3, 9.09 mol.% La_2O_3). The molar ratio of SiO_2 to Al_2O_3 was held constant (2:3) in both samples.

The gel formed in the course of synthesis was removed from the reactor and dried for 24 h under 150W IR lamp. The obtained samples were then calcined in box furnace in static air at a heating rate of 10 °C/h at 700 °C for 2 h in order to remove organics and nitrate phase. Yielding mass was subsequently grinded to form a fine powder by means of wet grinding in a

planetary mill with 200 rpm for 2 h and with propanol as a milling media. Grinded samples were dried and remaining propanol was removed by another calcification process at 700 °C for 2 h. Obtained mullite powders were uniaxially pressed into Φ 10 mm pellets with 100 MPa pressure. The pellets were then sintered in static air at a heating rate of 10 °C/h at temperature 1600 °C for 4 h. The Archimedes density of the samples sintered at 1600 °C for 4 h were 1.70 g/cm^3 and 3.03 g/cm^3 for samples A and B, respectively.

The thermal behavior of powder precursor was characterized with Differential Thermal Analysis (DTA) and Thermo-Gravimetric Analysis (TGA) using simultaneous DTA/TGA analyzer Netzsch STA 409. For the thermal analysis approximately 50 mg of material were placed in Pt crucibles and heated at a rate of 10 °Cmin^{-1} to 1350 °C in a synthetic air flow of 30 cm^{3}min^{-1}, α-alumina was used as a reference.

The crystal phases were identified by powder X-ray diffraction (XRD) on diffractometer Philips 1830 with CuKα radiation. Data were collected between 10 and 70 $^o 2\theta$ in a step scan mode with steps of 0.02 ^{o} and counting time of 2 s.

In order to investigate the chemical corrosion behavior of sintered pellets of samples the specimens were placed into a sealed polypropylene (PP) tubes with 10 ml of HNO_3 solution. The HNO_3 solution molarities were 0.3 mol/dm^3, 0.9 mol/dm^3 and 1.5 mol/dm^3. The static corrosion tests were carried out simultaneously on three samples at room temperature (25 °C) from 24 to 240 h. The measurements were conducted after 48, 96, 144, 192 and 240 hours of immersion. To avoid an enrichment of leached components at the surface of samples, the solution was occasionally stirred. After the exposure time, the specimens were removed from the tubes, rinsed with boiling distilled water and dried in a oven heated at 150 °C.

The determination of the amount of Al^{3+}, Si^{4+} and La^{3+} ions eluted in the corrosive solutions was carried out by means of the atomic absorption spectrophotometry (AAS, AA-6800, Shimadzu) and inductively coupled plasma-optical emission spectrometry (ICP-OES, Thermo Duo Iris Intrepid). Obtained results are expressed as the amount of eluted ions (M^{n+}) in μg per square centimeter of test sample area (μg M^{n+}/cm^2). All results are an average of three values.

Results and discussion

The thermal behavior of the samples is characterized by multistep weight loss in the temperature range of 100-500 °C (Figure 1). In the lower temperature region the DTA curves consist of series endothermic and exothermic effects with various intensity and mutual superposition. According to Tkalcec et al.[15], the peaks in the low temperature range are caused by dehydration, dehydroxylation and decomposition of nitrates and alkoxydes. Strong exotherm at ~980 °C is attributed either to the formation of mullite, or spinel, or both. When spinel crystallizes a small exotherm is also generally recorded at higher temperatures.[16] As can be seen in Fig.1, there is no evidence of additional exotherm between 1000 and 1300 °C in DSC scan. Therefore, an exotherm at 980 °C is attributed to mullite crystallization process. XRD analysis of the samples thermally treated at 1000 °C for 2 h (Fig. 2) provided evidence that no spinel was formed simultaneously with mullite at 980 °C. According to DSC and XRD results the prepared gels could be classified as type I by Schneider classification.[17,18] After calcinations/ grinding/ calcination cycle powders exhibit only exothermic peak at ~980 ºC (insert in Fig. 1). Slight temperature shift of doped sample exothermal peak towards higher temperatures can be noted for both, as received and calcined samples. The shifting of exothermic DSC peak samples doped with La_2O_3 to higher temperature has been described in literature.[19]

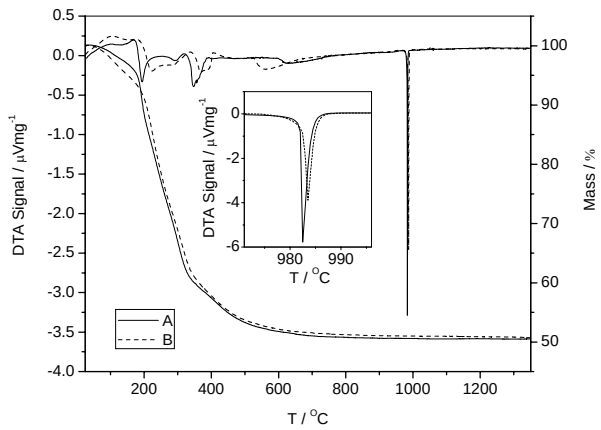

Figure 1: DTA/TGA curves of samples A (undoped sample) and B (La_2O_3 doped sample). Insert: calcined samples exothermal peaks.

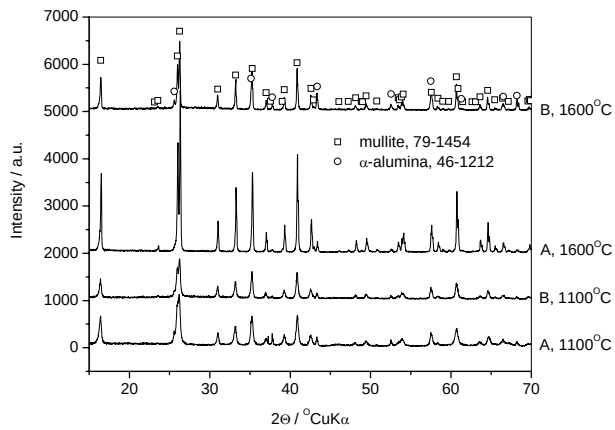

Figure 2: XRD patterns of the samples A (pure sample) and B (La_2O_3 doped sample) sintered at temperatures of 1100 and 1600 ºC for 4 h.

In this case so small temperature displacement is within method error range. On the other hand, the decrease of peak intensity of doped sample, observed for both, as received and calcined sample seems significant. According to the decrease in intensity the crystallization enthalpy for the doped sample is considerably smaller than for pure sample pointing out to decrease of the amount of mullite crystallized in doped sample.

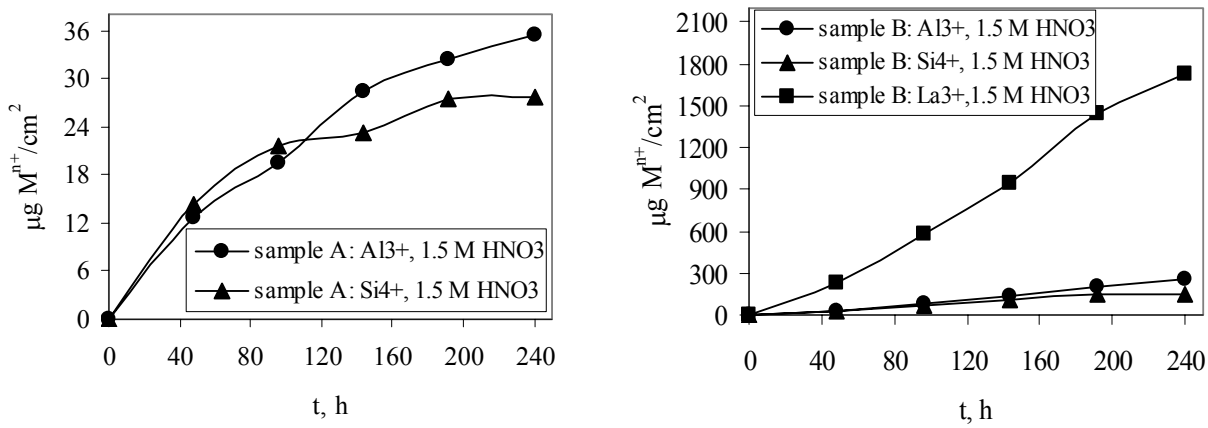

Figure 3: The amount of eluted Al^{3+} and Si^{4+} ions from mullite sample A; Al^{3+}, Si^{4+} and La^{3+} ions from mullite sample B in 1.5 M HNO_3 as function of corrosion time

XRD patterns of the pure and doped samples sintered at 1100 and 1600 °C are shown in Fig. 2. After sintering at 1100 °C, two phases are observed in XRD pattern of both samples: Mullite diffraction lines appear in XRD patterns of samples as a dominate phase, while α-alumina appears as a secondary phase. Neither La_2O_3 nor La_2O_3 related crystal phases were observed in the XRD patterns. The same phases are observed after sintering at 1600 °C. Since standard was added in this samples it could be observed that the content of crystalline mullite decreased and the background increased with La_2O_3 doping, suggesting the increase of amorphous phase. α-alumina peaks also increased with La_2O_3 doping. As we reported previously[13] hardly any lanthanum enters the mullite structural lattice and considerable amount of silicon and lanthanum rich glassy phase exist in doped sample. The chemical corrosion behavior of doped sample should reflect its partially amorphous nature, i.e. the existence of lanthanum rich glassy phase beside crystalline phases, mullite and α-alumina.

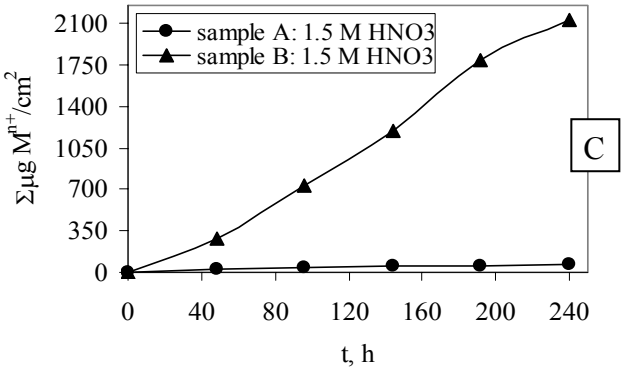

Figure 4: Total amount of eluted ions from mullite ceramics sample A and sample B in 1.5 M HNO_3 (C) as function of corrosion time

Mullite ceramics (sample A) corrosion kinetic can be put in form:

$$\left(\sum \mu gM^{n+} / cm^2\right)^2 = K_p \cdot t$$

For mullite ceramics sample B corrosion kinetic can be put in form:

$$\sum \mu gM^{n+} / cm^2 = K_1 \cdot t$$

Where:- K_p is the parabolic corrosion rate constant in $\mu g^2\ cm^{-4}\ s^{-1}$,

- K_1 is the linear corrosion rate constant in $\mu g\ cm^{-2}\ s^{-1}$,
- *t, s* is time of immersion in seconds,
- $\sum \mu gM^{n+} / cm^2$ is the sum of the amount of eluted ions (Al^{3+} and Si^{4+} for sample A), (Al^{3+}, Si^{4+} and La^{3+} for sample B) per square centimeter in $\mu g\ cm^{-2}$.

Significantly better dissolution can be observed for sample B on Fig. 4. (shown only 1.5 M HNO_3).

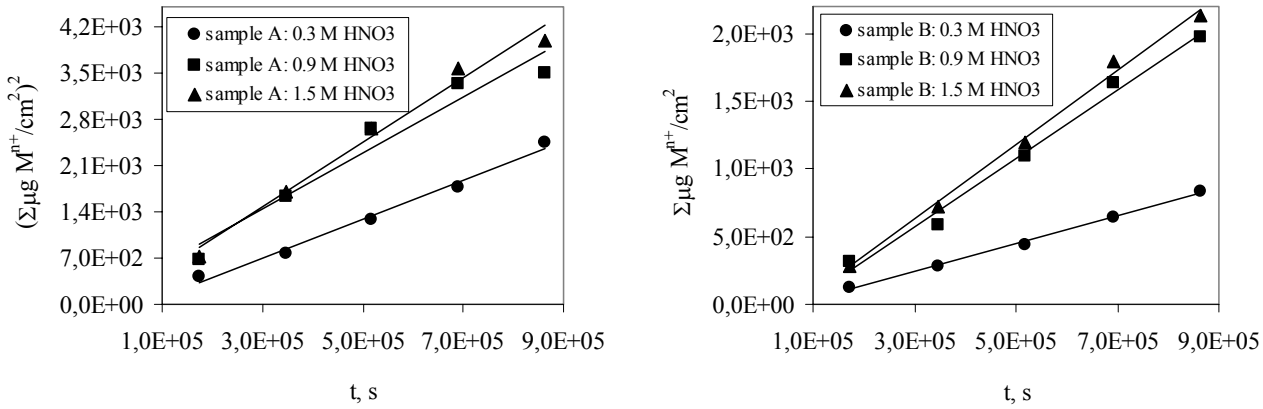

Figure 5: The square of the total amount of eluted ions Al^{3+} and Si^{4+} from mullite samples A and B vs. the corrosion time for different concentration of HNO_3 solution

The square of the total amount of eluted ions as a function of the corrosion time for different concentrations of HNO_3 solution are plotted in Fig 5. This correlation is linear with the correlation coefficient R^2 = 0.9870 for 0.3 M HNO_3, R^2 = 0.9462 for 0.9 M HNO_3 and R^2 = 0.9838 for 1.5 M HNO_3. The parabolic corrosion rate constants were evaluated from the slopes. The corresponding values of the parabolic corrosion rate constants are given in Table 2. The values of the parabolic and linear corrosion rate constants indicate maximum corrosion susceptibility of mullite ceramics at the highest concentration (1.5 mol/dm^3) of HNO_3 solution.

Table 2: The parabolic (Kp) and linear (K_1) corrosion rate constants for mullite ceramics sample A and sample B in different concentrations of HNO_3 solutions at 25 °C.

c(HNO_3), mol/dm^3 (M)	Sample A		Sample B	
	K_p, μg^2 cm^{-4} s^{-1}	R^2	K_p, μg^2 cm^{-4} s^{-1}	R^2
0.3	$2.9 \cdot 10^{-3}$	0.9870	$1.0 \cdot 10^{-3}$	0.9969
0.9	$4.2 \cdot 10^{-3}$	0.9462	$2.5 \cdot 10^{-3}$	0.9888
1.5	$4.9 \cdot 10^{-3}$	0.9838	$2.7 \cdot 10^{-3}$	0.9947

Conclusion

Monophasic mullite samples with and without La_2O_3 doping were synthesized by means of sol-gel method; thereafter dried, grinded, pressed into pellets and sintered at temperatures 1100 and 1600 °C for 4 h.

The crystallization path and corrosion behavior of samples was examined. Two crystal phases present in the samples are mullite and α-alumina. Neither La-silicate nor La-aluminate phases crystallize in the system. Samples reveal linear and parabolic dependence of amount of eluted ions to time of immersion and corodent concentration. Significantly better dissolution of samples upon doping with La_2O_3, also particularly the high amount of eluted La^{3+} ion are due to dissolution of an amorphous glassy part of sample. This confirms not only the existence of such phase yet lanthanum's tendency to form silicon rich phase.

Acknowledgement

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EFFECT OF TiO_2 ON SINTERING OF MAGNESIUM OXIDE OBTAINED FROM SEAWATER

UTJECAJ TiO_2 PRI SINTERIRANJU MAGNEZIJEVA OKSIDA DOBIVENOG IZ MORSKE VODE

Izvorni znanstveni rad / Original scientific paper

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Abstract: This study has examined the effect of the TiO_2 addition on properties of magnesium oxide obtained from seawater by substoichiometric precipitation. The addition of dolomite lime, used as the settling agent, was 80 % of the stoichiometrically required quantity. In sample preparation, the combined method of rinsing of the magnesium hydroxide precipitate was used (3+2), i.e. rinsing by decantation was done three times with alkalised distilled water with pH of 12.50 and twice with distilled water with pH of 6.74. Repeated rinsing on the filter paper (5 times) was done with fresh distilled water with pH of 6.74. Isothermal and activated sintering of MgO samples (80% precipitation) then took place without TiO_2 addition, and with the addition of 5 and 8 mass % TiO_2 at the temperature of 1700 ^oC during 1 hour, in order to determine the properties of these samples, particularly as regards the amount of B_2O_3 in samples after sintering. The results indicate that the addition of TiO_2 in the amount of 5 mass % is sufficient to bind the CaO present and thereby lead to significant evaporation of B_2O_3 in the process of activated sintering of seawater-derived magnesium oxide. Samples became significantly denser during sintering, i.e. all the samples examined had very low open porosity.
Key words: substoichiometric precipitation, TiO_2 addition, seawater, magnesia, activated sintering
Sažetak: U radu je ispitivan utjecaj dodatka TiO_2 na svojstva magnezijeva oksida dobivenog iz morske vode nestehiometrijskim načinom taloženja. Dodatak dolomitnog vapna, kao taložnog sredstva, iznosio je 80 % od stehiometrijski potrebne količine. Kod pripreme uzoraka primijenjen je kombinirani način ispiranja taloga magnezijeva hidroksida (3+2), tj. ispiranje dekantacijom vršeno je tri puta zaluženom destiliranom vodom pH vrijednosti 12.50 i dva puta destiliranom vodom pH vrijednosti 6.74. Višekratno ispiranje na filtar papiru (5 puta) vršeno je svježom destiliranom vodom pH vrijednosti 6.74. Izvršeno je zatim izotermno i aktivirano sinteriranje uzoraka MgO (80 %-tno taloženje) bez dodatka TiO_2 i uz dodatak 5 i 8 mas. % TiO_2 pri temperaturi 1700 ^oC u trajanju 1 sat, sa svrhom da se utvrde svojstva ovih uzoraka prvenstveno s obzirom na udjel B_2O_3 u uzorcima nakon procesa sinteriranja. Rezultati ispitivanja ukazuju da je dodatak TiO_2 u količini 5 mas. % dovoljan da veže prisutni CaO i time utječe na značajnije isparavanje B_2O_3 u procesu aktiviranog sinteriranja magnezijeva oksida iz morske vode. Tijekom sinteriranja postignuto je znatno zgušnjavanje uzoraka, tj. svi ispitivani uzorci imaju veoma malu brojnost otvorenih pora.
Ključne riječi: nestehiometrijsko taloženje, dodatak TiO_2, magnezijev oksid iz morske vode, aktivirano sinteriranje

1. INTRODUCTION

More than 70 % of the planet Earth is covered by seas i.e. oceans. Therefore seawater is an inexhaustible deposit and source of raw mineral materials, among which magnesium oxide holds a prominent place in view of high mass concentration of magnesium in seawater [1] which amounts to 0.13 g / dm^3. The technological process and procedures developed on the industrial scale in the last 50 years [2-6] are used to obtain magnesium hydroxide, which transforms into magnesium oxide in the process of calcination, and into refractory magnesium oxide [7] in the process of sintering at high temperatures.
Seawater-derived magnesium oxide contains boron (III) oxide as impurity, which has to be reduced to the lowest possible quantity by means of the appropriate method of rinsing of the magnesium hydroxide precipitate, and by adding TiO_2 in the process of activated sintering. Specifically, the properties of high-temperature sintered magnesium oxide are significantly affected by the content of B_2O_3 in the final product. This study has examined both effects.

2. EXPERIMENTAL

The composition of seawater used for the precipitation of magnesium hydroxide was:
MgO = 2.375 g dm^{-3}; CaO = 0.583 g dm^{-3}

The composition of the dolomite lime used as the precipitation agent was as follows (mass %):

CaO = 57.17 %	MgO = 42.27 %
SiO_2 = 0.099 %	Al_2O_3 = 0.051 %
Fe_2O_3 = 0.079 %	

The seawater was first acidified (by sulphuric acid) to lower its pH from the normal value of 8.2 to 4.0. Seawater was then passed through the desorption tower packed with Rasching rings where it flowed downward against a rinsing stream of air. At low pH, the bicarbonates (HCO_3^-) and carbonates (CO_3^{2-}) were converted to the CO_2 gas, which was stripped out of the falling water drops by the ascending airflow. The flow rate of the induced air was 120 $dm^3\ h^{-1}$ and the volumetric flow rate of seawater through the desorption tower was 6 $dm^3\ h^{-1}$.
The precipitation of magnesium hydroxide took place after the pre-treatment of seawater with 80 % of the stoichiometric quantity of dolomite lime as the precipitation agent.
The experimental procedure used to obtain magnesium hydroxide from seawater was similar to that employed in our previous studies [4,8].
The sedimentation rate was increased by the addition of the optimum amount of the anionic 818A flocculent (polyacrylamide) produced by the Dutch firm Hercules. The experimental procedure used to determine the optimum quantity of the anionic 818A flocculent has been described in a previous study [9].
After completed sedimentation, the clear layer was decanted, and the formed magnesium hydroxide precipitate rinsed using the combined method.
The rinsing agent was: - alkalised distilled water pH = 12.50 which was alkalised by the addition
of concentrated NaOH and
- distilled water pH = 6.74
The 3+2 combined rinsing method was used in rinsing by decantation, i.e. after the magnesium hydroxide precipitate was rinsed three times with alkalised distilled water with

pH = 12.50, it was rinsed twice with fresh distilled water. The volume of the rinsing agent was approx. 1 dm^3.
After decantation, the precipitate was filtered on a number of funnels (blue ribbon filter paper). Repeated rinsing on the filter paper (5 times) was done with fresh distilled water with pH of 6.74. The prepared magnesium hydroxide samples were dried at 105 ^oC after filtering and then calcined at 950 ^oC for 5 h to form caustic magnesium. Table 1 shows the operating conditions during rinsing of the magnesium hydroxide precipitate using the combined rinsing method and the results obtained for chemical composition of magnesium oxide from seawater by 80 % precipitation. Mixtures of magnesium oxide were then prepared with the addition of a mass fraction of 5 % and 8 % TiO_2. The doping oxide used was analytical reagent grade titania (TiO_2 p.a.) in the rutile form – produced by Merck. Table 2 shows its analysis.
Samples were homogenized by manual stirring in absolute ethanol (C_6H_5O p.a.). The mixtures were cold pressed into compacts in a hydraulic press at a pressure of 625 MPa. The compacts were then sintered in a gas furnace, made by the French firm Mecker (type 553), with zirconium (IV)-oxide lining, at 1700 ^oC with 1h of soaking at the maximum temperature.
It took approximately 2 h to reach the maximum temperature in the furnace. After sintering, the samples were left to cool in the furnace. The sample density after sintering (ρ) was determined from the volume of water displaced from a calibrated cylinder. The total (P_t), apparent (P_a) and closed (P_c) porosities in the samples examined were determined according to standard methods (HRN B.D8.302, B.D8.312, B.D8.313). The boron content in the magnesium oxide samples examined was determined potentiometrically. The variation coefficient for the method applied is ± 1 % [10]. The results shown represent the average of a number of measurements.

Table 1: Chemical composition (mass %) of magnesium oxide obtained from seawater

Sample	Rinsing water	No. of rinses by decantation*	CaO	MgO	B_2O_3
			mass %		
MgO (80 % precipitation)	Alkalised + Distilled	3+2	1.66	97.80	0.0871
	Without rinsing	-	2.44	97.24	0.1923

*- After rinsing by decantation, the sample of magnesium hydroxide was rinsed five times with distilled water (pH=6.74) on filter paper.

Table 2: Chemical analysis (mass %) of TiO_2 p.a. (Merck)

	TiO_2 (99 %)
Water-soluble matter	0.3 %
Chloride (Cl)	0.01 %
Sulphate (SO4)	0.05 %
Heavy metals (such as Pb)	0.001 %
Iron (Fe)	0.005 %
Arsenic (As)	0.0002 %

3. RESULTS AND DISCUSSION

This study has examined the effect of the TiO_2 addition on properties of magnesium oxide obtained from seawater by substoichiometric precipitation with 80% of the stoichiometric quantity of dolomite lime as the precipitation agent. Magnesium oxide obtained by substoichiometric precipitation from seawater contains boron (III) oxide as impurity. During reaction settling of magnesium hydroxide, boron present in seawater (in the form of non-dissociated orthoborate acid H_3BO_3, and partly as the borate ion $H_2BO_3^-$) adsorbs on the magnesium hydroxide precipitate, and should be reduced as much as possible using the appropriate method of rinsing of the $Mg(OH)_2$ precipitate. B_2O_3 is an undesirable admixture in seawater-derived magnesium oxide. The properties of special purpose magnesium oxide, i.e. high strength oxide, are significantly affected by the quantity of boron in the product. High quality sintered magnesium oxide contains a very small quantity of B_2O_3. According to N. Heasman [2], the boron impurity limit should not be higher than 0.05 mass % B_2O_3 in refractory magnesium oxide.

In this study, the MgO sample (80% precipitation) was prepared by means of the combined method of rinsing (3+2) of the magnesium hydroxide precipitate using the process of decantation in such a way that the precipitate was rinsed three times with alkalised distilled water (pH = 12.50) then twice with distilled water (pH = 6.74), and then repeatedly rinsed on filter paper (5 times) with the same rinsing agent (fresh distilled water with pH of 6.74). When this method of rinsing is applied to the magnesium hydroxide precipitate, the B_2O_3 content is reduced by 55% as compared to B_2O_3 in samples prepared without rinsing the magnesium hydroxide precipitate (0.1923 mass %). When the magnesium hydroxide precipitate is rinsed with fresh distilled water after having been rinsed with alkalised distilled water (pH = 12.50), this contributes to a significant reduction of CaO in the final product, i.e. calcined magnesium oxide obtained from seawater. In this way the quantity of CaO is reduced by 32 % relative to the quantity of CaO in the sample obtained without rinsing of the precipitate (2.44 mass %). Table 1 shows the operating conditions of rinsing the magnesium hydroxide precipitate, and the results of analysis of chemical composition of magnesium oxide obtained by 80 % precipitation. The experimental data obtained indicate that the MgO (80 % precipitation) sample obtained contains 0.0871 mass % B_2O_3 and a somewhat increased quantity of CaO (1.66 mass %). It can also be observed that the MgO sample thus obtained (80 % precipitation) has approximately the same chemical composition as regards CaO and B_2O_3 as the magnesium oxide obtained by overstoichiometric 120 % precipitation (if the magnesium hydroxide precipitate is rinsed by decantation and filtering with fresh distilled water).

Isothermal and activated sintering of MgO samples (80% precipitation) took place without the TiO_2 addition, and with the addition of 5 and 8 mass % TiO_2 in order to determine the properties of these samples, particularly as regards the amount of B_2O_3 in samples after sintering.

Specifically, studies so far [8,11-13] have indicated that the addition of TiO_2, together with temperature and duration of isothermal sintering, has a significant effect on boron removal from the sample into the atmosphere during sintering of seawater-derived magnesium oxide.

Examinations [12,14,15] using the X-ray diffraction method and EDAX analyses indicate that in the sintering process the added TiO_2 reacts with CaO from the solid MgO-CaO solution and transforms into calcium titanate, $CaTiO_3$. A study [16] using the X-ray diffraction method has shown that in the sintering process B_2O_3 reacts with CaO to form $Ca_2B_2O_5$, i.e. dicalcium borate content has been proven in sintered samples of seawater-derived magnesium oxide. Therefore, there are two reactions leading to reduction of the boron (B_2O_3) content in the sintering process. These are: $2CaO + B_2O_3 = Ca_2B_2O_5$ and $CaO + TiO_2 = CaTiO_3$.

Tables 3 and 4 show the results obtained for density, porosity and B_2O_3 content in sintered magnesium oxide samples at the indicated operating conditions. Experimentally determined values for density (Table 3) of sintered samples indicate that the addition of TiO_2 leads to a significant increase of density of the samples examined, i.e. the densities increase with the increase of TiO_2 addition and amount up to 98.80 % of the theoretical density (ρ_t = 3.576 g cm^{-3}).
During isothermal sintering at 1700 °C/ 1 hour, the samples without the TiO_2 addition attain ≈ 97 % of the theoretical density. Low open porosity has been observed in samples examined, i.e. open porosity, P_p, amounts to 0.39 % for samples without the TiO_2 addition, 0.24 for samples with the addition of 5 % TiO_2, and 0.20 % for samples with the addition of 8 % TiO_2. Values for the total, P_u, and closed porosity, P_z, are almost identical and are much lower for samples containing the addition of TiO_2. The comparison of values attained shows that the total and closed porosity of samples containing 5 % TiO_2 is less by approx. 47 - 48 %, and those containing 8 % TiO_2 by 63 - 65 % than of those sintered without the addition.

Table 3: Density (ρ), apparent (P_a), total (P_t) and closed (P_c) porosity for sintered magnesium oxide samples (80 % precipitation) with 0.5 and 1 mass % TiO_2, and no sintering aid,
t = 1700 °C, τ = 1h, p = 625 MPa

No. of sample	Rinsing water	No. of rinses by decantation*	TiO_2 addition	ρ	P_a	P_t	P_c
			mass %	g cm^{-3}	%		
1	Alkalised + Distilled	3+2	no sint. aid	3.4594	0.39	3.37	2.98
2			5	3.5138	0.24	1.77	1.53
3			8	3.5330	0.20	1.22	1.02

* - After rinsing by decantation the sample of magnesium hydroxide was rinsed five times with distilled water (pH = 6.74) on filter paper.

Low values for open porosity indicate that samples have somewhat thickened before the maximum sintering temperature was achieved, i.e. 1700 °C. The effect of the TiO_2 addition can be explained by Ti^{4+} cations entering the MgO lattice, forming defective structures (cation cavities), which increases the diffusion rate and the density of samples sintered. Mobility of the elements of the crystal lattice also increases with the increase in temperature. At higher temperatures the concentration of the addition ions becomes equal throughout the grain mass, and it may be assumed that the mass transfer in that case is governed by the diffusion of the O^{2-} ion through the MgO lattice as the slower diffusion species [17].
Table 4 shows the results of determination of the B_2O_3 content in sintered magnesium oxide samples. The comparison of results before and after the sintering process indicates that the B_2O_3 content in magnesium oxide is reduced during the process. This is due to the fact that already at 1000 °C, the boron present evaporates as B_2O_3 from the sample into the atmosphere [18]. In the sintered sample of MgO (80 % precipitation) the amount of B_2O_3 is 0.0321 mass %; in the samples of MgO (80 % precipitation) with the addition of 5 mass % TiO_2 the B_2O_3 amount is 0.0058 mass %, and with 8 mass % TiO_2 the B_2O_3 amount is 0.0041 mass %.
The comparison of results for MgO samples (80 % precipitation) after isothermal and activated sintering at 1700 °C / 1h shows that the addition of TiO_2 significantly affects the B_2O_3 content in the final product. The B_2O_3 content in the samples examined was reduced by 82 – 87 % relative to the B_2O_3 content in the sample without the TiO_2 addition. MgO samples

(80 % precipitation) can be characterised as refractory materials with a very low B_2O_3 content.

Table 4: Effect of TiO_2 on the B_2O_3 content in the sintered magnesium oxide samples (80 % precipitation) at t = 1700 ^oC, τ = 1h, p = 625 MPa

No. of sample	Rinsing water	No. of rinses by decantation*	TiO_2 addition	B_2O_3
			mass %	
1	Alkalised + Distilled	3+2	no sint. aid	0.0321
2			5	0.0058
3			8	0.0041

* - After rinsing by decantation the sample of magnesium hydroxide was rinsed five times with distilled water (pH = 6.74) on filter paper.

The experimental results were analysed to calculate the fraction of B_2O_3 evaporated in the sintering process (J_1) from the experimental data on the fraction of B_2O_3 in the sintered sample and the fraction of B_2O_3 in calcined magnesium oxide, as well as the fraction of CaO that has reacted with TiO_2 (J_2). Based on the experimental data for boron determination by potentiometrical titration in magnesium oxide samples sintered at 1700 ^oC / 1 h, the reaction yield degree, ξ, was calculated for the dicalcium borate formation reaction in all the samples examined, relative to the quantity of boron present in the calcined magnesium oxide. Table 5 shows the results obtained.

Table 5: Dependence of J_1, J_2 and ξ on different quantities of sintering aid in the sintered magnesium oxide samples (80 % precipitation) at t = 1700 ^oC, τ = 3h, p = 625 MPa

No. of samples	Rinsing water	No. of rinses by decantation*	TiO_2 addition	J_1	J_2	ξ
			mass %	%		
2	Alkalised + Distilled	3+2	5	93.22	45.82	6.66
3			8	95.17	28.68	4.70

* - After rinsing by decantation the sample of magnesium hydroxide was rinsed five times with distilled water (pH = 6.74) on filter paper.

The results obtained, shown in Table 5, indicate that the addition of TiO_2 in the amount of 5 mass % is sufficient to bind the CaO present and thereby lead to significant evaporation of B_2O_3 in the process of activated sintering of seawater-derived magnesium oxide.

4. CONCLUSIONS

- In activated sintering of magnesium oxide (80 % precipitation) from seawater at 1700 ^{o}C for 1 hour and with the addition of 5 and 8 mass % TiO_2, the B_2O_3 content in the samples examined was reduced by 82 – 87 % relative to the B_2O_3 content in the sample without the addition of TiO_2. MgO samples (80 % precipitation) can be characterised as refractory materials with a very low B_2O_3 content.

- The addition of TiO_2 in the amount of 5 mass % suffices to bind the CaO present and thereby lead to significant evaporation of B_2O_3 in the process of activated sintering of seawater- derived magnesium oxide.

- Samples became significantly denser during sintering, i.e. all the samples examined had a very low open porosity.

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UTJECAJ TEMPERATURE SINTERIRANJA NA TVRDOĆU I MIKROSTRUKTURU ALUMINIJ OKSIDNE KERAMIKE

INFLUENCE OF SINTERING TEMPERATURE ON HARDNESS AND MICROSTRUCTURE OF ALUMINA CERAMICS

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Izvorni znanstveni rad / Original scientific paper

Sažetak: U radu je ispitan utjecaj temperature sinteriranja na tvrdoću i mikrostrukturu aluminij oksidne keramike oblikovane hladnim izostatičkim prešanjem. Uzorci su sinterirani u električnoj peći na sljedećim temperaturama: 1550, 1600 i 1650 °C. Nakon sinteriranja i poliranja uzoraka Al_2O_3 keramike, određena im je poroznost i izmjerena tvrdoća metodom po Vickersu. Tvrdoća je izmjerena pri sljedećim opterećenjima: 1,962 N; 4,905 N i 9,807 N.
Nakon toplinskog nagrizanja, uzorcima je određena veličina kristalnog zrna metodom kruga i crte. Analiza mikrostrukture (poroznost i veličina kristalnog zrna) provedena je optičkim mikroskopom.
Nešto veće vrijednosti tvrdoće dobivene su za uzorak Al_2O_3 keramike koji je sinteriran na temperaturi od 1550 °C u odnosu na uzorke koji su sinterirani na temperaturama od 1600 i 1650 °C.
Rezultati mjerenja pokazali su da se mikrostrukturni parametri (poroznost i veličina kristalnog zrna) vrlo malo mijenjaju s promjenom temperature sinteriranja od 1550, 1600 i 1650 °C.
Ključne riječi: aluminij oksidna keramika, temperatura sinteriranja, tvrdoća, mikrostruktura.

Abstract: In this paper the influence of sintering temperature on hardness and microstructure of cold isostatic pressed alumina ceramics is investigated. All samples were sintered in an electric kiln at the following temperatures: 1550, 1600 and 1650 °C. After sintering, porosity and Vickers hardness were determined on polished surface of alumina ceramics samples. Hardness was measured at different loads: 1.962 N, 4.905 N and 9.807 N. After thermal etching grain size was determined by means of lineal-intercept and circular-intercept methods. Microstructure analysis (porosity and grain size) was performed by means of optical microscopy (OM).
It was found that the hardness values are slightly higher for the sample that was sintered at the temperature of 1550 °C in comparison to samples sintered at the temperature of 1600 and 1650 °C.
Obtained results of measured microstructure parameters indicate that the changes of porosity and grain size are negligible with the variation of sintering temperature.
Key words: alumina ceramics, sintering temperature, hardness, microstructure.

1. Uvod

Keramički su materijali anorganski materijali sastavljeni od metalnih i nemetalnih elemenata koji su povezani ionskim i/ili kovalentnim vezama. Najvažniji materijal zbog svoje izuzetno široke primjene iz grupe oksidne keramike je aluminij oksidna (Al_2O_3) keramika [1,2].

Specifična svojstva keramičkih materijala omogućuju njihovu široku primjenu. U izuzetno dobra svojstva ubrajaju se visoka tvrdoća, visoka tlačna i savojna čvrstoća, visoki modul elastičnosti, niska toplinska i električna vodljivost, visoka otpornost na trošenje, mala gustoća, niska toplinska rastezljivost i kemijska postojanost [1,2].

Mikrostruktura svih tehničkih materijala, pa tako i tehničke keramike, utječe na cijeli niz svojstava, među kojima su mehanička, tribološka, korozijska, toplinska, električka i dr. Znanstvena istraživanja često pokušavaju staviti u odnos svojstva i ponašanje materijala s karakteristikama mikrostrukture. Metode i uvjeti proizvodnje općenito se odražavaju na mikrostrukturu [1-3].

Jedno od najčešće određivanih mehaničkih svojstava tehničke keramike je određivanje tvrdoće. Istraživanja su pokazala da primijenjeno opterećenje utječe na tvrdoću kod metanih materijala (polikristali), anorganskog stakla, keramičkih materijala (monokristali i polikristali) i kod polimernih materijala [4-8].

U radu će se ispitati utjecaj temperature sinteriranja na tvrdoću i mikrostrukturne parametre (poroznost i veličinu kristalnog zrna) aluminij oksidne keramike oblikovane hladnim izostatičkim prešanjem.

2. Eksperimentalni dio

Za analizu mikrostrukture korišten je uzorak aluminij oksidne keramike oblikovane hladnim izostatičkim prešanjem (CIP- Al_2O_3), čistoće 99,8 %. Ispitivana Al_2O_3 keramika sadrži MgO kao pomoćno sredstvo za sinteriranje i uobičajene nečistoće SiO_2, CaO, Na_2O i Fe_2O_3. Priprema praha aluminij oksida (Al_2O_3) i oblikovanje uzorka obavljeno je u tvrtki Applied Ceramics, Inc., Fremont, Kalifornija, SAD.

Sirovci su sinterirani na Fakultetu kemijskog inženjerstva i tehnologije, Zavod za anorgansku kemijsku tehnologiju i nemetale, Sveučilište u Zagrebu. Temperature sinteriranja su:

- Uzorak A -1550 ºC (režim grijanja: od 20 do 700 °C, brzina grijanja 2 °C/min, izotermno na 700 °C u trajanju od 2 sata, od 700 °C do 1550 °C, brzina grijanja 5 °C/min).
- Uzorak B-1600 ºC (režim grijanja: od 20 do 700 °C, brzina grijanja 2 °C/min, izotermno na 700 °C u trajanju od 2 sata, od 700 °C do 1600 °C, brzina grijanja 5 °C/min).
- Uzorak C-1650 ºC (režim grijanja: od 20 do 700 °C, brzina grijanja 2 °C/min, izotermno na 700 °C u trajanju od 2 sata, od 700 °C do 1650 °C, brzina grijanja 5 °C/min).

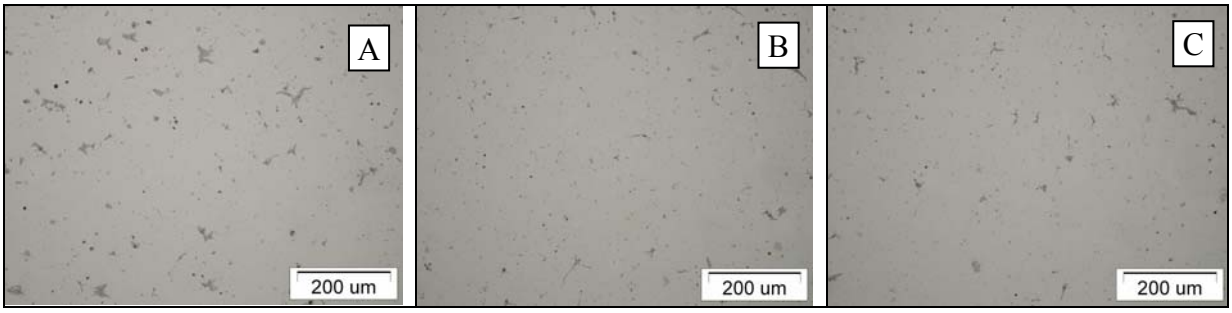
Nakon sinteriranja i rezanja uzorka Al_2O_3 keramike slijedi zalijevanje te brušenje i poliranje uzorka[3].

Na poliranim uzorcima određen je udio pora metodom crte. Za svaki su uzorak optičkim mikroskopom snimljene po tri fotografije ispolirane površine. Korišten je mikroskop Olympus GX 51. Nakon ispisa fotografija na papir metodom crte određen je udio pora.

Na istim je uzorcima određena i tvrdoća metodom po Vickersu (Instron, Wilskon-Wolpert Tukon 2100B, u Zavodu za materijale Fakulteta strojarstva i brodogradnje, Sveučilište u Zagrebu) pri sljedećim opterećenjima: 1,962 N, 4,905 N i 9,807 N. U svrhu određivanja veličine kristalnog zrna aluminij oksidne keramike, polirani uzorci toplinski su nagriženi na temperaturi od 1500 °C, u trajanju od 20 min, uz postupno grijanje i hlađenje. Veličina kristalnog zrna određena je metodama kruga i crte.

3. Rezultati i diskusija

Na poliranom uzorku A (temperatura sinteriranja 1550 °C), B (temperatura sinteriranja 1600 °C) i C (temperatura sinteriranja 1650 °C) određen je udio pora metodom crte. U tu su svrhu za svaki uzorak optičkim mikroskopom snimljene po tri fotografije (slika 1A, 1B i 1C) polirane površine i metodom crte određen je udio pora.



Slika 1. Polirana površine uzorka aluminij oksidne keramike (A) uzorak A (temperatura sinteriranja 1550 °C), (B) uzorak B (temperatura sinteriranja 1600 °C) i (C) uzorak C (temperatura sinteriranja 1650 °C).

Izmjerena vrijednost udjela poroznosti za uzorak A je 2,76 %, uzorak B 1,94 % i uzorak C je 2,72 %.

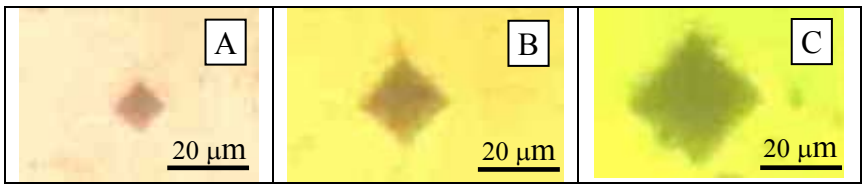
Utiskivanjem penetratora s opterećenjima od 1,961 N; 4,903 N i 9,807 N utisnute su u materijalu baze piramide (slika 2). Duljine njihovih dijagonala (d_1, d_2) izmjerene su optičkim mikroskopom.

Vrijednosti tvrdoće po Vickersu izračunate su pomoću sljedeće jednadžbe:

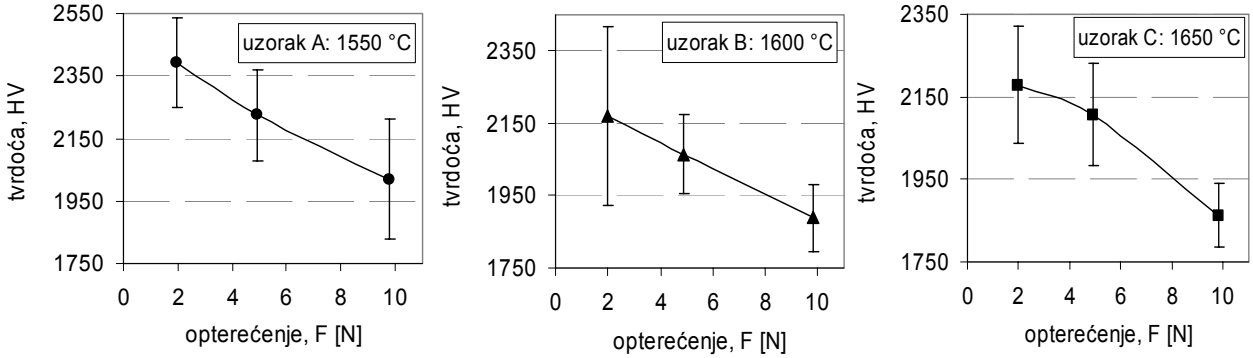
$$HV = \frac{0{,}1891 \cdot F}{d^2} \tag{1}$$

gdje je:

HV – tvrdoća po Vickersu,
F – primijenjeno opterećenje [N],
d – aritmetička sredina dviju duljina dijagonala [mm].



Slika 2. Otisak dijamantne piramide nakon mjerenja tvrdoće (A) HV0,2; (B) HV0,5 i (C) HV1 za uzorak koji je sinteriran na temperaturi od 1550 °C .



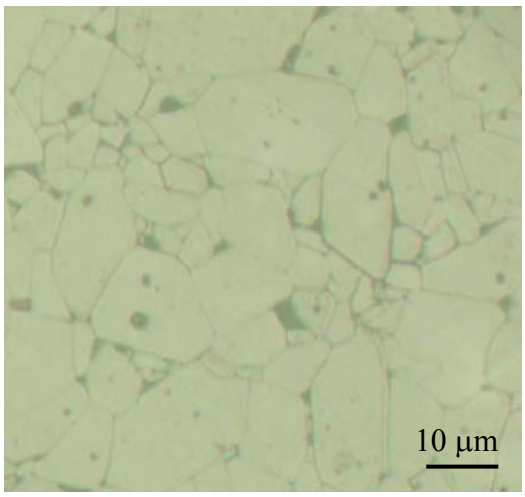
Slika 3. Vrijednosti tvrdoće mjerene Vickersovom metodom u ovisnosti o opterećenju za sljedeće uzorke Al_2O_3 keramike: uzorak A (temperatura sinteriranja 1550 °C), uzorak B (temperatura sinteriranja 1600 °C) i uzorak C (temperatura sinteriranja 1650 °C).

Za sva tri uzorka aluminij oksidne keramike tvrdoća se smanjuje s povećanjem opterećenja (slika 3). Ta se pojava naziva utjecaj opterećenja na tvrdoću. Postoji nekoliko objašnjenja o porijeklu utjecaja opterećenja na tvrdoću. Najuobičajenije objašnjenje odnosi se na pogreške koje proizlaze iz omjera elastične i plastične deformacije tijekom formiranja otiska. Ostala tumačenja pogreške vezana su uz:

- kočenje gibanja dislokacija, granice zrna, kao i elastičnih pomaka nakon rasterećenja;
- otvrdnjavanje tijekom utiskivanja;
- optičku rezoluciju leća objektiva koje se koriste;
- pojavu zaostalih napetosti na površini uzorka nastalih uslijed brušenja i poliranja površine prije mjerenja tvrdoće itd. [9, 10]

Usporedbom vrijednosti tvrdoća za ista opterećenja može se uočiti da uzorak A pokazuje nešto veće vrijednosti tvrdoće u odnosu na uzorak B i C. Vrijednosti tvrdoća za uzorak B i C približno su iste. Dakle, nešto veće vrijednosti tvrdoća postignute su pri najnižoj temperaturi sinteriranja (1550 °C).

U svrhu određivanja veličine kristalnog zrna aluminij oksidne keramike polirani uzorci A, B i C toplinski su nagriženi na temperaturi od 1500 °C, u trajanju od 20 min, uz postupno grijanje i hlađenje. Mikrostruktura uzorka Al_2O_3 keramike promatrana je i snimljena optičkim mikroskopom (slika 4). Veličina kristalnog zrna određena je metodama kruga i crte. Rezultati ispitivanja prikazani su u tablici 1.



Slika 4. Mikrostruktura aluminij oksidne keramike (uzorak A) promatrana optičkim mikroskopom nakon toplinskog nagrizanja.

Tablica 1. Rezultati mjerenja veličine kristalnog zrna Al_2O_3 keramike za različite temperature sinteriranja.

Način određivanja veličine zrna	Veličine kristalnog zrna, μm		
	Uzorak A	Uzorak B	Uzorak C
Metoda crte	6,18	6,11	6,29
Metoda kruga	7,59	7,54	7,70

Dobiveni rezultati pokazuju da se veličina kristalnog zrna aluminij oksidne keramike ne mijenja značajno s promjenom temperature sinteriranja. Nešto veće vrijednosti postignute su metodom kruga.

4. Zaključci

- Uzorci aluminij oksidne keramike sinterirani su u električnoj peći na tri temperature: 1550, 1600 i 1650 °C.
- Udio poroznosti poliranih uzoraka također se neznatno mijenja (ispod 3 %) s promjenom temperature sinteriranja.
- Na ispoliranim površinama sinteriranih uzoraka izmjerena je tvrdoća metodom po Vickersu pri sljedećim opterećenjima: 1,962 N, 4,905 N i 9,807 N.
- Izmjerene vrijednosti tvrdoća pokazuju da se tvrdoća za sva tri uzorka smanjuje s povećanjem opterećenja. Nešto veće vrijednosti tvrdoća postignute su za uzorak koji je sinteriran pri temperaturi od 1550 °C u odnosu na uzorke koji su sinterirani na temperaturi od 1600 i 1650 °C.
- Veličina kristalnog zrna aluminij oksidne keramike metodom crte je za sve uzorke oko 6,2 μm, a metodom kruga oko 7,5 μm. Dobiveni rezultati pokazuju da se veličina kristalnog zrna aluminij oksidne keramike ne mijenja značajno s promjenom temperature sinteriranja.

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COMMINUTION KINETICS OF PREMULLITE POWDER

KINETIKA MLJEVENJA PREMULITNOG PRAŠKA

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Izvorni znanstveni rad / Original scientific paper

Abstract: Pre-mullite powder has been synthesized by sol-gel process. Differential thermal analysis (DTA) of the powder yielded scan with two exotherms: stronger at ~980°C and weaker at ~1200°C. Using X-ray diffraction (XRD) analysis it has been determined that first exothermic peak is a consequence of Al-Si spinel crystallization, while second peak occurs due to mullite crystallization. The powder was wet milled in planetary ball mill within various time intervals. The particle size distribution of ground samples has been determined using particle size analyzer (PSA). Comminution kinetics of calcined pre-mullite gel is modeled using a classical batch grinding equation based on selection and breakage functions. Analysis of experimental data resulted with model suitable for prediction of particle size distribution of calcined amorphous gel comminuted in planetary ball mill if the duration of grinding is no longer than 128 min.
Keywords: pre-mullite gel, planetary mill, particle size distribution, grinding kinetics.

Sažetak: Sol-gel procesom pripravljen je premulitni prašak. Diferencijalnom termičkom analizom (DTA) praška dobiven je derivatogram karakteriziran s dva egzotermna efekta: jači, pri ~980°C, te slabiji pri ~1200°C. Rendgenskom difrakcijskom (XRD) analizom utvrđeno je da je prvi egzotermni efekt posljedica kristalizacije Al-Si spinela, dok do drugog egzotermnog efekta dolazi zbog kristalizacije mulita. Dobiveni prašak usitnjen je u planetarnom ZrO_2 mlinu uz različito trajanje usitnjavanja. Raspodjela veličina čestica mljevenih uzoraka određena je pomoću analizatora veličine čestica. Kinetika usitnjavanja kalciniranog premulitnog gela opisana je klasičnom jednadžbom diskontinuiranog usitnjavanja koja se temelji na funkcijama selekcije i loma. Analizom eksperimentalnih podataka dobiven je model prikladan za predviđanje raspodjele veličine čestica kalciniranog amorfnog gela nakon mljevenja u planetarnom kugličnom mlinu, primjenjiv za period mljevenja do 128 min.
Ključne riječi: premulitni gel, planetarni mlin, raspodjela veličine čestica, kinetika usitnjavanja.

Introduction

Mullite is a solid solution with a general formula $Al_{4+2x}Si_{2-2x}O_{10-x}$ where x represents the number of oxygen vacancies due to composition-induced substitution of tetrahedral Si^{4+} by Al^{3+}. [1] The high strength at high temperature, low thermal expansion, excellent creep resistance and good chemical and oxidation resistance make mullite an attractive ceramic material for advanced applications [2], for which ultra fine mullite precursor powders are of utmost importance [3]. In order to obtain high-purity mullite precursor powders, sol-gel process is employed [4]. Extensive work has been done related to the processing of sol-gel derived pre-mullite materials, but a complete understanding of all process parameters has not yet been fully achieved.

Traditional approach in comminution modeling is based on population balance models using first order kinetics which requires the determination of breakage and selection functions that are calculated from the batch grinding experiments using particle size range divided into a geometric sequence. The lack of methods for preparing narrow size intervals is often a problem when using population balance method of discretized sizes. Therefore, analytical solution that involves special form of the selection and the breakage functions is useful in kinetic analysis.

The investigation on grinding kinetics of amorphous powders is very scarce and, to the best of our knowledge, grinding kinetics of pre-mullite powders has not been investigated at all. Therefore, this work has been undertaken with aim to provide information about grinding kinetics and particle breakage mechanism of diphasic pre-mullite gel.

Experimental

Aluminum nitrate and tetraethylorthosilicate (TEOS) were used to prepare diphasic mullite gel with alumina/silica molar ratio close to 3/2. The $Al(NO_3)_3 \times 9H_2O$ (Kemika) was dissolved in H_2O and TEOS, (Merck) was mixed with ethanol and added dropwise to the nitrate solution. The mixture was stirred under reflux conditions at 60 ^oC for 8 days. The gel was dried at 110°C and calcined at 700 ^oC for 4 h to decompose the organics and remove the volatiles. The calcined gel was crushed and ground in a corundum mortar, seized to particles smaller than 63 μm and stored in a desiccator.

Calcined gel samples were grinded in planetary ball mill Fritsch GmbH, Pulverisette 6 using 250 mL zirconia bowl, and 30 ZrO_2 balls of 10 mm diameter with total weight of ~70 g. 10 g of premullite powder samples, mixed with 10 mL of isppropanol were grinded for 16, 32, 64, 128, 256 and 512 min at revolution speed of 200 rpm. After grinding, the samples were dried at 110°C and calcined at 700°C for 4h.

The particle size distribution of ground samples has been determined using particle size analyzer Coulter Counter ZM, (Coulter Electronics Ltd., Luton, UK). Samples were dispersed in 1 wt.% NaCl aqueous solution previously filtered to eliminate background count.

The powder samples morphology was investigated with Scanning Electron Microscopy (SEM) TESCAN, VEGA TSS 136LS. Prior to scan, powders were applied to the adhesive graphite tape.

X-ray diffraction analysis (XRD) has been performed on computer controlled difractometer Philips 1830 with CuKα radiation. Data were collected between 5 and 70° 2θ in a step scan mode with steps of 0.02^o and counting time of 2s.

Grinding kinetics is commonly described using population balances. Partial integro-differential equation for size-continuous time-continuous model, assuming well mixed batch process can be written in form [5-8]:

$$\frac{\partial^2 D(x,t)}{\partial t \partial x} = -S(x)\frac{\partial D(x,t)}{\partial x} + \int_{y=x}^{x_{\max}} S(y)\frac{\partial B(x,y)}{\partial x}\cdot\frac{\partial D(y,t)}{\partial y}dy \qquad (1)$$

where $D(x,t)$ is the mass fraction of particles less than size x, t is the time of batch grinding, x is the size of particle to be broken and $x_{\max}$ is the maximum particle size present. $S(x)$ is the specific rate of breakage (fracture) representing the probability of particle of size x to be selected for breakage and $B(x,y)$ is the cumulative primary (fracture) breakage distribution equal to mass fraction of fragment sizes less than x produced from particles of size y. Assuming that the product of selection and breakage function is of the following form:

$$S(x)\cdot B(y,x) = Kx^n \cdot \left(\frac{y}{x}\right)^m \qquad (2)$$

Nakajima and Tanaka [9] obtained analytical solution of the batch grinding equation (Eq. 1) in cumulative oversize form:

$$R(x,t) \approx R(x,0)\cdot\exp\left[-\left(\mu K x^n t\right)^\nu\right] \quad \text{for } m \neq n \qquad (3)$$

$$R(x,t) = R(x,0)\cdot\exp\left(-Kx^n t\right) \quad \text{for } m = n \qquad (4)$$

where m and n are constants, K is the grinding rate constant, and μ and ν are determined by the m/n ratio.

Results and discussion

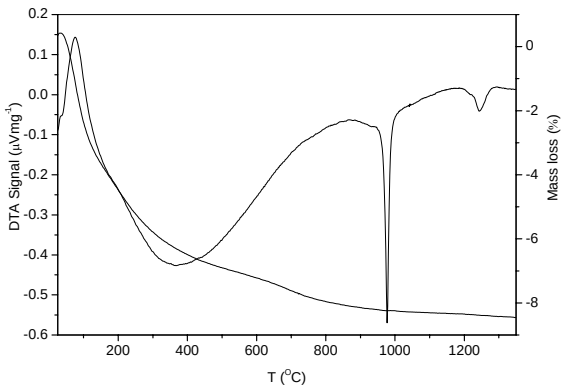

Fig. 1. DTA curves of premullite powder samples grinded for various times. Curves are shifted for visualization purpose.

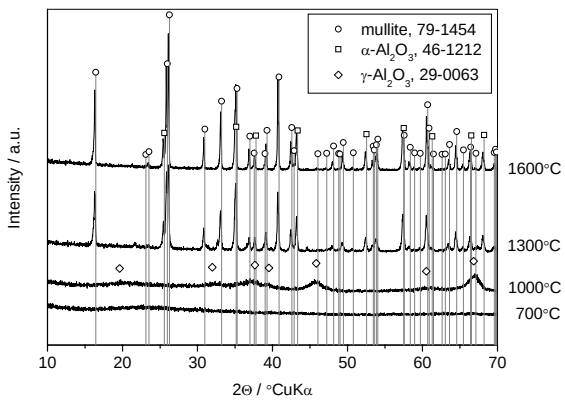

Fig. 2. Powder XRD patterns of the feed sample heat treated to a various temperatures.

The crystallization path of calcined premullite powders was examined by DTA. The DTA curve of as-received sample prior to calcinations (Fig. 1) is characterized with the peaks in the low temperature range, caused by dehydration, dehydroxylation and decomposition of nitrates and alkoxides and the combustion of organics [10], which correspond to a great mass loss in this temperature area. The DSC curve is further characterized with exotherms at 978°C and 1250°C. The diphasic gel contains polycondensed and polymerized particles without sufficient homogeneity for direct mullite formation below 1000°C. Instead, primary cristallization Al-Si spinel occurs followed by mullite crystallization at ~1200°C. In DTA scans of samples calcinated at 700°C for 2 h, milled for various time and re-calcinated the low-temperature region, endothermal peaks, except the peak due to a dehydration, are missing and high-temperature exothermal peaks are more pronounced due to an increased concentration.

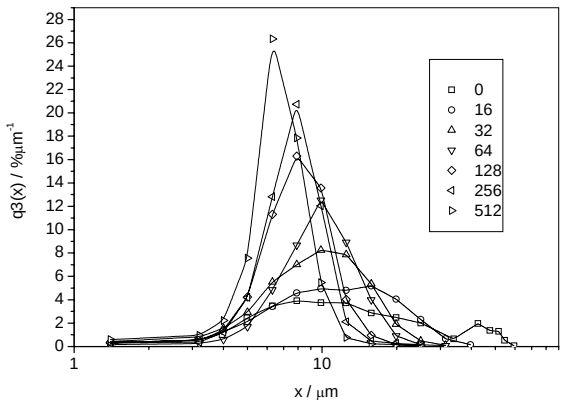

Figure 3a. Dynamic evolution of product particle size distribution.

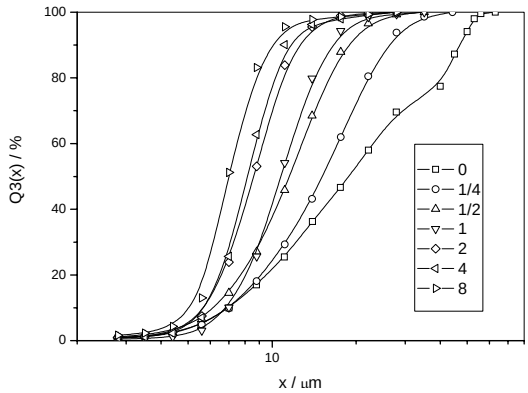

Figure 3b. Cumulative product particle size distribution.

In order to assign the DSC exothermic events and to establish the crystallization path of the gel, the samples were thermally treated for 4 hours at various temperatures and then subjected to XRD analysis. XRD patterns of non-milled sample specimens are shown in Fig. 2, as an example. Analysis reveal that the gel is amorphous up to the first exotherm on DSC curve at 977°C, after this point the XRD pattern displays typically broad reflections attributable to weakly crystallized aluminosilicate spinel. As evidenced by XRD, spinel phase transforms into orthorhombic mullite at temperatures below 1300 °C. The gel thermal evolution corresponds to type III precursors according to Schneider's classification formation path [4]. At 1300°C and 1600°C an α-alumina lines could be seen. That is the consequence of initial stoichiometry positioned in mullite+alumina phase field of Al_2O_3-SiO_2 phase diagram.

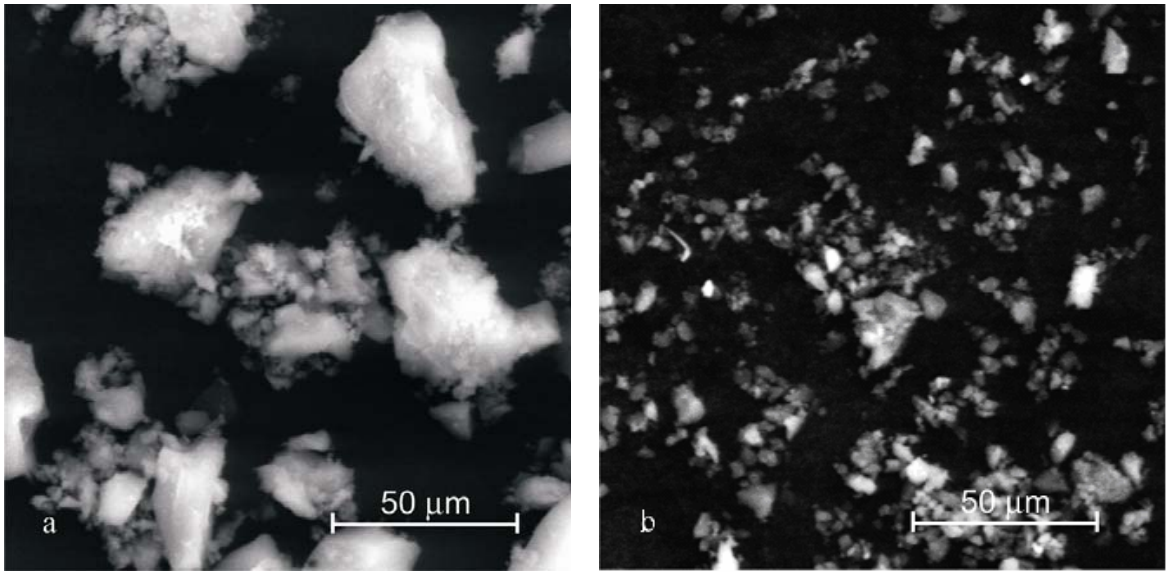

Figure 4. SEM micrographs of feed sample (a) and sample grinded for 512 min (b).

Fig. 3 shows product particle size distributions for the pre-mullite calcined gel obtained at various grinding times in the planetary ball mill. As can be seen, size distribution shifts progressively to finer sizes with the increase of grinding interval. The shift is slightly better pronounced at low comminution duration. The shape of the size distribution curve of feed sample indicates bimodal size distribution. The size distribution of samples grinded for 15 and 30 min is also bimodal but less expressed than for feed sample. With further increase

of grinding time the curves become monomodal reflecting samples monodisperse distribution.

For a detailed view of the size and morphology of the particles, SEM investigation of the powders was carried out. Fig. 4 shows the SEM micrographs of the feed sample (Fig. 4a) and powder milled for 512 min (Fig. 4c). Feed sample, as well as grinded sample, is characterized with particles of irregular shape. As far as it can be estimated, the particle size obtained by the Coulter Counter correlates with calcined powders particle sizes.

Analysis of grinding data was performed according to Eq. (3), previously converted to linear form by taking the logarithm of both sides [5-8]:

$$\ln\left[-\ln\left(\frac{R(x,t)}{R(x,0)}\right)\right] = \nu\ln(\mu Kt) + n\,\nu\ln(x) \tag{5}$$

where

$$\nu\ln(\mu Kt) = \nu\ln(\mu K) + \nu\ln(t) \tag{6}$$

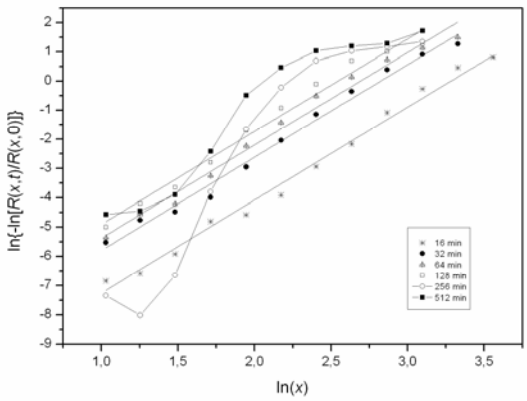

Figure 5a. Normalized cumulative particle size distribution

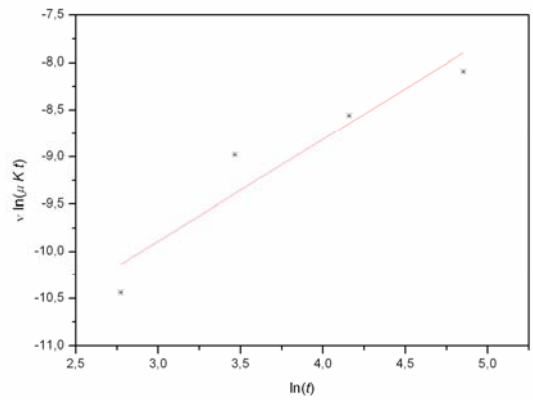

Figure 5b. Variation of intercept $\nu\ln(\mu Kt)$ with grinding time.

As can be seen in Fig. 5a linear dependence of normalized cumulative oversize functions, ln{-ln[$R(x,t)/R(x,0)$]}, on particle size in logarithmic scale, ln$x$, exist only for data corresponding to grinding interval of 16, 32, 64 and 128 min. For increased duration of grinding, the data could not be fitted to Eq. 5. Therefore, the experimental data for extended grinding periods were not used in kinetic modeling.

Regression analysis of data corresponding to grinding interval of 16, 32, 64 and 128 min, using least-square method (Fig. 5a), resulted with constant value of $n\nu$ (fixed to 3.18) and intercept $\nu\ln(\mu Kt)$ varying with time. The intersects of straight lines in Fig. 5a on the ordinate for grinding intervals of 16, 32, 64 and 128 min are plotted against the grinding time in Fig. 5b. Parameter ν was then obtained as a slope from linear regression analysis of Eq. (6). Furthermore, model parameter μ was obtained from Nakajima and Tanaka chart [9] using known values of ν and m/n ratio. Finally, grinding rate constant was calculated from intercept value of Eq. (6) and known values of parameters μ and ν. Grinding kinetics analysis of experimental data resulted with model suitable for prediction of particle size distribution during grinding of calcined pre-mullite gel in planetary ball mill:

$$R(x,t) = R(x,0)\cdot\exp\left(-2\cdot10^{-6}x^{3.18}t^{1.076}\right) \tag{7}$$

where x is the particle size in μm, and t is the grinding time in minutes.

Conclusions

The kinetics of comminution of calcined pre-mullite gel in planetary ball mill was investigated. The grinding kinetics approach was successfully applied to the analysis of product size distribution.

A classical batch grinding equation was used for the modeling of comminution process. The analytical solution equation, as well as parameters of grinding kinetics was obtained through Nakajima and Tanaka approach.

Grinding kinetics analysis of experimental data resulted with model suitable for prediction of particle size distribution for grinding of calcined amorphous gel in planetary ball mill if the duration of grinding is no longer than 128 min.

Acknowledgement

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TEHNOLOŠKA ISPITIVANJA INOX DIMNJAKA

TEHNOLOGICAL TESTING OF INOX CHIMNEY

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Stručni članak / Professional paper

Sažetak: Montažni inox dimnjaci ispituju se tehnološki, odnosno na način da se kompletan dimnjak kakav će biti u upotrebi ispita u realnim uvjetima djelovanja tribokorozijskih i mehaničkih opterećenja.
U tu svrhu potrebno je definirati područje nominalne veličine dimnjaka, temperaturnog razreda, razred tlaka, razrede otpornosti na kondenzat i koroziju, razred otpornosti gorenja čađe, vlačnu i tlačnu čvrstoću, otpornost na opterećenje vjetra, te otpornost na kišu.

Ključne riječi: Montažni dimnjak, inox, sanacija dimnjaka, mehanička opterećenja, korozija.

Abstract: Assembling inox chimneys have been tested technologically in the way that complete chimney, as will be used in practice, has been tested under real conditions of tribocorosional and mechanical loadings effects.
For this purpose it is necessary to define the range of nominal chimney size, temperature class, pressure class, condensate resistance class, corrosion resistance class, soot fire resistance class, tensile and compressive strength, resistance to wind load and resistance to rain water.

Key words: Assembling chimney, inox, chimney recovery, mechanical loadings, corrosion

1. Uvod

Za ispravno funkcioniranje inox dimnjaka najvažniju ulogu ima pravilan izbor materijala. Nakon toga montažni inox dimnjaci ispituju se tehnološki, odnosno na način da se kompletan dimnjak kakav će biti u upotrebi ispita u realnim uvjetima djelovanja tribokorozijskih i mehaničkih opterećenja.

U tu svrhu potrebno je definirati područje nominalne veličine dimnjaka, temperaturnog razreda, razred tlaka, razrede otpornosti na kondenzat i koroziju, razred otpornosti gorenja čađe, vlačnu i tlačnu čvrstoću, otpornost na opterećenje vjetra, te otpornost na kišu.

Način na koji se montažni dimnjaci ispituju na određena opterećenja dan je u slijedećim primjerima.

2. Opis sistema dimnjaka

Tablica 1. Radne karakteristike dimnjaka

Karakteristika	**Radne karakteristike prema deklaraciji proizvođača**
nominalna veličina	Ø 80- Ø 705
temperaturni razred	T450 (temperatura plinova u dimu ≤ 450°C)
dodirne površine	zaštita je potrebna gdje je moguć slučajan kontakt s čovjekom
razred tlaka	N1 (podtlak, brzina propuštanja ≤ 2l/sm^2)
razred otpornosti na kondenzat	D (suhi radni uvjeti) W (vlažni radni uvjeti)
razred otpornosti na koroziju	V2 V3
razred otpornosti na gorenje čađe	G (otporan na gorenje čađe)
minimalna udaljenost da bi se osigurala zaštita od požara	udaljenost ≥ 75 mm udaljenost ≥ 50 mm
tlačna čvrstoća (maksimalna visina i stabilnost ulaza dimnih plinova)	≤ 2,12 kN za Ø80 ≤ 2,25 kN za Ø300 ≤ 1 ,25 kN za Ø705
tlačna čvrstoća (maksimalna visina i stabilnost nosača)	radne karakteristike nisu definirane
vlačna čvrstoća	radne karakteristike nisu definirane
sigurnost horizontalnih instalacija	radne karakteristike nisu definirane
otpornost na opterećenje vjetra	maksimalna udaljenost između nosača: ≤ 4 m do Ø 405 / ≤ 3 m počevši od Ø 455 maksimalna duljina slobodnog kraja: ≤ 3 m do Ø 405 / ≤ 2 m počevši od Ø 455
otpornost na kišu	otporan na kišu
krajnja vremenska otpornost na kišu	radne karakteristike nisu definirane
krajnja vremenska otpornost na utjecaj vjetra	radne karakteristike nisu definirane
toplinska otpornost	≥ TR37
otpor strujanju	vrijednosti prema [1]

Norma po kojoj se definira sistem je [2].

3. Opis sistema dimnjaka i usporedba s ispitnim uzorcima

Tablica 2. Procjena deklaracije komponenata dimnjaka.

komponenta	karakteristika	deklaracija[1)]	procjena[2)]
unutarnja cijev dimnjaka	materijal	čelik AISI 316L	3)
	duljina	4)	1001 mm
	instalirana duljina	4)	961 mm
	debljina stijenke	≥ 0,5 mm	0,60 mm
	promjer (vanjski)	200 mm	200, 8 mm
	dubina spojnice	4)	57,5
	duljina kraja naglavka	4)	nema ograničenja
	promjer spojnice	202 mm	203,0 mm
	promjer kraja naglavka	4)	201,0 mm
	konstrukcija spoja	naglavak-i-spojnica, cilindričan	kao u deklaraciji
	brtve	bez	kao u deklaraciji
izolacijska ploča	materijal	mineralna vuna tipa: Superwool Blanket X 607	kao u deklaraciji
	debljina	25,0	26,0 (2x13,0)
	gustoća	128 kg/m^3	155 kg/m^3
vanjska cijev dimnjaka	materijal	čelik AISI 304 BA	3)
	debljina	≥ 0,5 mm	0,58 mm
	duljina	955 mm	954 mm
	instalirana duljina	4)	994 mm
	promjer (vanjski)	248 mm	251,5 mm
	dubina spojnice	50 mm	48,0 mm
	duljina kraja naglavka	40 mm	37,6 mm
	promjer spojnice	258 mm	257,5 mm
	promjer kraja naglavka	248mm	248,5 mm
	konstrukcija spojeva	naglavak-i-spojnica, cilindričan	kao u deklaraciji
	brtve / spojni elementi	bez / s	kao u deklaraciji
ravna cijev	instalirana duljina L [mm]	3)	1001
ulaz dimnih plinova	konstrukcija	T- komad s pričvršćenim ispustom	kao u deklaraciji
	otklon	90°	90°
ispitni element	konstrukcija	kružni otvor, izolirani kružni zatvarač	kao u deklaraciji
	veličina ispitnog otvora	Ø 200 mm	Ø 200 mm
	konstrukcija vrata	naglavak-i-spojnica, cilindričan	kao u deklaraciji
	brtve	bez	kao u deklaraciji
element za odvođenje kondenzata	konstrukcija	središnji ispust	kao u deklaraciji
	veličina	3)	3/4″ cijev
	nepropusnost		zatvorena cijev od strane laboratorija za ispitivanje

priključak	konstrukcija	vanjska stijenka konusno smanjena i zavarena za unutarnju cijev	kao u deklaraciji
nosač	konstrukcija	teleskopska osnovica (podupirač) sa spojnom pločicom	kao u deklaraciji

1) dano od strane naručitelja
2) provjereno na ispitnim uzorcima
3) nije provjereno
4) detaljni opisi cjevovoda, izolacije i spojeva nisu dostupni laboratoriju za ispitivanje

4. Mehanička čvrstoća (otpornost na opterećenje vjetra)

Uzorci:

- 11 ravnih cijevi (instalirana duljina=960 mm), 3 zidna nosača (ø 80, ø 405)
- 8 ravnih cijevi (instalirana duljina=960 mm), 3 zidna nosača (ø 455, ø 705)

Raspored pri ispitivanju:

- horizontalna instalacija dimnjaka sa zidnim nosačima na čeličnu konstrukciju, zidni nosači u sredini između spojeva
- udaljenost između zidnih nosača 4,00 m do ø 405 / 3,00 m od ø 455 m, duljina slobodnog kraja 3m do ø 405 / 2,00 m od ø 455 m
- 1 spoj iznad i 1 spoj ispod gornjeg (prvi) zidnog nosača je brtvljen spojnim elementima

Ispitivani uzorci:

- 45 (ø 80, ø 405), 33 (ø 455), 65 (ø 705) jednake mase, tolerancija ± 1 g
- duljina, tolerancija ± 1 mm
- masa, tolerancija ± 1,0 g

Slika 1. Ispitivanje otpornosti na opterećenje vjetra.

Uvjeti ispitivanja:

Procjena težina:

- početno opterećenje(=težina dimnjaka + spojni elementi) (ø 80) 0,466 kN
- početno opterećenje(=težina dimnjaka + spojni elementi) (ø 405) 1,903 kN
- početno opterećenje(=težina dimnjaka + spojni elementi) kN (ø 455) 1,71966
- početno opterećenje(=težina dimnjaka + spojni elementi) (ø 705) 2,555 kN

- ispitno opterećenje (projicirana površina*1,5 kN/m^2 - početno opterećenje) (ø 80) 1,346 kN
- ispitno opterećenje (projicirana površina*1,5 kN/m^2 - početno opterećenje) (ø 405) 4,494 kN
- ispitno opterećenje (projicirana površina*1,5 kN/m^2 - početno opterećenje) (ø 455) 3,448 kN
- ispitno opterećenje (projicirana površina*1,5 kN/m^2 - početno opterećenje) (ø 705) 5,170 kN

Postupak ispitivanja:

- mjerenje otklona pri početnom opterećenju
- povećenje opterećenja dodavanjem pojedinačnih utega
- mjerenje otklona nakon 10 minuta s ispitnim opterećenjem
- mjerenje otklona nakon uklanjanja utega

Tablica 3. Rezultati mjerenja otklona.

položaj	otklon [mm] [1)]							
	Ø 80		Ø 405		Ø 455		Ø 705	
	s opterećenjem	bez opterećenja	s opterećenjem	bez opterećenja	s opterećenjem	bez opterećenja	s opterećenjem	bez opterećenja
M1	20	-4	22	19	-10	-10	35	21
M2	2	-7	4	2	-10	-9	4	2
M3	-10	14	9	7	0	-3	75	54
M4	-6	-3	5	4	-8	-6	8	4
M5	213	211	72	60	77	45	123	78

[1)] Negativna vrijednost znači savijanje u suprotnom smjeru od smjera opterećenja

5. Nepropusnost dimnjaka

Ispitivanje je provedeno na dimnjaku ø 200 prije i poslije pokusa toplinskog naprezanja i pokusa gorenja čađe

Ispitivani uzorci:

- kuglasti zatvarači za dovod zraka

Uređaji za ispitivanje

- mjerač protoka zraka točnost ±0,1 l/h, raspon 0,5-10 l/h;

±1 l/h, raspon 10-100 l/h;
±10 l/h, raspon 100-1000 l/h;
±100 l/h, raspon > 1000 l/h

- Tlakomjer točnost ±1 Pa, raspon ≤ 1000 Pa
  ±10 Pa, raspon > 1000 Pa

Uvjeti ispitivanja:

- nepropusnost plina poslije instalacije:
  - ispitni tlak 40 Pa
  - okolna temperatura 19,1°C
- nepropusnost plina poslije toplinskog naprezanja:
  - ispitni tlak 40 Pa
  - okolna temperatura 18,1°C
- nepropusnost plina poslije pokusa gorenja čađe:
  - ispitni tlak 40 Pa
  - okolna temperatura 18,3°C

Slika 2. Ispitivanje nepropusnosti dimnjaka.

Tablica 4. Rezultati mjerenja propusnosti.

uzorak	ispitni tlak	stanje poslije	izmjerena vrijednost	relativna vrijednost[1)]
Ø 200	40 Pa	instalacija	0,291 l/s	0,086 l/sm^2
Ø 200	40 Pa	toplinsko naprezanje T450	0,361 l/s	0,107 l/sm^2
Ø 200	40 Pa	gorenje čađe	0,488 l/s	0,144 l/sm^2

[1)] odnosi se na unutrašnje površine
[2)] pokus sekcija dimnjaka svih proizvedenih promjera nije bio predmet ovog izvještaja

6. Ispitivanje korozijske otpornosti

Montažni inox dimnjak sastoji se od dvije cijevi ø120mm, dužine 1000 mm, jedne cijevi ø120mm dužine 500 mm, jednog elementa ø120mm za odvod kondenzata i jednog "T komada" ø120mm. Svi segmenti načinjeni su od identičnnog materijala, identične debljine stijenke i usporedivog proizvodnog procesa (identični postupci, identična kvaliteta alata)

- unutrašnja površina: 1,02m^2
- debljina metala 0,6 mm odnosno 1,0 mm

- materijal, površina — AISI 316L (odgovara 1.4404), III-D, bez specijalne obrade
- proces proizvodnje — - rezanje plazma uređajem ili mehaničko rezanje
  - valjčani alati izrađeni od legiranog čelika,
  - zavarivanje s automatskim plazma uređajem
  - spajanje s neabrazivnim / polimernim alatom

Ispitni segment instaliran je u odgovarajuću ispitnu opremu i spojen s uljnim bojlerom.
Za ispitivanje potrebno je slijedeće:

- ispitni valjak s dvostrukom stijenkom s vodom kojom se vrši hlađenje, duljine 2,5 m
- uređaj za grijanje i hlađenje vode
- bojler s uljnim plamenikom i opskrbnim tankom s 1000lit modificiranog ulja
- NiCr-Ni termoparovi, točnost ±0.5%
- mjerač protoka zraka, točnost ±0.1 m/s
- analizator dimnih plinova točnost ±0.1% O_2, ±1 ppm CO, ±1 ppm SO_4, ±1 ppm Cl^-
- masa, točnost ± 1g
- jedinica za prikupljamje podataka potpomognuta računalom

6.1. Uvjeti ispitivanja korozijske otpornosti

Pokus je proveden kroz 30 ciklusa, od kojih se svaki sastoji od faze grijanja (8h) i faze sušenja (16h) [2].

Faza grijanja (izlaganje kondenzirajućim dimnim plinovima izvan kotla):

- temperatura dimnih plinova (srednja vrijednost) — 59,7°C
- temperatura unutarnje stijenke (donja, srednja vrijednost) — 41,2°C
- temperatura unutarnje stijenke (gornja, srednja vrijednost) — 43,0°C
- brzina dimnih plinova — 0,75.m/s

Faza sušenja (grijanje ispitne sekcije izvana):

- temperatura unutarnje stijenke (donja, srednja vrijednost) — >60°C
- temperatura unutarnje stijenke (gornja, srednja vrijednost) — >60°C

Po završetku tretiranja cijevi izvršili smo rastavljanje dimnjaka tako da su cijevi izrezane na pola. Unutrašnje površine ispitali smo vizualno s ciljem utvrđenja oštećenja od korozije. Kritične točke ispitane su detaljnije uz pomoć mikroskopa. Također je napravljena kemijska analiza goriva, kondenzata i kvalitete nerđajućeg čelika.

7. Rezultati ispitivanja korozijske otpornosti

Pokus je proveden prema korozijskoj klasi 2 [2].
Dobiveni su slijedeći rezultati:

• analiza ulja:	klor (Cl)	100 ppm
	sumpor (S)	0,30 g/l
• analiza nerđajućeg čelika:	krom (Cr)	17,33%
	nikal (Ni)	11,29%
	molibden (Mo)	1,97%

	sumpor (S)	0,002%
	fosfor (P)	0,031%
	silicij (Si)	0,59%
	mangan (Mn)	1,63%
	titan (Ti)	--%
	ugljik (C)	0,031%

udovoljava 1.4404 [3].

- analiza kondenzata:

klor (Cl)	39,7 mg/l
sulfat (SO_4)	117,5 mg/l
Ph-vrijednost	2,4[4]
željezo (Fe)	3,1 mg/l
nikal (Ni)	1,1 mg/l
krom (Cr)	1,2 mg/l [5]

- maksimalna dubina korozije u vertikalnim sekcijama > 20% debljine*)
- srednja dubina korozije u vertikalnim sekcijama < 10% debljine

*)korozija koja razara s maksimalnom dubinom jamice >20% debljine stijenke nastupa u jednom od tri spoja. Analiza je pokazala da je ovaj spoj izrađen primjenom neadekvatnog alata. Drugi spojevi su pokazali dovoljnu korozijsku otpornost, ako su i alati i proizvodni proces adekvatni. Neispravan spoj je izuzet od procjene.

8. Zaključak

Neosporna je činjenica da je za ispravno funkcioniranje saniranog dimnjaka najbitnije pravilan izbor materijala. No tijekom proizvodnje dimnjaka postoje brojne operacije kod kojih može doći do pogreške, prvenstveno zbog ljudskog faktora. Primjeri za to bili bi: izbor krivog alta za rezanje lima, neodgovarajuće zavarivanje i slično. Sve to upućuje da je neophodno izvršiti ispitivanje kompletnog dimnjaka kakav je on na mjestu upotrebe.

LITERATURA

[1] Norma EN 13 384-1
[2] Norma DIN EN 1856-1
[3] Norma DIN EN 10088-2
[4] Norma DIN 38404-C5
[5] Norma DIN ISO 11885

NASTANAK SIGMA FAZE I NJEZIN UTJECAJ NA SVOJSTVA DUPLEKS ČELIKA

THE FORMATION AND INFLUENCE OF SIGMA PHASE ON PROPERTIES OF DUPLEX STEEL

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Izvorni znanstveni rad / Original scientific paper

Sažetak: U radu je ispitan utjecaj temperature i vremena zagrijavanja na promjenu mikrostrukture dupleks čelika i njezin odraz na svojstva. Uzorci dupleks čelika 1.4462 grijani su na 700 i 850°C a vrijeme zagrijavanja iznosilo je 30, 60 i 120 minuta. Na tako pripremljenim uzorcima provedena je kvalitativna i kvantitativna analiza mikrostrukture te mjerenje tvrdoće (HV1 i HV0,2). Pokazalo se da žarenje na 700°C nije izazvalo značajnije izlučivanje sigma faze, već samo smanjenje volumnog udjela ferita. Kod uzoraka žarenih na 850°C došlo je do značajnijeg formiranja sigma faze već nakon 30 min. Produljenjem vremena žarenja volumni udio sigma faze je rastao, kao i udio austenita, a smanjivao se udio ferita. Povećanjem udjela sigma faze u mikrostrukturi dupleks čelika rasla je tvrdoća.

Ključne riječi: dupleks čelici, mikrostruktura, sigma faza, tvrdoća

Abstract: The formation and influence of sigma phase on properties of duplex steel was determined in this paper. Samples were cut from a 1.4462 pipe and heat treated at 700 °C and 850 °C for three different annealing times - 30, 60 and 120 min.Qualitative and quantitative microstructural analysis of the samples was performed, as well as the Vickers hardness measurement (HV1 and HV0.2). The annealing at 700 °C did not cause significant formation of the sigma phase, but the volume fraction of the ferrite was decreased. Higher temperature (850 °C) and longer annealing time resulted in significant formation of sigma phase, increase of volume fraction of austenite, and decrease of volume fraction of ferrite. It was found that the microstructural transformations significantly influence the hardness in the investigated case.

Key words: duplex stainless steels, microstructure, sigma phase, hardness

Uvod

Dupleks čelici pripadaju skupini korozijski postojanih čelika zajedno s feritnim, austenitnim, martenzitnim i precipitacijski očvrsnutim. Osobiti su po tome što na sobnoj temperaturi posjeduju kombinaciju feritne i austenitne mikrostrukture u omjeru 1:1.

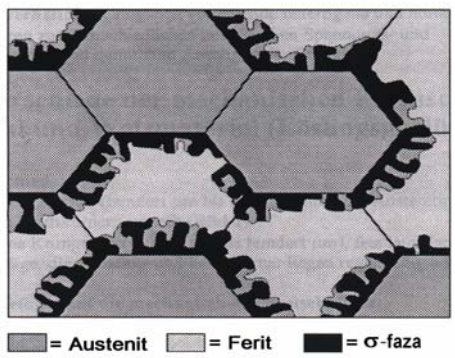
Pri unosu topline u visoko legiranom sustavu dupleks čelika postoji velika opasnost od izlučivanja intermetalnih faza i karbida. Ukoliko se izlučevine pojave u većoj mjeri, konačni rezultat je pad svojstava čvrstoće, žilavosti i korozijske otpornosti. Nastanak ovih faza i karbida najviše ovisi o temperaturi, vremenu te količini i vrsti legirnih elemenata. Za svojstva su najnepoželjnije α' faza, σ faza i χ faza. Povećavaju tvrdoću, a smanjuju žilavost, vlačnu čvrstoću i otpornost koroziji.

U radu su prikazani rezultati istraživanja utjecaja temperature i vremena na nastanak σ faze, a zatim i djelovanje σ faze na mehanička svojstva dupleks čelika. Na uzorcima je napravljena kvalitativna i kvantitativna analiza mikrostrukture te izmjerena makro- i mikrotvrdoća.

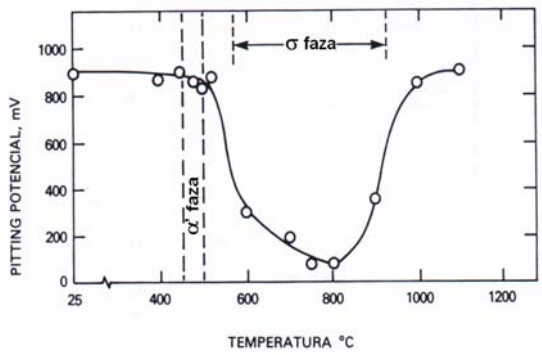
Tvrda, intermetalna σ faza nastaje u temperaturnom području od 560°C do 980°C. Bogata je kromom, a njezin nastanak potiču svi alfageni elementi, posebno Mo. Nukleusi σ faze formiraju se po granicama između feritnih i austenitnih zrna i rastu na račun ferita. Istodobno se povećava udio austenita. Na slici 1 prikazan je model nastanka i progresivni smjer σ faze, [1].

Tvrdoća σ faze iznosi oko 940 HV što je dovoljno da izazove ozbiljne probleme mehaničkim svojstvima, pogotovo žilavosti i duktilnosti povisujući makrotvrdoću dupleks čelika i do 450 HV50.

Korozijska otpornost također dosta opada već pri minimalnoj prisutnosti sigma faze u mikrostrukturi. Dijagram na slici 2 zorno prikazuje utjecaj dugotrajnog izotermnog žarenja (4 sata) na PRE dupleks čelika Fe-26Cr-5,5Ni-1,5Mo-0,2N. Pad otpornosti u intervalu od 560°C do 980°C je evidentan, [2].



Slika 1. Model nastanka σ faze, [1]



Slika 2. Utjecaj dugotrajnog izotermnog žarenja na PRE dupleks čelika Fe-26Cr-5,5Ni-1,5Mo-0,2N, [2]

1. Eksperimentalni dio

Sva ispitivanja provedena su na uzorcima izrezanima iz cijevi od dupleks čelika oznake 1.4462, odnosno X2CrNiMoN22–5–3. Kemijski sastav čelika prikazan je u tablici 1.

Uzorci su toplinski obrađeni u Laboratoriju za toplinsku obradu, Fakulteta strojarstva i brodogradnje u Zagrebu. Temperatura i vrijeme žarenja prikazani su u tablici 2, a na slici 3 prikazani su uzorci nakon žarenja.

Tablica 1. Kemijski sastav dupleks čelika X2CrNiMoN22-5-3, [3]

	Maseni udio elemenata, %								
	C	**Ni**	**Cr**	**Mn**	**Si**	**P**	**S**	**N**	**Mo**
min		4,50	21,00					0,10	2,50
max	0,03	6,50	23,00	2,00	1,00	0,035	0,015	0,22	3,50
izmjereno	0,018	5,49	22,64	1,87	0,28	0,027	0,0004	0,15	2,88

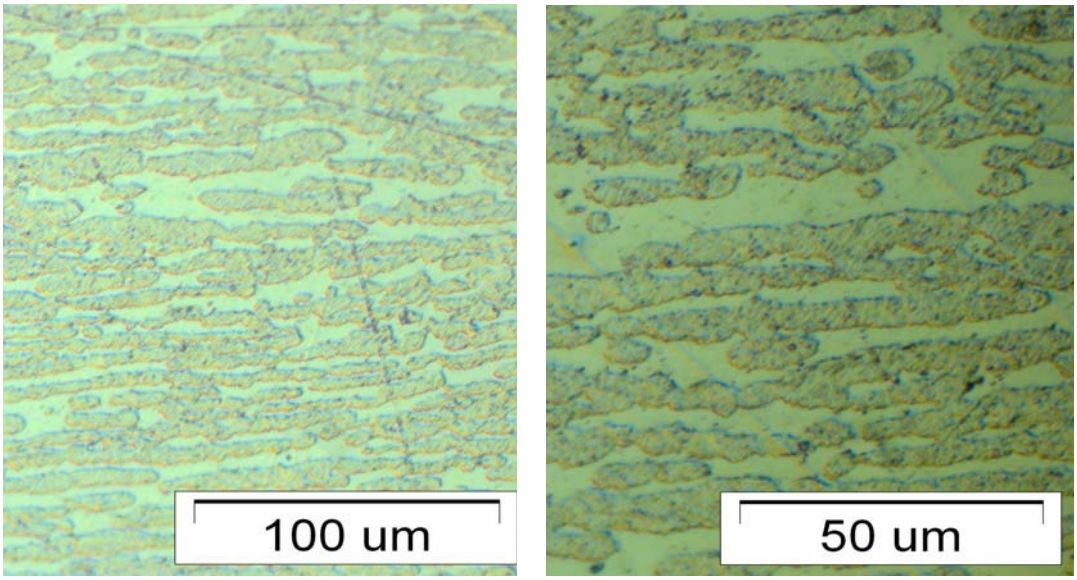
Tablica 2. Uzorci za istraživanje

Uzorak	Vrijeme	Temperatura
A1	30 min	700°C
A2	60 min	
A3	120 min	
B1	30 min	850°C
B2	60 min	
B3	120 min	

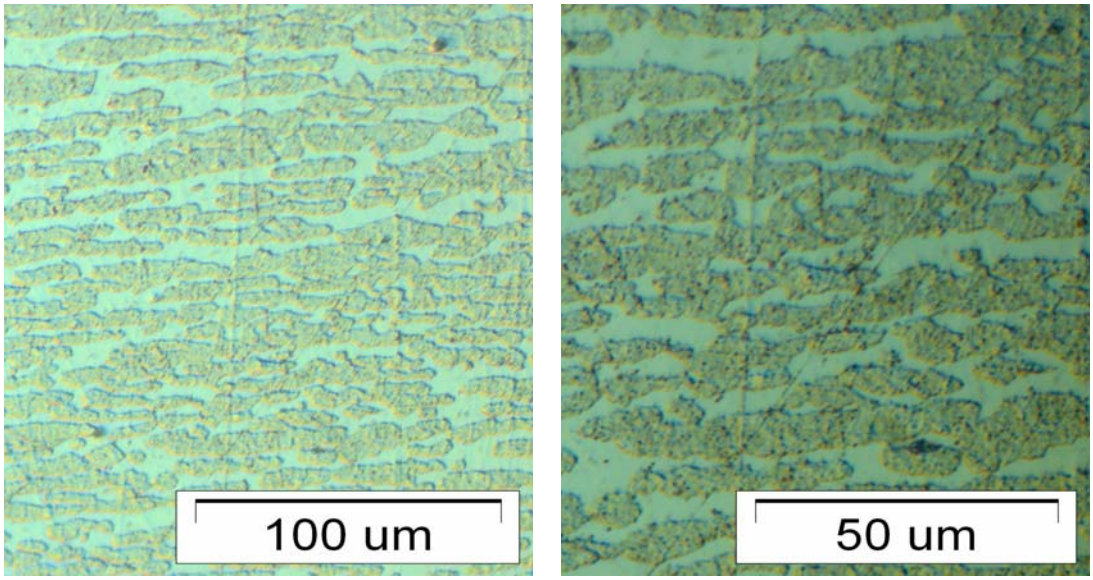
Slika 3. Uzorci nakon toplinske obrade

2. Rezultati

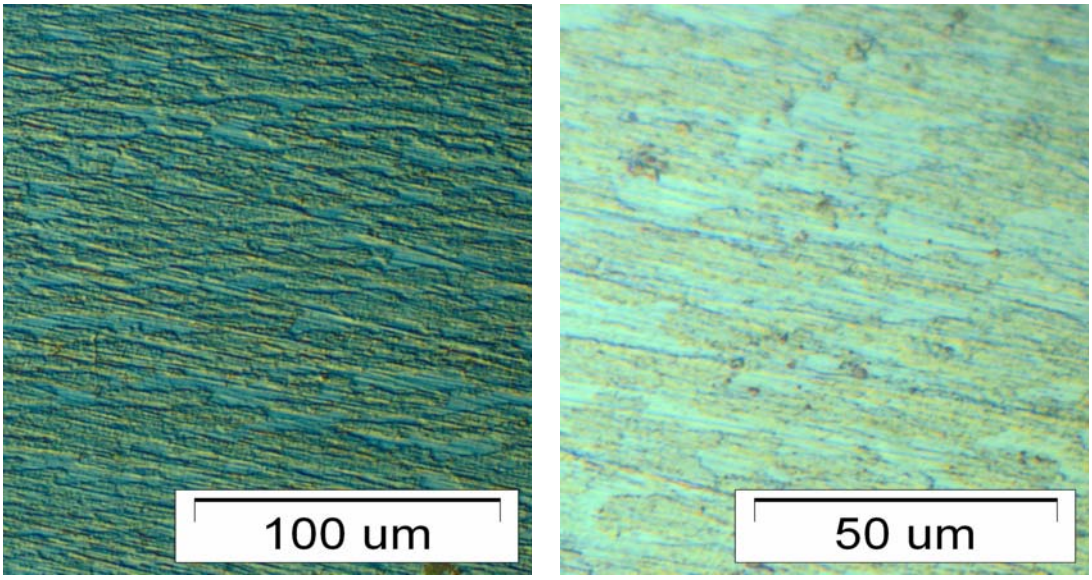
Uzorci su propisno pripremljeni za analizu mikrostrukture: izrezani, zaliveni u masu, brušeni, polirani i nagriženi u odgovarajućem sredstvu, [3]. Analiza mikrostrukture provedena je na svjetlosnom mikroskopu u Laboratoriju za materijalografiju Zavoda za materijale i tribologiju. Kvalitativna analiza mikrostrukture pokazala je da kod uzoraka žarenih na 700°C nije došlo do značajnijeg formiranje σ faze. No, uzorci žareni na 850°C pokazali su, već pri žarenju u vremenskom trajanju od 30 min, nastanak σ faze po granicama zrna između ferita i austenita. Na fotografijama od 4 do 9 prikazana je mikrostruktura svih uzoraka pri dva različita povećanja, [4].



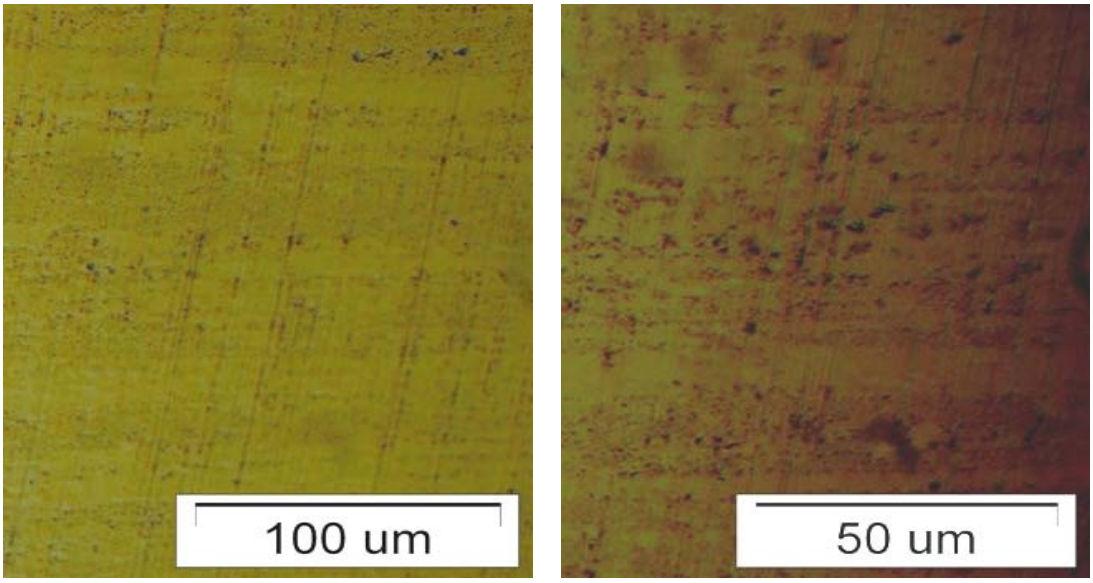
Slika 4. Prikaz mikrostrukture uzorka A1



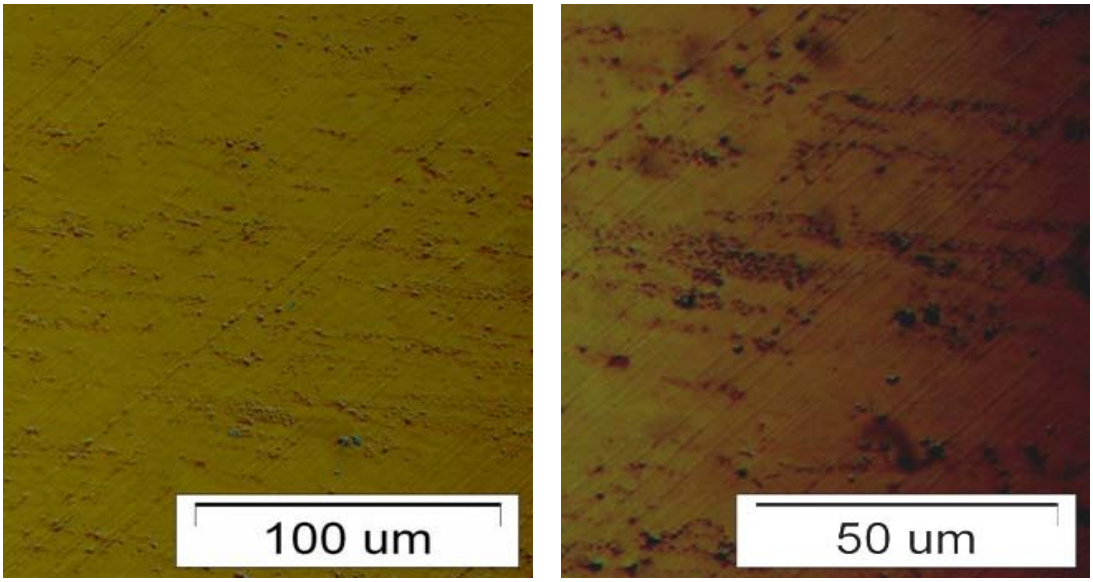
Slika 5. Prikaz mikrostrukture uzorka A2



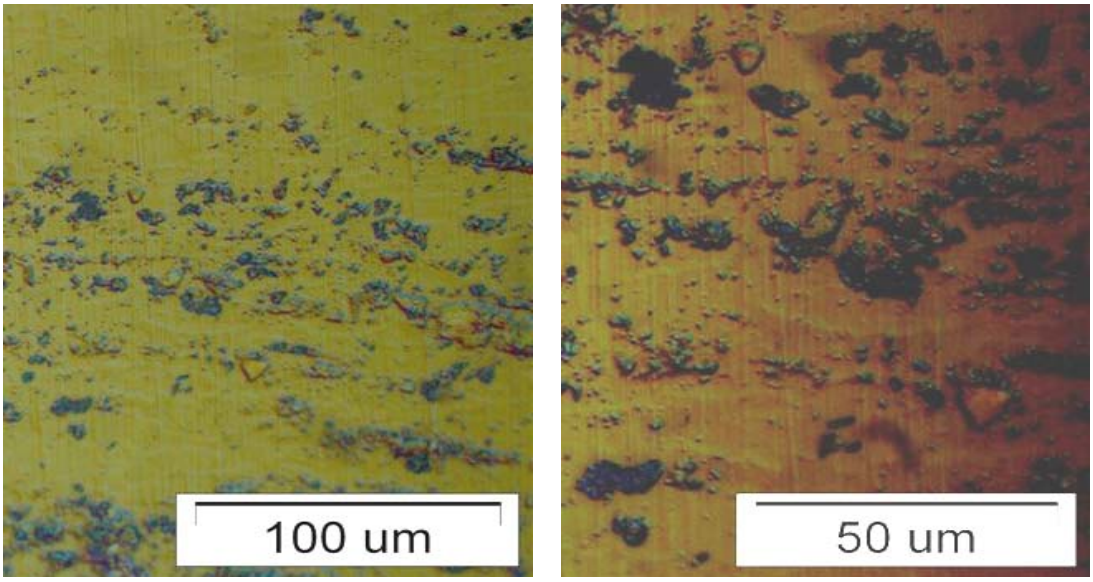
Slika 6. Prikaz mikrostrukture uzorka A3



Slika 7. Prikaz mikrostrukture uzorka B1



Slika 8. Prikaz mikrostrukture uzorka B2



Slika9. Prikaz mikrostrukture uzorka B3

Rezultati mjerenja volumnog udjela ferita u mikrostrukturi svih uzoraka prikazani su u tablici 3. Prikazani rezultati su srednje vrijednosti od deset mjerenja. Udio ferita izmjeren je feritmetrom. U tablici 4 prikazani su rezultati ispitivanja mikrotvrdoće HV0,2 - srednje vrijednosti od 5 mjerenja. U tablici 5 nalaze se rezultati mjerenja makrotvrdoće HV 1, također srednje vrijednosti od 5 mjerenja.

Tablica 3. Rezultati mjerenja volumnog udjela ferita u mikrostrukturi.

	Volumni udio ferita, %					
	A1	**A2**	**A3**	**B1**	**B2**	**B3**
Av	**30,60**	**30,40**	**30,20**	**10,20**	**6,85**	**4,80**

Tablica 4. Rezultati mjerenja mikrotvrdoće *HV 0,2*

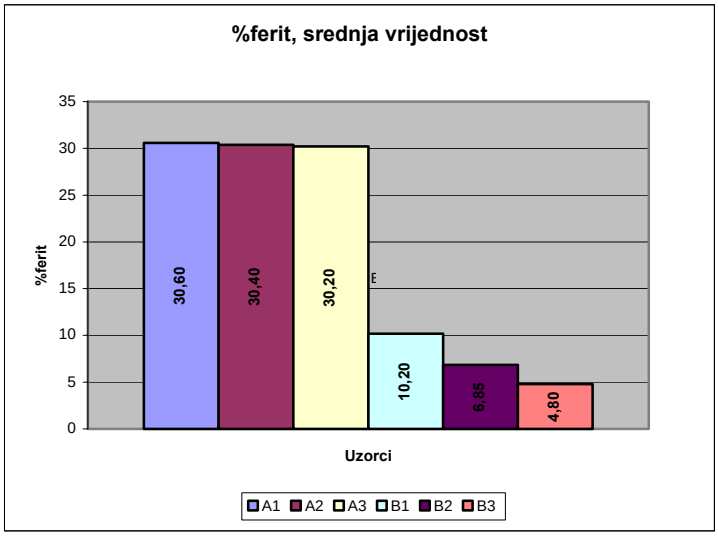
	HV 0,2					
	A1	**A2**	**A3**	**B1**	**B2**	**B3**
Av	271	266,2	260,2	300	346,4	353,4

Tablica 5. Rezultati mjerenja makrotvrdoće *HV 1*

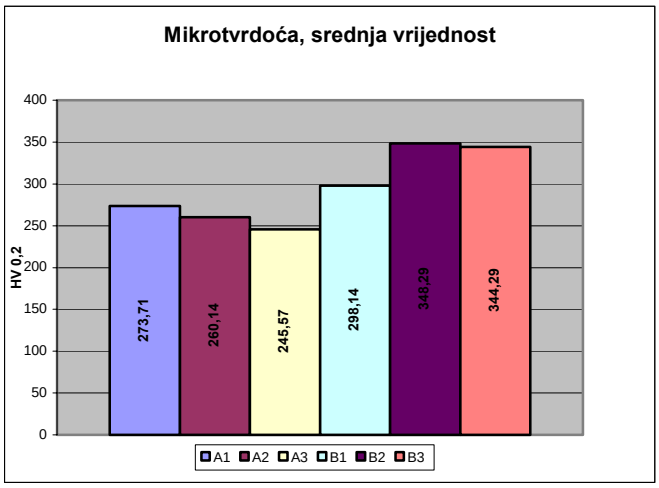
	HV 1					
	A1	**A2**	**A3**	**B1**	**B2**	**B3**
Av	253,8	255,4	254,2	300,4	334,8	340,4

3. Analiza rezultata

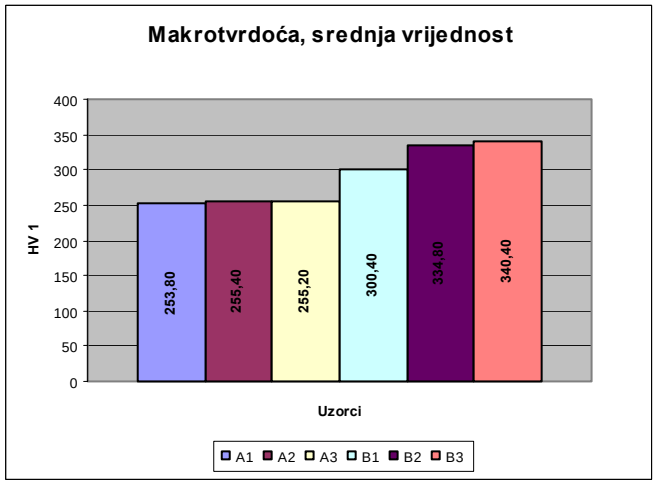
Rezultati dobiveni kvalitativnom analizom pokazali su da temperatura od 700°C ne izaziva izlučivanje sigma faze u značajnijoj količini ali je znakovita promjena volumnog udjela ferita koji je s 50% pao na oko 30%. Ova promjena bitno je narušila izbalansirani odnos ferita i austenita u osnovnom materijalu. Trajanje žarenja nije utjecalo na promjenu mikrostrukture. Temperatura žarenja od 850°C izazvala je značajnije izlučivanje sigma faze i još veći pad udjela ferita u mikrostrukturi. Produljenjem vremena žarenja količina sigma faze se povećala a udio ferita se još više smanjio. Dijagramom na slici 10 grafički su prikazani rezultati mjerenja volumnog udjela ferita za sve uzorke.
Mikrostrukturne promjene odrazile su se na svojstva, konkretno na vrijednosti tvrdoće, što je predočeno dijagramima na slikama 11 i 12.



Slika 10. Dijagram srednje vrijednosti volumnog udjela ferita u mikrostrukturi



Slika 11. Dijagram srednjih vrijednosti mikrotvrdoće HV 0,2



Slika 12. Dijagram srednjih vrijednosti makrotvrdoće *HV 1*.

4. Zaključak

Na temelju rezultata dobivenih tijekom ispitivanja, može se zaključiti slijedeće:

- Žarenje na temperaturi od 700°C izazvalo je pad volumnog udjela ferita i prirast udjela austenita. Izlučevine sigma faze u mikrostrukturi jedva se uočavaju (samo kod uzorka koji je najduže žaren)
- Trajanje žarenja nije utjecalo na promjenu tvrdoće kod uzoraka žarenih na 700°C
- Žarenjem na temperaturi od 850°C nastala je znatna količina σ faze, a njezin volumni udio rastao je proporcionalno porastu vremena žarenja. Volumni udio ferita se još više smanjio
- Mikrotvrdoća je značajno porasla s povećanjem volumnog udjela sigma faze u mikrostrukturi dupleks čelika.

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UTJECAJ ODABIRA PODLOGE ZA ISPIS NA KARAKTERISTIKE DIGITALNE FOTOGRAFIJE REALIZIRANE DIGITALNIM LASERSKIM FOTOGRAFSKIM PRINTEROM

INFLUENCE OF SUBSTRATE SELECTION ON THE CHARACTERISTICS OF DIGITAL PHOTOGRAPHS REALIZED WITH DIGITAL PHOTOGRAPHIC LASER PRINTER

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Stručni članak / Professional paper

Sažetak: Pri ispisu digitalnog zapisa fotografske slike, fotografi na raspolaganju imaju različite tehnike ispisa, ali i, unutar određene tehnike ispisa, mogućnost odabira podloge za ispis. Izbor karaktera efekta podloge, sjajni ili mat, ovisi o motivu, formatu i namjeni fotografije, ali se, u idealnom slučaju, očekuje da promjena načina dorade površine podloge za ispis bitno ne utječe na reprodukciju boja i tonova. U ovom je radu na temelju kolorimetrijskih mjerenja ispitan utjecaj odabira podloge za ispis različitog načina dorade na boje i tonove fotografije realizirane tehnikom digitalnog laserskog fotografskog ispisa. Rezultati upućuju na bitne razlike tonova i boja realiziranih digitalnih fotografija.

Ključne riječi: digitalna fotografija, digitalni laserski fotografski printer, podloga za ispis, razlika boja, prenosne krivulje

Abstract: When printing digital photographic image files photographers have available different printing techniques, but also, within certain printing technique, a choice of substrates for printing. Selection of substrate finishing, glossy or matt, depends on subject, format and purpose of photography, but, in the ideal case, it is expected that finishing of the substrate surface does not substantially affect the reproduction of colors and tones. In this paper, based on colorimetric measurements the impact of selecting a substrate for printing with different ways of finishing on colors and tones of photographs realized with digital laser photographic printing technique is examined. The results indicate significant differences of tones and colors of realized digital photographs.

Key words: digital photography, digital laser photo printer, substrate, color difference, transmission curve

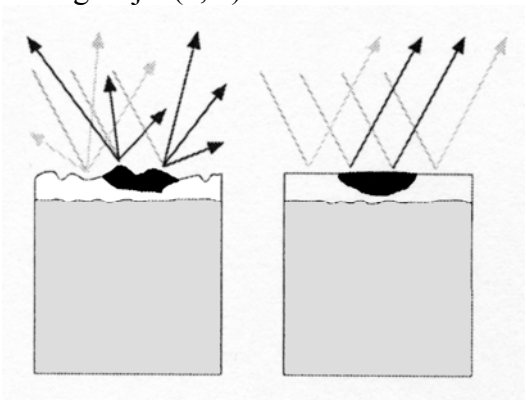
1. UVOD

Digitalna je fotografija jedno od područja najbržeg i najočiglednijeg razvoja zadnjih dvadesetak godina. Pojava i razvoj digitalnih fotografskih tehnika utjecala je na razvoj fotografije i u tehničkom i u kreativnom smislu, ali pri tome fotografija zadržava svoja osnovna semantička i sintaktička svojstva i, bez obzira da li se radi o "klasičnoj" ili digitalnoj fotografiji, radi se o istom mediju određenih načela izražavanja koja se razvijaju još od sredine 19. stoljeća - tj. od pojave fotografije. Niti tehnički niti kreativno nije potrebno stvarati umjetne granice između "klasične" i digitalne fotografije - tehnike rada vrlo se često isprepleću te je danas, često, nemoguće i, prije svega, nepotrebno inzistirati na tome da li je neka fotografija "klasična" ili "digitalna".
Profesionalno, digitalna je fotografija u prvo vrijeme bila prihvaćena u području primijenjene fotografije koja se ostvaruje kroz tisak ili Internetom, a amaterska se digitalna fotografija najčešće realizirala kao prikaz na monitoru računala. Međutim, povećanje kvalitete digitalnih fotografskih aparata, "digitalnih fotografskih laboratorija" (programa za obradu fotografija), a time i fotografske slike koja se dobivala snimanjem digitalnim fotografskim aparatom, digitalna fotografija postaje zanimljiva u svim područjima profesionalne i amaterske fotografije što dovodi do potrebe kvalitetnog ispisa takvih fotografija - ispisom koji neće zaostajati za ispisom fotografija "klasičnih" fotografskih sustava.
Od sredine devedesetih godina dvadesetog stoljeća razvija se niz različitih tehnika ispisa koje svojim karakteristikama imaju ili ulogu aparata za povećavanje ili fotografskih (studijskih) printera. Među tehnikama ispisa digitalne fotografije danas dominantnu ulogu imaju tehnika bubble jet ispisa, piezoelektričnog ink jet ispisa, sublimacijskog ispisa i ispisa laserskim digitalnim fotografskim printerom.
Uz mogućnost izbora tehnike ispisa, fotograf ima na raspolaganju i odabir različitih materijala - prvenstveno podloga. Pri tome se, ovisno o motivu i namjeni fotografije, biraju podloge različitog načina dorade (mat, sjajni i sl.), a u idealnom bi slučaju odabir podloge različite dorade površine minimalno utjecao na reprodukciju boja.

2. TEORETSKI DIO

Fotografski studiji koji nude izradu fotografija kao uslugu fotografima (profesionalcima i amaterima) sedamdesetih i osamdesetih godina dvadesetog stoljeća napuštaju "pojedinačnu" izradu kolor fotografija koja podrazumijeva rad s aparatom za povećavanje i prelaze na visokoautomatizirane uređaje za kemijsku obradu filmova ("razvijanje") i izradu fotografija pomoću tzv. fotografskih printera. Razvoj amaterske fotografije sredinom devedesetih godina dvadesetog stoljeća sve je više dovodio do potrebe za automatiziranom izradom kolor fotografija snimljenih digitalnim fotografskim aparatom što je dodatno naglašeno sve većim prihvaćanjem digitalne fotografije u najrazličitijim područjima profesionalne fotografije.
Kako ink jet i sublimacijski printeri za ispis digitalnih fotografija prvenstveno pokrivaju potrebe pojedinačne izrade fotografija, mogu se usporediti s aparatima za povećavanje u klasičnoj fotografiji što ne odgovara potrebama velikih automatiziranih fotografskih laboratorija (studija) koji su orijentirani velikoj brzini i kapacitetima izrade više stotina (pa i tisuća) fotografija u satu (1). Uz to je kvaliteta ispisa i njihova svjetlostalnost, prvenstveno ink jet ispisa, krajem 20. stoljeća bitno zaostajala za ispisom klasične fotografije fotografskim printerom pa se kao logično rješenje nametnulo adaptacija fotografskih printera digitalnom zapisu fotografije (2).
Prvi digitalni fotografski printeri su koristili LED tehnologiju osvjetljavanja slike formirane na LCD-u. Takvi fotografski printeri omogućuju i osvjetljavanje fotografskog papira kroz film, ali kod izrade digitalno zapisane fotografije ova tehnologija daje “mrežastu” strukturu

fotografije (kao na monitoru) što je naročito naglašeno kod većih povećanja pa se danas za izradu digitalnih fotografija sve rjeđe koriste i to isključivo pri izradi fotografija manjih formata (okvirno do 10 x 15 cm). (2)
Moderni digitalni fotografski printeri u pravilu koriste lasersko osvjetljavanje fotografskog papira pa se često nazivanju i laserski (digitalni) fotografski printeri. Temelj ove tehnike je kolor fotografski papir - papir (obostrano oslojen polietilenskim slojem - tzv. RC ili "plastificirani papir") na kojem je nanesen nesenzibilizirani sloj - nositelj "žute slike", ortokromatski sloj - nositelj "magenta slike" i pankromatski sloj - nositelj "cijan slike". Fotografski printer osvjetljava fotografski papir plavim, zelenim i crvenim svjetlom djelujući na pojedine slojeve (nositelje slike u komplementarnoj boji onoj izvora svjetla) te se gotova fotografija dobiva kontinuiranim prelazom tonova suptraktivnom (CMY) izgradnjom boja nakon kemijske obrade koja, u osnovi, podrazumijeva kromogeno razvijanje (stvaranje crne-srebrene slike u svakom sloju redukcijom osvijetljenih zrnaca srebrenog halogenida u fotoosjetljivim slojevima papira u metalno srebro te reakcijom kolorkomponente u pojedinom sloju i oksidacijskog produkta razvijanja čime se u slojevima stvara cijan, magenta i žuta slika), izbljeđivanje (tj. uklanjanje razvijene crne-srebrene slike) i fiksiranje (uklanjanje nerazvijenih zrnaca srebrenih halogenida). Kako u digitalnoj fotografiji ne postoji materijalna slika (film) kroz koju se osvjetljava plavim, zelenim i crvenim svjetlom, digitalni fotografski printer, prema uputi računala, laserom osvjetljava fotografski papir. Općenito, digitalni fotografski printeri danas omogućuju izradu fotografija iz najrazličitijih medija - digitalnih (CF, SM, memory stick, CD, fotografije poslane Internetom i sl.) i "klasičnih" (negativ, dijapozitiv).
Ovisno o načinu dorade površine pri proizvodnji fotografskog papira, nakon izrade fotografija, fotografije imaju različite efekte – mat, sjajni, raster i sl. Među njima se prvenstveno koriste fotografski papiri mat ili sjajne površine (slika 1), a izbor podjednako ovisi o afinitetu fotografa-autora, namjeni fotografije, motivu i formatu. Nije rijedak slučaj da se ista i za ispis jednako pripremljena fotografija, ovisno o namjeni i formatu, realizira i na sjajnom i na mat fotografskom papiru i da, pri tome, fotograf sa stanovišta reprodukcije tonova i boja očekuje „iste" fotografije. (2, 3)



Slika 1: Fotografski papiri mat i sjajne površine

3. EKSPERIMENTALNI DIO

Za ispis je pripremljena Gretag Macbeth tablica boja koja se sastoji od 24 kvadratičnih polja kojima je obuhvaćen široki raspon boja karakterističnih za snimanje, obradu i ispis u različitim fotografskim sustavima i polja s pokrivenostima površina 0-100 % (koraci po 10%) u cijanu, magenti, žutoj i crnoj. Gretag Macbeth tablicom boja obuhvaćene su boje karakterističnih fotografskih motiva (npr. boja kože, boja plavog neba, maslinastozelena i sl.), primarne boje aditivne i suptraktivne izgradnje boja, akromatske boje (bijela, sive, crna) i ostale boje koje omogućuju objektivnu ocjenu reprodukcije boja u određenom fotografskom

sustavu i uvjetima. Za ovo je ispitivanje korišten standardni JPEG zapis ove tablice boja (tablica 1).

Tablica 1: Gretag Macbeth tablica boja

NAZIV	L	a	b	NAZIV	L	a	b
tamna koža	38,02	14,78	12,17	**plava**	29,66	29,75	-54,78
koža	66,37	16,93	13,50	**crvena**	41,22	54,06	23,91
plavo nebo	51,04	3,39	-26,03	**zelena**	55,48	-38,30	31,13
maslinastozelena	43,21	-14,37	19,72	**žuta**	81,35	0,43	76,64
ljubičica	56,39	16,01	-29,69	**magenta**	51,61	52,53	-19,50
plavozelena	71,62	-26,96	-3,05	**cijan**	51,61	-17,58	-45,07
narančasta	61,74	31,41	56,10	**bijela**	96,00	5,16	-5,53
purpurnoplava	41,22	20,37	-47,12	**siva 8**	81,35	4,48	-4,81
umjerenocrvena	51,61	46,41	11,88	**siva 6.5**	66,67	3,81	-4,08
purpurna	30,88	28,46	-26,41	**siva 5**	51,61	3,11	-3,34
žutozelena	72,43	-24,72	56,89	**siva 3.5**	35,98	2,39	-2,57
narančastožuta	71,62	16,45	64,70	**crna**	20,44	1,68	-1,80

Gretag Macbeth tablica boja (tablica 1) ispisana je laserskim digitalnim fotografskim printerom Agfa d-lab.3 na kolor fotografskim papirima sjajne i mat površine: Agfa Sensatis Glossy i Agfa Sensatis Lustre.
Uvjeti kemijske obrade osvijetljenog papira navedeni su u tablici 2, a osnovne karakteristike korištenih podloga za ispis u tablici 3.

Tablica 2: Kemijska obrada u printeru Agfa d-lab.3

FAZA KEMIJSKE OBRADE	OZNAKA KEMIKALIJE	VRIJEME (s)	TEMPERATURA (^{0}C)
razvijanje	94 CD-R	45	35 +/_ 0,5
izbjeljivanje-fiksiranje	94 BX-MR	45	30 - 36
ispiranje	voda	90	30 - 40
sušenje	-	64	max 80

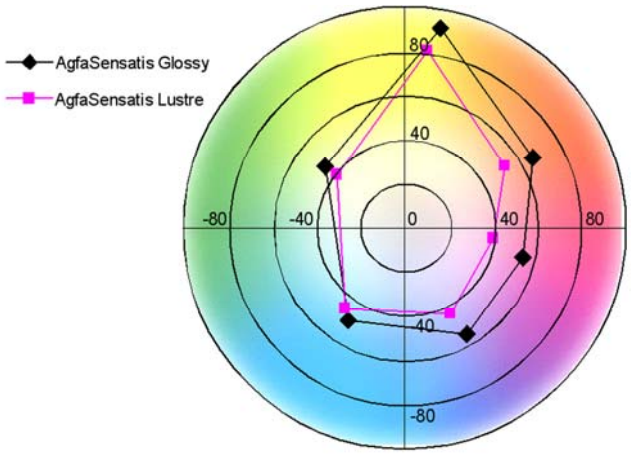
Tablica 3: Osnovne karakteristike korištenih podloga za ispis fotografija

OZNAKA PODLOGE	GRAMATURA (gm^{-2})	DEBLJINA (mm)	LUMINACIJA (L)	EFEKT ISPISA	TEHNIKA ISPISA
Agfa Sensatis Glossy	250	0,24	93%	visoki sjaj	Agfa d-lab
Agfa Sensatis Lustre	250	0,24	92%	mat	Agfa d-lab

Za mjernu je ocjenu ispisa korišten spektrofotomertar X-RiteColor Digital Swatchbook podržan ColorShop softverom. Pomoću spektrofotometra izmjerene su L, a i b vrijednosti polja Gretag Macbeth tablice boja pojedinih ispisa te su izračunate razlike boja (ΔE_{00}) za pojedino polje u odnosu na standardne vrijednosti (4). Primarne boje aditivne i suptraktivne sinteze pojedinih ispisa su prikazane i u CIE ab dijagramu kromatičnosti. Pomoću istog su uređaja određene gustoće obojenja ispisa cijana, magente, žute i crne za polja zadane optičke pokrivenosti 10 - 100 % na osnovi čega su izračunate ostvarene optičke pokrivenosti te izrađene prenosne krivulje.

4. REZULTATI

Na slici 2 je prikazan CIE Lab dijagram kromatičnosti za fotografije realizirane na Agfa Sensatis Glossy i Agfa Sensatis Lustre podlozi.



Slika 2: CIE ab dijagram kromatičnosti - usporedba ispisa Agfa d-lab 3 printerom na različitim podlogama

U tablicama 3 i 4 su prikazane L, a i b vrijednosti boja na realiziranim fotografijama te razlike boja ΔE_{00}. u odnosu na standardne boje tablice boje.

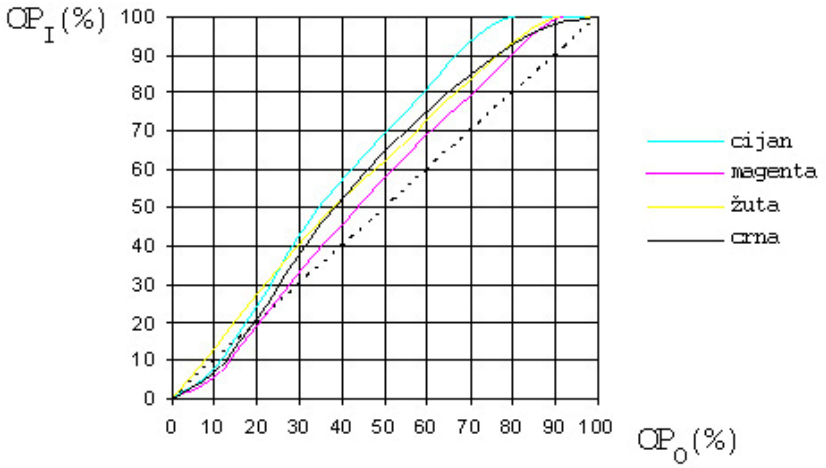
Tablica 3: L, a, b, ΔE_{00} vrijednosti ispisa Agfa d-lab 3 printerom na podlozi Agfa Sensatis Glossy

broj	naziv boje	L	a	b	$\overline{\Delta E}_{00}$
1	tamna koža	41.59	20.27	17.71	5.08
2	koža	67.07	23.42	17.40	3.80
3	plavo nebo	49.48	1.32	-27.71	2.93
4	maslinastozelena	42.39	-11.25	16.61	2.42
5	ljubičica	55.40	12.91	-27.16	1.84
6	plavozelena	62.87	-26.52	-18.11	12.11
7	narančasta	61.03	33.13	62.68	2.02
8	purpurnoplava	39.66	16.5	-41.14	2.29
9	umjerenocrvena	54.05	45.03	17.60	4.16
10	purpurna	32.43	27.76	-22.3	2.89
11	žutozelena	66.25	-11.58	59.53	8.95
12	narančastožuta	70.29	21.79	78.71	3.70
13	plava	27.38	28	-48.79	2.84
14	zelena	43.62	-35.85	27.88	11.93
15	crvena	42.49	58.54	31.92	3.67
16	žuta	73.97	16.35	90.72	10.33
17	magenta	52.45	54.01	-13.05	3.11
18	cijan	37.83	-25.64	-42.54	13.62
19	bijela	91.45	1.62	-2.85	5.39
20	siva 8	79.49	4.57	-1.42	1.15
21	siva 6.5	65.93	5.77	-1.92	3.08
22	siva 5	52.36	4.09	-3.53	1.39
23	siva 3.5	37.50	5.13	-1.65	3.67
24	crna	21.05	2.35	-2.47	1.12
					$\overline{\Delta E}_{min}$ 1.12
					$\overline{\Delta E}_{max}$ 13.62
					$\overline{\Delta E}_{00}$ 4.93

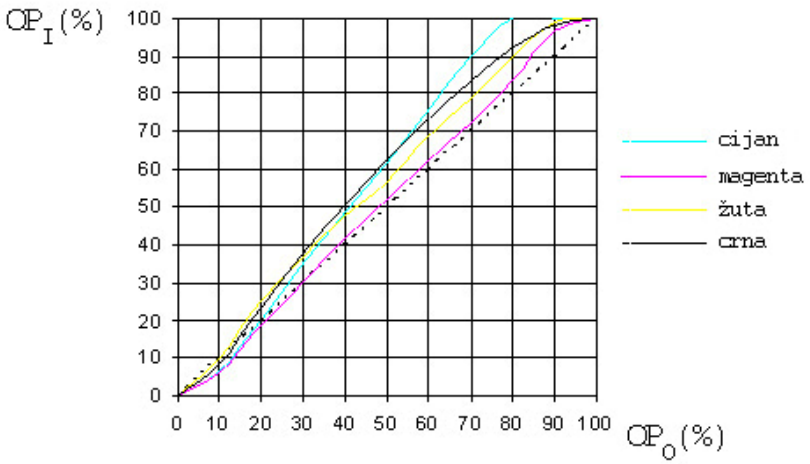
Tablica 4: L, a, b, ΔE_{00} vrijednosti ispisa Agfa d-lab 3 printerom na podlozi Agfa Sensatis Lustre

broj	naziv boje	L	a	b	$\overline{\Delta E}_{00}$
1	tamna koža	42,34	15,90	18,98	5,76
2	koža	67,42	17,68	19,20	3,71
3	plavo nebo	51,28	-0,85	-18,92	3,79
4	maslinastozelena	42,92	-10,15	17,72	2,87
5	ljubičica	58,04	9,30	-16,40	7,18
6	plavozelena	62,77	-22,77	-7,14	8,07
7	narančasta	59,46	25,87	53,74	3,38
8	purpurnoplava	43,55	11,38	-26,22	8,43
9	umjerenocrvena	54,85	34,48	18,68	7,88
10	purpurna	34,46	23,16	-14,47	6,79
11	žutozelena	64,42	-9,33	52,10	10,32
12	narančastožuta	66,95	17,71	63,75	3,76
13	plava	29,47	20,76	-88,96	5,23
14	zelena	43,99	-30,37	23,96	12,03
15	crvena	41,11	45,25	28,10	4,87
16	žuta	71,75	10,64	80,52	9,07
17	magenta	54,12	40,55	-4,69	7,76
18	cijan	37,66	-26,63	-36,92	14,29
19	bijela	90,45	1,28	-2,48	6,17
20	siva 8	78,43	2,80	-0,08	4,86
21	siva 6.5	65,94	3,36	-0,46	3,22
22	siva 5	52,26	2,19	0,86	3,98
23	siva 3.5	37,22	1,10	0,83	3,72
24	crna	21,16	-0,62	0,60	3,99
					$\overline{\Delta E}_{min}$2,87
					$\overline{\Delta E}_{max}$14,29
					$\overline{\Delta E}_{00}$6.47

Slike 3 i 4 prikazuju prenosne krivulje za fotografije realizirane na Agfa sensatis glossy i Agfa sensatis lustre podlozi.



Slika 3: Prenosne krivulje za višebojni ispis agfa d-lab.3 printerom na podlozi Agfa sensatis glossy



Slika 4: Prenosne krivulje za višebojni ispis agfa d-lab.3 printerom na podlozi Agfa sensatis lustre

5. DISKUSIJA I ZAKLJUČCI

Boje 1-5 Gretag Macbeth tablice predstavljaju boje karakterističnih fotografskih motiva - tamna koža, boja kože, plavo nebo, maslinastozelena, ljubičica. Ispis Agfa d-lab.3 printerom na Agfa Sensatis Glossy podlozi (prosječno ΔE_{00}=3,21) kod ovih boja pokazuje manje promjene od ispisa na Agfa Sensatis Lustre podlozi (prosječno ΔE_{00}=4,66), ali se, kako se radi o otvorenom sustavu uz korištenje renderiranja uz percepcijske namjere, može se razlike u oba slučaja smatrati prihvatljivim. Međutim, ako se promatra srednja vrijednost razlika primarnih boja aditivne i suptraktivne izgradnje boja u odnosu na one definirane Gretag Macbeth tablicom boja (boje 13-18) odstupanja su bitno veća - za Sensatis Glossy (prosječno ΔE_{00}=7,58), a za Sensatis Lustre (prosječno ΔE_{00}=8,88).

Općenito, ispis laserskim digitalnim fotografskim printerom Agfa d-lab.3 na podlogama Agfa Sensatis Glossy i Agfa Sensatis Lustre pokazuje vrlo široke raspone razlika boja. Ispis na podlozi Agfa Sensatis Lustre općenito pokazuje veće razlike boja.

Slika 2 prikazuje CIE ab dijagrame kromatičnosti s prikazom primarnih boja aditivne i suptraktivne izgradnje boja za ispise laserskim digitalnim Agfa d-lab.3 printerom na podlogama Agfa Sensatis Glossy i Agfa Sensatis Lustre. CIE ab dijagram kromatičnosti za ispis na Agfa Sensatis Glossy podlozi pokazuje najveće odstupanje u ispisu žute promjenom tona i povećanjem zasićenja u odnosu na žutu zadanu Gretag Macbeth tablicom boja što rezultira i povećanjem gamuta ispisa u području žuta-crvena (ispis crvene, također, pokazuje određeno povećanje zasićenja u odnosu na zadanu boju). Kod ispisa na Agfa Sensatis Lustre podlogu pomak u ispisu žute je manji, a uočljivo je i bitno smanjenje zasićenja u području crvene, magente i plave što uzrokuje smanjenje gamuta u tim područjima.

Prenosne krivulje za ispise laserskim digitalnim fotografskim printerom na podlogama Agfa Sensatis Glossy i Lustre (slike 3, 4) pokazuju značajniji prirast u reprodukciji tonskih vrijednosti za cijan od 30% - Agfa Sensatis Glossy, odnosno 40% - Agfa Sensatis Lustre, uz jednaku reprodukciju svih tonova optičke pokrivenosti 80% i veće i crnu od 40%. Prenosne krivulje za magentu ne pokazuju izrazite priraste optičkih pokrivenosti dok je bitna razlika uočljiva kod prenosnih krivulja za žutu - kod ispisa na Agfa Sensatis Glossy podlozi do

značajnijeg prirasta dolazi u vrijednostima iznad 30%, dok kod ispisa na Agfa Sensatis Lustre podlozi prenosna krivulja za žutu ne pokazuje značajne priraste.

Prirasti optičkih pokrivenosti prvenstveno su posljedica softvestkih korekcija kojima se nadoknađuje uže područje reprodukcije tonova ispisom od područja tonova koje se potencijalno bilježi snimanjem, odnosno dobiva nakon obrade fotografija, ali, određene su karakteristike tih krivulja posljedica mogućnosti i odstupanja koja se javljaju prilikom ispisa konkretnom kombinacijom printera i podloge za ispis (i ostalih elemenata). Pri ispisu fotografija problemi prevladavanja pojedine boje mogu se prvenstveno očekivati ako prenosne krivulje nisu međusobno usklađene, tj. ako su prirasti optičkih pokrivenosti za neka područja nagli te ako su naglašeni za neku boju u određenom području.

Dobiveni rezultati upućuju da je ispis laserskim digitalnim fotografskim printerom orijentiran brzoj studijskoj izradi fotografija te uključuje niz automatskih korekcija tonova, boja i oštrine čime se fotografije pokušavaju dovesti u "standardne vrijednosti". Ovakve korekcije mogu povećati prihvatljivost neobrađenih fotografija, eventualno pogrešno snimljenih (krivo određeni elementi ekspozicije, smanjena oštrina), ali i poništiti neke namjerne autorske efekte. Stoga je ova tehnika ispisa primarno optimalno rješenje za ispis kolor amaterskih fotografija i općenito fotografija "standardnih" motiva (fotografija vani, portret) koji se temelje na izrazitim bojama.

Iako fotografi očekuju da će primjenom iste tehnike ispisa na podlogama različite dorade (sjajna, mat) postići približno iste boje, ispitivane su podloge za ispis pokazale da odabir podloge za ispis bitno utječe na karakteristike postignutih boja. Ovo upućuje i na mogućnost različite pripreme fotografija ovisno o odabiru podloge za ispis.

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ANALYSIS OF WEAR MODELS FOR ADVANCED COATED MATERIALS

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Abstract:

Tribological tests, mathematical modelling and simulations have been conducted over the last few decades to investigate the nature and effects of mechanical wear in coated and uncoated materials. Mathematical models have been developed and in unison with specifically designed empirical tests, the veracity/capability of these models has been investigated. In more recent cases advanced engineering analysis tools, such as FEA and DOE, are used to further compliment and refine experimental techniques.

Studies have focused on the various wear mechanisms: abrasion, adhesion, erosion, corrosion wear, fatigue wear and also on different combinations of these. The intrinsic importance of the material in these studies has lead to a wide range of coated and uncoated materials being used in experimentation and modelling. From analysis, some models are based wholly on established/ classical wear theory while more recent work on wear models have been based on micro and nano scaled scientific approaches.

In practical wear tests, some mathematical models assume certain wear profiles and symmetry for calculating wear volume or mass loss. These assumptions do not account for the very irregular patterns that are the result of most wear mechanisms. Modern instrumentation on the other hand can capture precise profiles and dimensions to produce a more accurate measurement of material loss.

Some authors also use certain parameters such as hardness, fatigue or tensile strength to represent the resistance of a material to wear. Hardness does give an indication of the wear resistance of a material; however studies have demonstrated that the addition of certain alloying elements increases the wear resistance but not the hardness. Therefore hardness alone cannot describe the wear resistance properties of a material.

The objective of this work was to examine a number of models that have been used for analysing wear of materials. It highlights some key details and techniques used by authors to ascertain wear rates and gives examples of modern approaches to wear measurement for coated engineering samples. Figures 1 to 5 show examples of wear on materials and components that are difficult to measure and model in terms of material loss due to their irregular shapes.

Keywords: Tribology, Wear models, Mathematical analysis of wear, FEA, wear Instrumentation

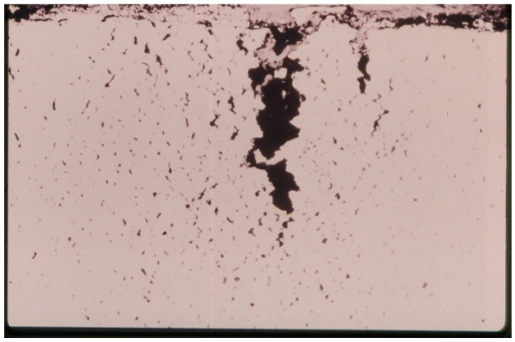

Figure 1 inter-granular corrosion.

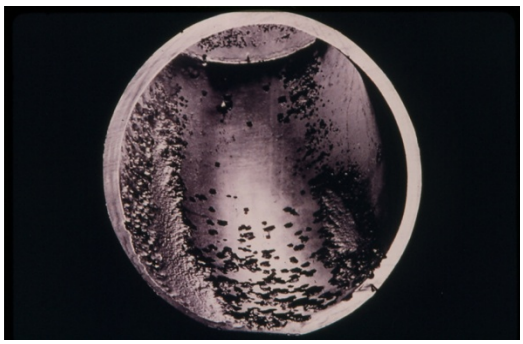

Figure 2 erosion wear in a pipe.

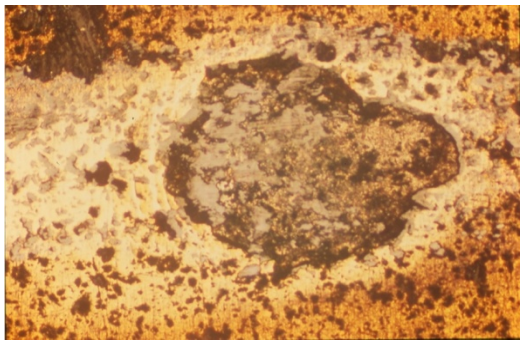

Figure 3 abrasive wear

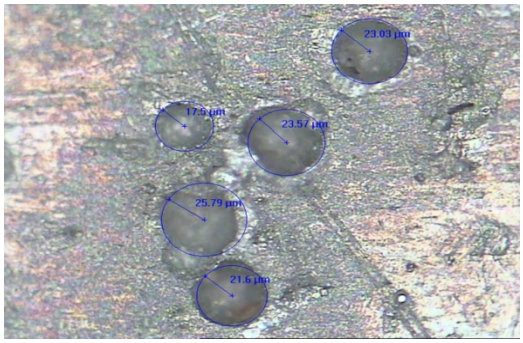

Figure 4 pitting wear.

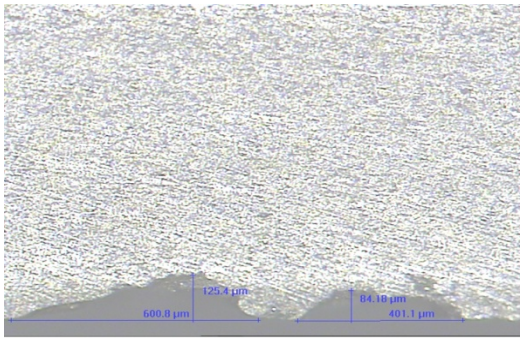

Figure 5 profile of pitting wear.

1. Introduction

Surface Engineering can be defined as the study, characterisation and improvement of a material's surface properties. This surface will be exposed to an external environment and will therefore deal with a different set of constraints/ conditions than the bulk material. Consequently the bulk material can be selected based on structural requirements and the surface of the material can be altered in a number of ways to suit external conditions[1].

This enhancement must be achieved in a cost effective manner without a detrimental effect on the beneficial properties of the bulk material. Common cases where surface treatment is essential are: a cutting tool, punch and dies or dental tools. A classic example of a surface engineering challenge is the gas turbine blade. The turbine environment is highly corrosive and maintained at extreme temperatures; the blade will need to resist these demanding conditions at the surface while also being strong enough, structurally, to transmit a torque to the central shaft of the turbine.

There are three typical methods of improving materials; heat treatment, alloying or surface engineering. Tribology is the science and study of interactions between surfaces in relative motion. Friction, wear and lubrication are fundamental concerns that make up this field [2]. Materials that are in contact have, at the interface, two material surfaces that will have individual characteristics and therefore a different effect on the tribological relationship.

There are a number of inter-related variables that govern how two materials will react in a contact/ Tribological situation. The load applied to bring the materials into contact, the degree of contact

between the materials, the presence of a lubricant, sliding speed of the surfaces with reference to each other and the individual material properties. Each variable will have an effect on the system as a whole and it is very difficult to separate out/ differentiate the individual contributions. The material properties of chief concern are the toughness, porosity, hardness and surface roughness. If a surface coating has been applied to a material then the adhesion of the coat to the substrate is important. A major challenge in this field of tribology is found in the accurate measurement of these properties, especially in the case of coated materials. An example of this is the phenomenon of varying hardness with the load applied, or the depth reached in a given material, during an indentation test. This is known as the indentation size effect (ISE)[3] [4] and has led to much discussion and debate.

Wear can be defined as: "The progressive loss of substance from the operating surface of a body as a result of relative motion of the surface with respect to another body"[5]. *Kloss et al*[6] stated that it is a complicated thermal, mechanical and chemical process and is therefore present in an extremely broad range of situations; from the rotating components in a motor to the impeller of a pump to the leading edge of a cutting tool. The loss of material has an obvious effect on the working life of a machine, tool or surface that is exposed to a wear process.

Wear models are used to predict the reaction of a material to a wear situation and to forecast the rate of material removal from the surface of a body. Classical wear theory begins by considering the rate of material removal as a function of the sliding speed, the hardness of the material, the load applied and the probability of a material to produce a wear particle in a given contact situation[7, 8]. There are four main theories that are used as a basis to begin a wear model: a mass balance approach, an energy balance approach, a stress/strain analysis and a contact mechanics approach to determine material behaviour.

Wear can occur in a number of different forms and these processes differ from each other when you consider the bodies that are in contact, the way in which material is removed and in what amount. The processes do not always occur exclusively i.e. several might be present in a given situation. The primary processes are: abrasion, adhesion, erosion, fretting and cavitation. For example abrasion occurs as a physical gouging effect where the harder of the two surfaces will dig into the softer material and subsequently remove material. Fretting operates by a fatigue type action where a build up of incremental strains will lead to material failure. The differences between the wear processes result in possible differences in the failure mechanism of the material e.g. through shearing away of material or through crack initiation and propagation; hence the wear process must be considered when modelling. Research that is focused on a specific application or material in a wearing environment may also include process-specific parameters that will therefore increase the consistency of a model with the application. An example of this would be the inclusion of disparate material regions within a nano-composite coating[9], modelled in an FEA package, or the incorporation of a linked thermo-mechanical simulation to represent a tool wearing situation where heat generation is a very significant factor[10].

Empirical testing is a vital stage in the development of any theoretical model. Through experimentation a proposed model can be verified and problems or inconsistencies are highlighted. It is vital again to account for which wear mechanism is present and to define/ design the test to best represent the situation under examination (WRT bodies interacting, materials, sliding speed, loads etc.).

2. Classical Wear Theory

According to the literature [11], there have been three major stages or trends observed in the development of wear models from the mid to late twentieth century. They are as follows: those based on empirical equations, those founded on a contact mechanics approach and those based on a failure mechanics approach. No general agreement has been achieved, at any level, with regard to wear: its effects, its governing variables and the best method to approach and study this phenomenon. For example during his study *Meng*[11] found that a total of 100 variables have been employed in over 180 models and that no two papers agree on the importance of any one variable in the wear process.

Friction is a very important concept and is intrinsically linked to wear. It remained as a relatively esoteric topic until figures such as Amonton [12, 13] began to study in this field. Equation 1 gives the hypothesis proposed:

$$F_F = \mu F_N \tag{1}$$

Where F_F is the friction force, μ is the coefficient of friction and F_N is the normal load applied. This equation for friction is based on two primary assumptions; firstly the stress distribution is independent of the normal load. Secondly that the load applied is proportional to the real area of contact; if each surface is considered to be composed of a complex topography of asperities then the real area of contact is said to be the common area shared between meeting asperities.

In isolation from Amonton's work, Coulomb [14, 15] also developed the same theory for governing the frictional behaviour of two materials subjected to a normal load. Further to Amonton, Coulomb also proposed that the coefficient of friction was independent of the relative velocity of the bodies.

2.1 Reye (1860) [16]

Reye begins his examination of wear by defining a situation where two bodies are in contact and are in a loaded condition. Figure 6 depicts a rectangular body in contact with a flat surface and a force applied to its top surface. The resultant pressure will be equally opposed from the surface supporting the body. Reye proposed to examine the wear resulting from a tangential stress applied as shown; this would result in an equal force, acting in the opposite direction, at the interface between the two surfaces. He stated that if this tangential stress reached a given value, dependant on the normal pressure and a friction factor *f*, that the body would start to slip. Therefore the equation he derived is very similar to Amonton's friction law:

$$q = fp \tag{2}$$

Where q is the tangential stress and p is the applied pressure. From this point Reye hypothesised that the wear occurring at the material interface, as indicated by the depth of material removed from the surface of the body is proportional to the pressure applied to the material surface

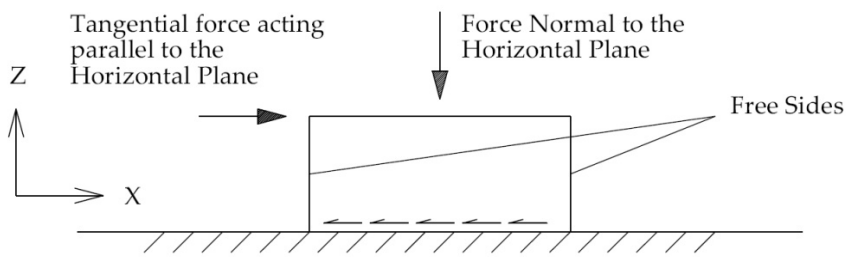

Figure 6. sliding block subjected to a normal and a tangential force (*after Villaggio et al*)

The wear relationship is defined by Equation 3:

$$L_w = K_R p \tag{3}$$

Where L_w is the depth of the wear scar, K_R is a constant of proportionality dependant on the material conditions at the contact boundary and p is the pressure applied over the contact. There have been two major questions that have been raised regarding this theory. The first point of note is the fact that the conditions assumed to be present for the normal load and tangential stress will result in a tangential stress at the free sides of the body, which is not accurate; i.e. a non-uniform distribution of shear stress would actually be the case. Secondly it is assumed that the shear stress is due only to the tangential stress applied at the top surface of the body and it does not take into account the pressure applied. Reye now considered that the volume of material removed form a body was proportional to the energy dissipated into it by the relative motion of the two contacting surfaces[17, 18].

$$V = k_R W \tag{4}$$

Where V is the volume of material removed, K_R is Reye's wear constant and W is the work dissipated into the material. Reye's method was one of the first methods to look at the wear of material from an

energy consideration standpoint. Since 1860 there have been a number of investigations that have refined his model or used it as a basis to begin a new model [16, 18, 19].

2.2 *Tabor (1939)[20]*

D. Tabor posited that the actual amount of contact between two bodies is actually much less than the apparent contact area. He has described this phenomenon by saying *"flat surfaces are held apart by small surface irregularities which form bridges"*[20]. His description of surface asperities in contact was substantiated by his empirical investigation into this phenomenon. Tabor and his associate, Bowden, have referenced a number of key developments in the area of contact mechanics. Firstly Hertz'[21] theory on elastic deformation and calculation of the variance of contact area with load was a fundamental beginning. Following on from this Bidwell [22] investigated the conductance between two crossed cylinders. Employing this theoretical basis Tabor *et al*[20] began to investigate the actual area of contact between two bodies. He proposed that since the materials are held apart by the surface asperities an applied load would force greater contact between the bodies and the conductance would therefore be increased. He developed two theoretical equations to predict behaviour of the contact. Using an elastic assumption he stated that the conductivity between the bodies would be dependant on the cubed root of the load applied; similarly, using a plastic assumption, he stated that the conductivity would be dependant on the square root of the load applied.

This hypothesis was tested and verified using a crossed-cylinders apparatus. The findings showed that the actual conductivity (and hence the actual contact area) increased with increasing load and greatest correlation was found with the equation developed using a plastic deformation assumption. Through this work the authors have contributed to the confirmation of Amonton's law of friction. They state: *"The total cross section of the junctions and hence the tangential force required to break them will be directly proportional"*

2.3 *Holm (1946)[23, 24]*

Holm began to consider the process of wear with reference to the relative motion of surface asperities. He envisaged that the individual atoms on opposing asperities were moving towards each other and colliding. His hypothesis stated that the amount of material removed during these atomic interactions was a function of the properties of the materials in contact and the load applied over the contact. This relationship is governed by Equation 5.

$$V = Z\frac{P}{p_m} \tag{5}$$

In the above equation V is the volume of material removed per unit sliding distance, z is the probability of removal of an atom per atomic encounter and would depend on the properties of the materials in contact, P is the load applied and P_m is the flow pressure of a worn surface, which is comparable to the hardness of a material.

2.4 *Archard (1953)[7, 8]*

Archard examined the wear process and decided that there were a number of key considerations that must be included in a wear model. He endeavoured to incorporate these disparate variables into one predictive equation. These considerations are as follows: the wear mechanism (adhesion), the area of contact, the contact pressure, the sliding distance and the material properties[11]. Archard's model is based upon the motion and interaction of opposing asperities on either contacting body. It should be noted that he has referenced Holm in his publications and his work could be thought of as an extension or furthering of Holm's wear equation; they are both centred on a contact mechanics approach, but Archard has decided that the wear regime will depend on a greater number of influences than Holm.

Furthermore he assumed that the deformation occurring was of a plastic type and that the material property of greatest importance was the *"flow pressure"* of the softer metal. Equation 6 is Archard's wear equation.

$$\frac{V}{S} = K \times \frac{P}{p_m} \tag{6}$$

Where V is the volume of material removed (m^3), s is the sliding distance (m), k is the wear coefficient, P is the load applied (N), p_m is the flow pressure of the material under examination. It can be seen that the rate of material removal is directly proportional to the load applied and that independent of the apparent area of contact.

This predictive equation is of great importance and has been used and cited in many empirical and theoretical studies [11, 25-30]. It has been adapted and utilised to model different forms of wear e.g. a fretting wear[30] situation which is a cyclic procedure where incremental stress and strains lead to failure in the material.

There are a number of problems with the assumption that the wear rate is directly proportional to the load, as stated by *Archard*[8]. He had followed on from his pivotal paper in 1953 to document his experimental investigations into wear of metal. He found during these experiments that there were not many situations where this law was substantiated by results obtained. There were two reasons suggested by way of explanation: firstly the surface characteristics of the materials in contact will be changing as a result of material being removed, they will generally become rougher and therefore a change in the friction coefficient by a factor of two or three could result in an alteration of the rate of wear by one or more orders of magnitude. Secondly *Archard* also considered the thermal effects in a wear regime, where surface temperatures is a major factor in the removal of material. He then investigated the heat energy produced at the surface of two connecting bodies that are moving relative to one another[31].

3. Modern Mathematical Wear Models

There are four dominant methodologies employed with regard to modern studies in this field. They are the energy balance, mass balance, stress/ strain analysis and finally a contact mechanics approach. There is no direct connection or agreement between the diverse models and equations to be found in the literature and with reference again to the work of *Meng et al* there is a range of variables and mechanisms in existence that will be seen in only one or two works. There have been a very large number of investigations into very specific applications and wear situations. In some cases authors appear to have arbitrarily chosen not only the variables that are of greatest concern to wear of the contacting materials but also the best manner in which to approach or solve the problem. There has been no formal standardisation as such in this field and this creates difficulties for both researchers and engineers that are trying to combat the effects of wear in its many different forms.

3.1 Fouvry et al (2001)[32]

Fouvry et al began an investigation into the energy absorbed by a hard material subjected to fretting wear. This method centres on a concept whereby the Kinetic energy entered or applied to the tribo-system will be reduced by the dissipative effects of the situation; i.e. a portion of the energy applied will be consumed or used up. There are a number of ways in which this energy can be spent: work done to the contacting materials against friction, to produce heat and to deform the surface asperities (in either an elastic or plastic manner) and hence the production of wear particles. Initially they investigated the suitability of the Archard equation with reference to a situation where the frictional characteristics of the system were not constant. They achieved this by utilising a range of samples with varying porosity in which a solid lubricant was suspended. Thus the coefficient of friction was varied through changes in the material porosity (over which they had control).

These samples were divided into two categories: those with a coefficient of friction (μ) greater than 0.3 and those with a co-efficient of friction less than 0.3. Subsequently a fretting analysis was executed on the samples described above using an apparatus, shown in Figure 1, which oscillates a spherical indenter in a linear pattern over the test material. To investigate Archard's model the product of the normal load and sliding was varied for each cycle (one of each coefficient of friction) of samples to be tested. Once this testing was complete the wear volume resulting was calculating by measurement of the wear scar. A considerable difference was observed between samples that had different coefficients of friction. Archard's wear equation does not incorporate this important criterion and this is,

according to Fouvry and the results he produced, a limitation that detracts from the useful potential of his equation and its principal assumptions.

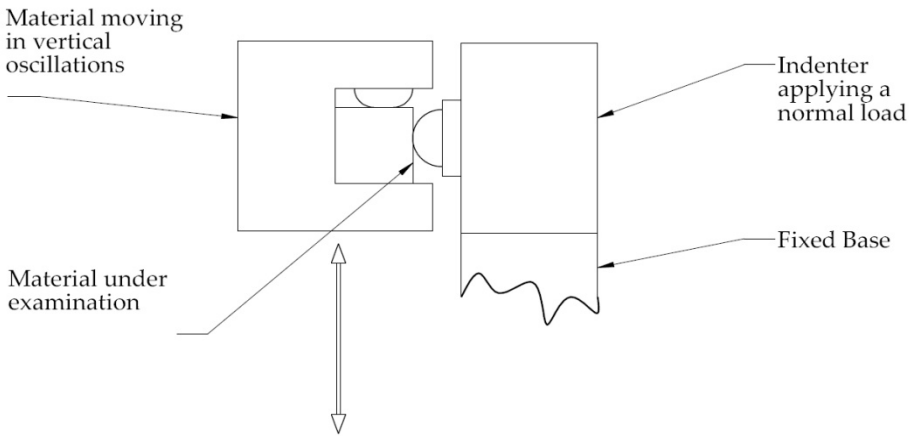

Figure 7 linear fretting apparatus (*after Fouvry et al*).

From here the author considered the energy balance method. He stated *"the wear volume can be compared with the accumulated friction work dissipated through the interface"*. Once again this friction work can contribute to a number of destructive processes e.g. abrasion, heat generation, wear fragment formation and removal etc. To begin the author states that the volume of wear matter produced will be a result of the total energy dissipated into the material, the energy needed to activate wear and will also depend on an energy wear coefficient. This relationship is shown in Equation 7:

$$V = \alpha_V(\Sigma E_D - E_{DA}) \tag{7}$$

Where V is the volume of material removed, α_V is the wear energy coefficient, ΣE_D is the accumulated energy dissipated into the material and E_{DA} is the energy required to activate wear. For the fretting experiment the energy dissipated is equated to the area within the fretting loop, which is a product of the tangential force applied vs. the deflection of the contact plotted on a scatter graph. In addition the energy applied before wear begins is derived from this experiment.

The next stage in the development of this model is the derivation of the energy wear coefficient. To achieve this the author proposes to compare the wear energy components, detailed above, to physical energy components; i.e. binding energy between molecules of constituent material, activation energy required to initiate oxidation and mechanical energy (kinetic, shear). In the following equation the wear energy needed to yield one mole of material from the interface is compared to the yield stress of the materials and the volume produce. This is therefore a comparison of the mechanical elements of energy:

$$E_{\sigma y} = \sigma_y \times V_o \times N \tag{8}$$

Where $E_{\sigma y}$ is the wear energy to yield the material (J/mole), σ_y is the yield strength of the material, V_o is the atomic volume and N is the Avogadro number. Now the energy of wear is considered to be a function of the energy needed to mechanically deform the surface of the material coupled with the activation energy needed to begin oxidation. The energy per mole of material worn is given by equation 9:

$$\varphi_{mol} = C_f(E_{\sigma y} + E_a) \tag{9}$$

Where φ_{mol} is the wear energy required, C_f is a constant related to the contact arrangement, $E_{\sigma y}$ is the mechanical energy to yield the material and E_a is the activation energy of oxidation. This molar energy for wear can now be used to define the energy wear coefficient - by dividing the total volume of material removed by the energy needed per mole of material.

$$\alpha_V = \frac{V}{\varphi_{mol}} = \frac{M}{\rho} \times \frac{1}{C_f(E_{\sigma y} + E_a)} \tag{10}$$

Where M is the molar weight and ρ is the density of the material. From this derivation Equation 7 is now a usable description of the wear of material using an energy approach. Through the use of an energy based examination the author has incorporated the friction coefficient of the materials in contact and has therefore eliminated one of the discrepancies of the Archard wear model. Furthermore through the presentation of the activation energy of wear and the use of a wear coefficient the author states that mechanisms of wear can be better understood. In particular the transformation a materials microstructure during the period of "wear activation" can be better studied and understood due to these definitions.

3.2 *Savio et al (2008)[33]*

Savio et al selected, as a focus for their research, the polishing of glass moulds and the inherent material removal process. This is a very complex application where two primary wear or "damaging" mechanisms will be in operation at any one time. There will be a polishing element due to the polishing tool and an abrasive action due to the slurry used to aid in material removal. In addition there may also be an erosive element but this is not discussed by the author.

This particular application has received a wide range of interest and attention in the literature and a number of key theorems have been recognised[34]. The first hypothesis is that of a chemical action: a film of material is produced due to diffusion of the slurry into the upper levels of the glass and subsequent removal of this layer. The second theory proposes an abrasive type of action whereby a large number of fine cracks are induced into the material due to mechanical contact, the subsequent failure is due to the fracture of asperities. Thirdly a plastic flow concept is introduced where peaks of the material are heated due to friction and then deformed due to the pressure applied to them. Finally a frictional wear hypothesis is a development of the chemical action described whereby the mechanical removal of the film is now attributed to a further chemical interaction between the grains suspended within the slurry and the constituents of the glass.

After study of the pertinent literature in his chosen area the author has decided that the most suitable method for his examination is that of the abrasion deterioration. He proposes to examine the variables of concern to the process, namely: tool deformation, sliding speed, tool dimensions and the initial surface roughness. The wear apparatus of interest consists of a spherical tool which is articulated on three dimensions in a Cartesian co-ordinate system centred on the top of the work piece. As the glass is polished there will be a significant deterioration of the tool and it the apparatus will account for this degradation in order to apply a constant pressure. Thus the contact area will have a circular form that will have a Hertzian [21] type distribution of pressure.

The author now references Reye's approach to the modelling of a wear application i.e. relating the energy dissipated into the material to the volume of debris removed. In this case the formula is written in a differential form to define the rate of volume lost with respect to time. In order to do this the sliding velocity and the pressure are introduced to derive Equation 11:

$$\frac{dV}{A} = K_R p v dt \tag{11}$$

Where dV is the incremental change in volume, A is the contact area, p is the pressure applied over the contact area, v is the sliding velocity and dt is the incremental change in time. This function can now be integrated to determine the volume lost over the total experiment in the following manner.

$$\frac{\Delta V}{A} = \int_0^{\tau} K_R p v dt \tag{12}$$

$$\frac{\Delta V}{A} = K_R v \int_0^{\tau} p dt \tag{13}$$

In Equation 13, the velocity of the tool is assumed constant and so too is the wear coefficient; therefore the pressure will be integrated with respect to the time it is applied over. In the case of equation 12 the tool speed is not assumed constant and nor is the Reye coefficient. The term on the left hand side of this equation is the cumulative frictional work applied. If this term is integrated with respect to the

local pressure distribution the frictional work can be described as a function of the experiment parameters, as show below:

$$\int_0^{\tau} K_R p v dt = K_R \frac{4v_{tr}}{3v_{av}} E_{eq} \sqrt{R_{eq}} \frac{\Delta^{1.5}}{p_a} \tag{14}$$

Where v_{tr} is the tangential tool velocity, v_{av} is the tool feed rate, E_{eq} is the equivalent modulus of elasticity R_{eq} is the equivalent radius of curvature and p_a is the feed step. Equation 14 is a function of the specific process parameters and as such is a semi-empirical examination of this wear process. It begins on a purely theoretical basis and continues on to integrate process specific and experimentally derived variables to relate the friction work done to the resulting wear parameters. The author has found good correlation with work produced by other authors in the field of polishing wear/ machining[35] with regard to the wear co-efficient.

3.3 Kassman, et al(1991)[25]

This work is of vital importance as it develops a mathematical model for the wear of a coated material and its substrate and then verifies its usefulness through empirical testing. The mechanism of wear that is under investigation is abrasion and the apparatus used to simulate this process is shown in figure 8. The author's goal is to determine the wear behaviour of the coating material and the substrate simultaneously; he states that the difficulties of determining coating properties stem from the fact that most testing performs a composite wear process of the substrate and the coating together. Therefore this methodology is applied with the aim of examining the materials individually.

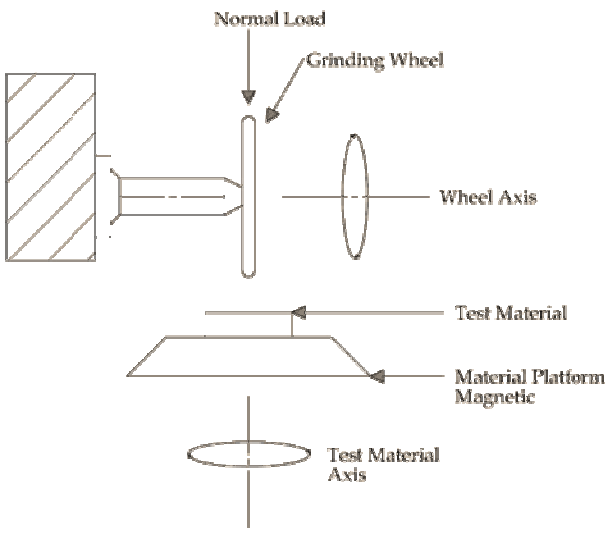

Figure 8 crater grinding apparatus (after Kassman et al).

The *"crater grinding method"* that is proposed is based on a contact mechanics approach and has as its foundation point the wear equation developed by Archard (see equation 6). The derivation of a new model begins by an initial adaptation of this equation. Rather than using the "flow pressure" of the material which is a relatively ambiguous tern, this author uses the load applied and the hardness of the material to formulate:

$$\frac{V}{S} = K\frac{L}{H} \tag{15}$$

Where L is the Load applied and H is the hardness of the material. As the material is essentially a composite there will not be a unified value for the wear coefficient, as each material will have a different affect on the tribo-system. The author introduces a new term to combine the hardness and wear coefficient for each material and this is the wear constant k, given in equation 16.

$$\square_k = \frac{\mathbf{K}}{H} \tag{16}$$

In addition as the coating is worn and the crater deepens the substrate will have a greater effect on the behaviour of the system; therefore it is proposed to use a weighted mean procedure to ascertain the global wear constant. The rate of debris formation will not be constant either and hence a derivative equation is formed.

$$\frac{dV}{dS} = kL \tag{17}$$

Where *dV/dS* is the rate of change of volume removed with respect to the sliding distance i.e. the wear rate of the material. This equation can be further refined by introducing the volume removed from the coating and the substrate respectively.

$$\frac{dV}{dS} = \frac{d(V_c + V_s)}{ds} = \frac{dV_c}{dS} + \frac{dV_s}{dS} = k_c L_c + k_s L_s \tag{18}$$

Where *Vc* is the volume removed from the coating, *Vs* is the volume removed from the substrate, *kc* is the wear constant of the coating, *ks* is the wear constant of the substrate, *Lc* is the load applied to the coating and *Ls* is the load applied to the substrate. From this point the volume of material removed and the sliding distance travelled is now investigated. The aim of the derivation undertaken is to determine the values of *ks*, *kc* and *t*, where *t* is the depth/ thickness of the coating.

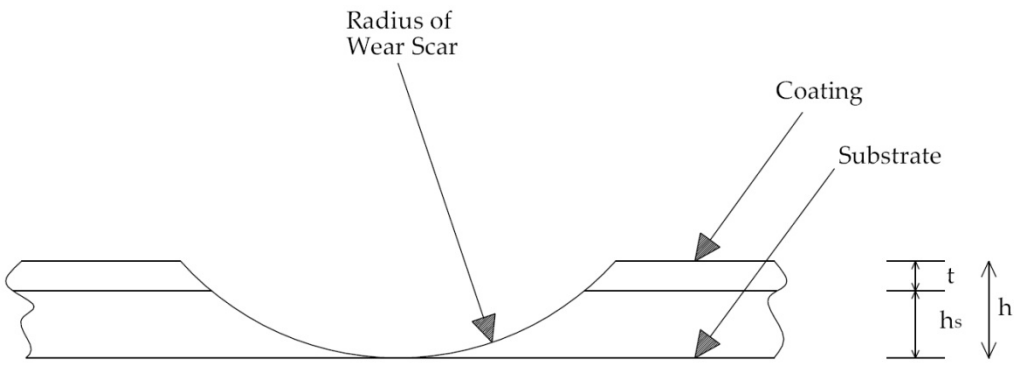

Figure 9 wear scar geometry (*after Kassman et al*)

A wear scar, as shown in figure 9, is used to begin the theoretical undertaking. Through standard geometry the total volume of debris removed from both the coating and the substrate can be found from equation 19 and the volume of material removed from the substrate is given by equation 20

$$V = \frac{\pi}{3} h^2 (3r - h) \tag{19}$$

$$V_s = \frac{\pi}{3} h_s^2 (3r - h_s) \tag{20}$$

Where h_s is the depth of the crater in the substrate alone, *h* is the total depth of the wear scar and *r* is the radius of the crater. He now separated the differential relationship *dV/dS*, as it is not possible to obtain a solution from this form, to obtain equation 20 below:

$$\frac{dV}{dh}\frac{dh}{dS} = kL \tag{21}$$

Where *dV/dh* is the rate of change of volume with respect to crater depth *h*, and *dh/dS* is the rate of change of crater depth with respect to the sliding distance. Both of these derivatives can be found: *dV/dh* can be obtained from equation 19, which will result in an equation with *r*, *h* and *t* as the variables. Similarly *dh/dS* can be obtained from derivation and manipulation of the equations given here to find a function with *r*, *t*, *h*, k_s and k_c as the parameters. Through the integration of *dh/dS*, as given in equation 22, the desired theoretical function is obtained and can be used to find the wear constant of both the coating and the substrate independently. In addition there have been two expressions derived dependant on whether the coating has been worn through or not, as can be seen in equation 23.

$$\frac{dh}{dS} = \frac{Lk_c k_s}{\pi}\left(\frac{1}{k_s(2rt - 2ht + t^2) + k_c(2r(h-t) - (h-t)^2)}\right) \tag{22}$$

$$s = \frac{\pi}{L}\begin{cases} \dfrac{rh^2 - \frac{h^3}{3}}{k_c} & when\ h \leq t \\ \dfrac{2rt\left(h - \frac{t}{2}\right) - th^2 + t^2h - \frac{t^3}{3}}{k_c} + \dfrac{r(h-t)^2 - \frac{(h-t)^3}{3}}{k_s} & when\ h > t \end{cases} \tag{23}$$

The apparatus, show in figure 8 is now used to investigate a number of advanced material coatings applied to a substrate of high speed steel (HSS). It is important to note that a datum material of the HSS is used to provide an arbitrary reference point for testing. The experiment was also tested for consistency of results by using a silicon plate. As silicon is a very homogenous material the test is repeated a number of times to see if there is any change for different samples subjected to the same load and sliding distance. It was found that the test will respond to changes of 5% or greater in the wear properties and that there is no appreciable change in wear rate.

The sliding distance of the test was found from the angular velocity of the grinding wheel and its diameter. Now k_s and k_c are found by forming two simultaneous equations from a simplified version of equation 23, hence two h values must be obtained during one experiment. The author states that this method can be used to determine the wear characteristics of very thin coatings while only removing a very small area of material. In addition the characteristics that are primary interest have been found independently as desired. However the assumption that the wear scar will be a perfect segment of a sphere may detract slightly from this approach.

3.4 Fillot et al (2007)[36]

This author begins by firstly referring to Archard and the many other works that have used his law as a basis to begin an investigation into wear. He notes however that the majority of works present in the literature centre on studying a particular application or experiment; therefore they are not suitable as predictive equations for general wear applications. It is proposed in Fillot's paper to approach the concept of wear from a new perspective rather than try and refine an established wear law.

In order to achieve this, the author proposes to approach this phenomenon from a *"global standpoint"* rather than focusing on the particular process of material removal. The author states that Archard's model does not account for the role that wear debris can play on the behaviour of the system and this must be addressed. Godet[36, 37] posited the third body theory to incorporate the particles produced, and contained within the contact area. He defined three important contributions that such a collection would have on the tribo-system: that it would support part of the load applied over the contact, that it will intervene in the contact relationship of the surfaces and that it will participate in *"accommodation velocity"*. It should be noted that in his work, Fillot assumed that the presence of wear particles in the system will act as a dry lubricant, therefore protecting the materials in contact, and not as an exacerbating agent as in the three body abrasion concept.

To formulate an analytical model the author first composes a particular definition of the third body concept stating that wear is a process characterized by three distinct phases: material detachment from the surface of a body, the mass of particles within the contact area and finally the ejection of particulate matter from the system; referring to figure 10 these are *Qs*, *Mi* and *Qw* respectively. As a result the change in mass of particles within the system can be written as a function of the two volume flow rates, as given in equation 24; the author refers to this as the mass equilibrium equation (i.e. it is a mass balance).

$$\frac{dM_i}{dt} = Q_s - Q_w \tag{24}$$

Subsequently the author defined two relationships that were essential in this wear analysis, these are the connection between Qs and Mi and secondly between Qw and Mi.

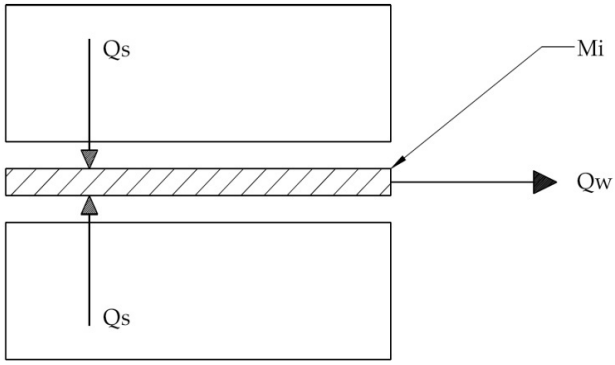

Figure 10 graphical representation of three body concept.
(*after Fillot et al*)

The first relationship (Qs - Mi) is referred to as the source flow activation and represents the particle generation process; as discussed, this was the sole concern of Archard's wear law. The author considers this in three stages. Firstly he states that the normal pressure applied across the contact will be equally shared by the surfaces and the third body. Furthermore he states that the total sliding distance occurring in the system will be composed of the sliding distance of the two surfaces and the sliding distance of the third body, which represents the shear occurring between particles, and uses this definition to arrive at equation 25.

$$dX_{total} = dX_{FB} + dX_{TB} \tag{25}$$

Where dX_{total} is the total sliding distance, dX_{FB} is the sliding distance of the contacting surfaces and dX_{TB} is the sliding distance of *Mi*. The total velocity of the system is the rate of change of distance with respect to time and therefore can be written as in equation 26.

$$u = \frac{dX_{FB}}{dt} + \frac{dX_{TB}}{dt} \tag{26}$$

Where u is the total velocity of the system. The author now considers the occurrence of shear within the system, stating that, as a preference, shear will occur in the third body rather than at the contacting surfaces as long as it is "easier" to do so. This will cease to be the case when the maximum value of shear stress has been obtained within the third body; hence at τ_{max}. The shear rate can then be expressed as a function of the max shear stress and therefore a function of the velocity within the third body and its thickness as shown in equation 27.

$$\dot{\gamma} = \frac{1}{H_{TB}} \frac{dX_{TB}}{dt} \tag{27}$$

Where γ is the shear rate, H_{TB} is the height of the third body. If the shear rate of the system is assumed to be a constant then the velocity of the third body is proportional to its height. Therefore the mass of the third body can be related to the sliding velocity:

$$\frac{dX_{TB}}{dt} = aMi \tag{28}$$

Where *a* is a constant of proportionality. No the variable Q_s is considered with respect to the sliding velocity of the bodies in contact. Referring to Archard the volume of material removed from the body is proportional to the sliding distance; hence the rate of change of volume produced (volume flow-rate Qs) will be proportional to the rate of change of sliding distance (i.e. velocity)

$$\frac{dX_{FB}}{dt} = bQ_s \tag{29}$$

$$Q_s = C_s(M_i^{max} - Mi) \tag{30}$$

Where b is a constant of proportionality. Equations 29, 28 and 26 can now be combined to find a relationship between *Qs* and *Mi*, as can be seen in equation 30. From this last equation it can be seen that the flow of material from the contact surfaces is proportional to the mass of material already

trapped in the contact area. The author does not examine the process of material removal from the surfaces in great detail but he proposes that material removal will occur when the energy present in the system cannot be absorbed by the third body.

The next stage is the development of the *"wear flow activation"* relationship (Qw – Mi). It is stated that the volume of material (per unit time) that will pass through a surface, or area, is found from the double integral of the velocity with respect to the area.

$$Q = \iint_{da} u \, da \tag{31}$$

Where u is the velocity of material passing through the incremental area da. The profile of the velocity as a function of distance from the surfaces is assumed to be analogous to that observed in fluid lubrication, therefore parabolic in profile. As a result the velocity of material at the contacting surfaces will be zero and it will be at a maximum at the centre point of the area da. Using a parabolic equation to describe this relationship between velocity and the thickness of the third body it is possible to perform the double integration in Equation 31 to obtain the following:

$$Q_w = \frac{4}{3}\rho L_x H u_{max} \tag{32}$$

Where ρ is the density of the material, L_x is the length of the contact area in the sliding direction and u_{max} is the maximum velocity of material being removed. Now the flow-rate of material can now be related to the mass of the third body at a particular time and the mass of the third body at the start of the wear regime in the following manner:

$$Q_w = C_w(Mi - Mi^{start}) \tag{33}$$

These two relations can now be solved with respect to a specific duration through the formulation of two sets of ordinary differential equations, one for the initial period of contact and another for the steady state period of wear. To verify the analytical model produced a test was devised in which a drill press was used to apply a pressure and sliding action, thus producing a wear situation. As it is very difficult to measure the actual flow rates of material the authors decided to concentrate on the change in mass produced at a number of locations: the mass of material ejected, the mass of the third body in the contact area and the mass of material removed from one surface. To ensure this was possible one of the materials was chosen to be a degradable surface and one was selected to be a "non-degradable".

The results for this test are as follows: the third body mass rose initially in line with the mass of particles produced then it achieved a steady state and remained at this level for the remainder of the test, the total mass of particles produced and the total mass of particles ejected from the system rose at a constant rate throughout the experiment and therefore the flow-rates, *Qw* and *Qs*, are also constant.

To conclude the author restates that the aim of this work was not to refine or continue existing wear laws and thinking but to look at this problem from a new angle in order to better describe, predict and understand wear. The author also raises the question surrounding the pin on disc test: i.e. why the wear process is dependant on the orientation in which the apparatus is configured. Therefore the author incorporates the way in which a particle leaves the contact area to try and account for this phenomenon. He suggests that a large amount of time has been spent in defining and investigating the various wear mechanisms but there is a distinct dearth of information on the methods of material expulsion

4. Discussion

There are four main methods of analysis with respect to wear. In this work the papers selected represent three of these four. It should be noted that three of those have referenced, and in some cases used/worked upon, Archard's Law; therefore demonstrating the impact of his work on this field. *Kassman* has used this law as a fundament to begin his study, developing a differential relationship and working to resolve this with reference to a particular geometry produced during testing. Conversely, other authors [32, 36] have stated that the assumptions inherent in Archard's law do not accurately represent the wear process; Fouvry refuted, based on investigation, the assumption that

the wear coefficient will not effect the wear process. While on the other hand *Fillot* has questioned the overall approach used by Archard in confining the investigation to a study of the mode of material removal only and not the effect this debris will have on wear performance.

Two of the authors in section 3 have selected an energy balance approach, one utilises a contact mechanics approach and one has used a three body mass balance. An importantly the mass balance approach is significantly different from the other three in that it examines the system from a global point of view i.e. considering the inputs and flow of mass rather than specific processes of material degradation. As a result of this difference in approach the variables used to relate the wear process to the removal of material will also be relatively diverse. The volume removed from a surface is a fundamental variable that is common to all papers; for the contact mechanics and the mass balance the sliding distance is also common but this is where the similarities end. The energy balance approach is concerned with the energy dissipated into the material, however both of the examples above [32, 33] examine this in a different manner: *Savio* begins by developing Reye's wear law whereas *Fouvry* begins an independent investigation into this phenomenon. These two have dissimilar variables even though they employ the same principal model (energy balance). *Fillot's* examination is concerned with the mass and flow rate of material in the system.

Each of the models selected have combined a physical testing procedure with the theoretical aspect of the investigation. However the models begin to differ in the application of these experimental techniques. The ideal case is exemplified by *Fillot et al* whereby the testing apparatus is used to verify the analytical model; *Savio et al* on the other hand first developed a theoretical hypothesis and then began to introduce terms that were specific for the testing procedure and therefore his is a semi-empirical investigation. *Fouvry* began his work by studying Archard's wear law, using a fretting wear test, with respect to the influence the coefficient of friction can have on the wear process; he then used the dissipated energy, recorded during the test to develop his relationship between wear volume and energy dissipated. Finally *Kassman et al* began their mathematical model based solely on the wear scar produced during a very specific testing procedure.

The materials in consideration are fundamental to the behaviour of the tribosystem. With respect to the studies in section 2 there have been a number of different materials used. The most relevant experiment, with regard to the materials employed, is that of *Kassman*. He investigated the behaviour of a two different coated material specimens; the substrate in both cases was HSS and the two coatings were Titanium Nitride and Titanium Carbide. *Savio* investigated glass in a grinding and polishing application, *Fillot* looked at a sintered material (easily deteriorated) and similarly *Fouvry* also used a sintered material in his work.

There is one deficiency to be observed in the examples selected and that is the lack of a sensitivity analysis. In the current literature [11] most authors, when conducting a sensitivity analysis, vary only one parameter at a time to determine the sensitivity of a model to a change in that parameter. It has been suggested that a global approach to sensitivity analysis should be employed using a modern mathematical scheme of weighted variables that interact during the analysis.

In conclusion there is a number of areas in which work is required and a wide range of benefits that can be achieved from a better understanding of wear. The strengths and findings of current models and investigations should be utilized to allow new work to progress and therefore improve our knowledge. It is in the view of this author that a multi disciplinary approach might be very beneficial; this would incorporate a global view to investigate the motion of debris during the process and then a more detailed study of the material removal process to bring an older way of thinking together with a new concept.

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NEW PERSPECTIVES FOR COAL - ASH UTILISATION: SYNTHESIS OF GEOPOLYMERIC MATERIALS

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Prethodno priopćenje / Preliminary note

Abstract: The present paper described and interprets experimental data on the synthesis and properties of fly ash-derived geopolymers, as an alternative use for coal-fly ash. In this study, Class F fly ash, which is high in aluminosilicate and low in calcium, from the Croatian coal-fired thermal power plant (HEP TE Plomin2, Plomin) was used. The fly ash (FA) was treated with sodium silicate solution (a technical grade water glass, SiO_2/Na_2O = 3.1), and then thermally cured at 85 ^oC for different periods of time. Furier transforms infrared spectroscopy (FTIR), X-ray diffraction (XRD) and scanning electron microscopy (SEM/EDS) have been used to identify the new phases and to follow the progress of their formation. It is observed that the glassy component of FA used reacted with water glass and the main reaction products formed in the alkaline activation FA (AAFA), or geopolymeric materials, was amorphous alkali aluminosilicate gel that induce a shift in the T-O (T = Si or Al) asymmetric stretching band towards lower wavenumber (1023 cm^{-1}) related to ones in the original FA (1089 cm^{-1}). The mean values of mechanical strengths of the AAFA mortars increase as reaction time increases. The lineal correlation equations among flexural and compressive strength exists for all ages studied.
Key words: Class F fly ash; alkaline activation, geopolymers, mortar, mechanical strengths.
Sažetak: U radu su prikazani i raspravljeni eksperimentalni rezultati sinteze i svojstava novih anorganskih polimernih veziva, tzv."geopolimera" temeljenih na alkalijskoj aktivaciji letećeg pepela klase F (FA) iz domaće termoelektrane (HEP TE Plomin 2, Plomin). Kao alkalijski aktivator rabljena je otopina natrijevog silikata (SiO_2/Na_2O = 3.10) uz toplinsku obradu pri temperaturi od 85 ^oC. Metodama rendgenske difrakcije (XRD), infracrvene spektroskopije (FTIR) i pretražne elektronske mikroskopije (SEM/EDS) praćen je razvoj i karakterizacija reakcijskih produkata. Uočeno je da staklasta faza iz FA reagira s otopinom natrijevog silikata, a glavni produkt alkalijske aktivacije letećeg pepela (AAFA), tj. geopolimernog materijala, je amorfni alkalijski alumosilikat što potvrđuju absorpcijske vrpce karakteristične za asimetrično istezanje veze T-O (T = Si ili Al) prema nižim valnim brojevima (1023 cm^{-1}) u odnosu na iste prisutne u izvornom uzorku FA (1089 cm^{-1}). Vrijednosti mehaničkih čvrstoća AAFA mortova rastu s vremenom. Nađena je linearna međuovisnost savojne i tlačne čvrstoće za sva vremena ispitivanja.
Ključne riječi: leteći pepeo klase F; alkalijska aktivacija; geopolimeri; mort, mehaničke čvrstoće.

INTRODUCTION

Power station, using coal like fuel, are worldwide energy sources and then high quantities of fly ash are nowadays generated. Fly ash (FA) is being usually applied in cement and concrete industry, but the material has favourable properties for more valuable application, such as the conversion into the alkali-activated aluminosilicate materials, or inorganic polymers, referred as "geopolymers" by Davidovits [1]. Geopolymers can best be viewed as the amorphous equivalent of certain synthetic zeolites and would generally have more or less the same chemical composition although the distinctive zeolitic structure is absent which makes them amorphous to X-rays. Davidovits [1] proposed that geopolymers consist of a polymeric Si-O-Al framework, not unlike that found in zeolites, with alternating SiO_4 and AlO_4 tetrahedra joined together in three directions by sharing all oxygen atoms. The fact that aluminium is four co-ordinated with respect to oxygen creates a negative charge imbalance and therefore the presence of cations such as Na^+ and K^+ is essential to maintain electric neutrality in the matrix. According to the structure, geopolymers can be expressed by the following empirical formula: $M_n[-(SiO_2)_z - AlO_2 -]_n \cdot wH_2O$, where z is 1, 2 or 3; M is an alkali cation (Na or K); n is the degree of polymerization; and w is binding water amount [1].

The basic properties of these geopolymeric materials are their fast-setting and fast-hardening at room temperature or a slightly higher temperature. They find their applications in construction materials required to have high early-age strength, resistance to acids, stability and durability, and can also be used for immobilisation of toxic and radioactive waste [2].

The alkali activation of fly ashes (AAFA) can be described as a physical-chemical process in which this powdery solid is mixed with a concentrated alkali solution (in a suitable proportion to produce a workable and mouldable paste) and stored at mild temperatures (T< 100 ^oC) for a short period of time to produce a material with good binding properties [3]. The alkaline solution most often utilised is a sodium silicate solution, although potassium silicate solutions and other alkaline solutions have also been used. The final structure and physical properties of the AAFA depends heavily on the chemical composition of the starting material, nature and concentration of alkali activator, synthesis temperature, and thermal curing time [2 – 5].

This paper deals with the alkaline activation of the Croatian fly ash for production of a novel cementitious material and with the effect of curing conditions on the compressive strength and microstructure development of the reaction products.

EXPERIMENTAL PROCEDURE

The chemical composition of the Croatian fly ash (FA) used in this work is shown in Table 1. Commercial available (Galenika-Magmasil, Serbia), technical grade sodium silicate solution – water glass, type S with the SiO_2/Na_2O = 3.10 was used as alkaline activator. The mortar was prepared according to the Croatian standards (HRN EN 196-1:2005). The size of the prisms was 4 x 4 x 16 cm. The aggregate/FA ratio used was 3/1 and the alkaline solution/FA ratio was 0.55. The fresh mortars were precuring at room temperature (about 26 ^oC) for 24 h and exposed to heat curing in a laboratory convection oven at 85 ^oC for 8 h (the C sample) and 24 h (the A sample), respectively. In the case of the B sample, the fresh mortars were

heat curing at 85 ^{o}C for 24 h without precuring at room temperature. Flexural and compressive mechanical strengths were measured at 3, 7, and 28 days (HRN EN 196-1:2005).

SEM (Tescan VEGA Electron Microscope Oxford INCA EDS), XRD (Philips X' Port Pro, the PW spectrometer 3040/60 model), and FTIR (the Spectrum One model) were used to identify the new phases and to follow the progress of their formation.

Table 1. Chemical composition of the fly ash (Plomin, Croatia), in mass %

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	LOI
48.46	19.19	10.09	2.81	1.35	4.96

RESULTS AND DISCUSSION

The chemical composition of the Croatian type F fly ash, which is high in aluminosilicate and low in calcium, is given in the Table 1.

Figure 1 shows the XRD patterns for the original FA and AAFA systems. A comparing the XRD pattern of the original fly ash with those of the geopolymeric materials, it can be seen that the crystalline phases originally existing in the fly ash (quartz, mullite and hematite) have not been apparently altered by the activation reaction. This relative large amount of fly ash still present in the hardened samples is an indication of the geopolymerisation reaction not being completed yet. Results also suggest that the structure of these geopolymers is typically glass-like. The glassy phase, reflected by board "hump" in the XRD diffractograms (Fig. 1) is convoluted partially with that of the original fly ash. In addition, the broad amorphous background feature (in the region 10 – 16° 2 theta), presented in all the AAFA samples, suggesting that the main reaction product formed is "alkaline aluminosilicate gel" with low-ordered crystalline structure[2,3].

The FTIR spectra for all the AAFA systems, as well as the spectrum for the original FA, are plotted in Fig 2. These spectra reveal the differences between the originally fly ash and geopolymers formed when the main band at 1089 cm^{-1} of the original fly ash used that corresponding to Si-O and Al-O vibrations becomes sharper and shifts towards lower wave number (1023 cm^{-1}). The appearance of the new bands at 1023 cm^{-1} could be due to polymerisation or structural reorganisation of the glassy aluminosilicate phases originally located at 1089 cm^{-1}. This is indicative of significant depolymerisation of the silicate and/or aluminosilicate networks, suggesting that the glass component of fly ash is reacting with the water glass activator and therefore a new reaction product was an amorphous alkaline aluminosilicate gel[2,3]. This observation of changes in FTIR spectra of the AAFA materials indicate that the geopolymerisation reaction occurred, leading to the formation of a main product of reaction, an amorphous aluminosilicate gel in all samples examined.

In all the AAFA samples, new bands in the regions of 1657 and 3488 cm^{-1} that were attributed to bending vibration (H-O-H) and stretching vibration OH-groups, were observed, respectively.

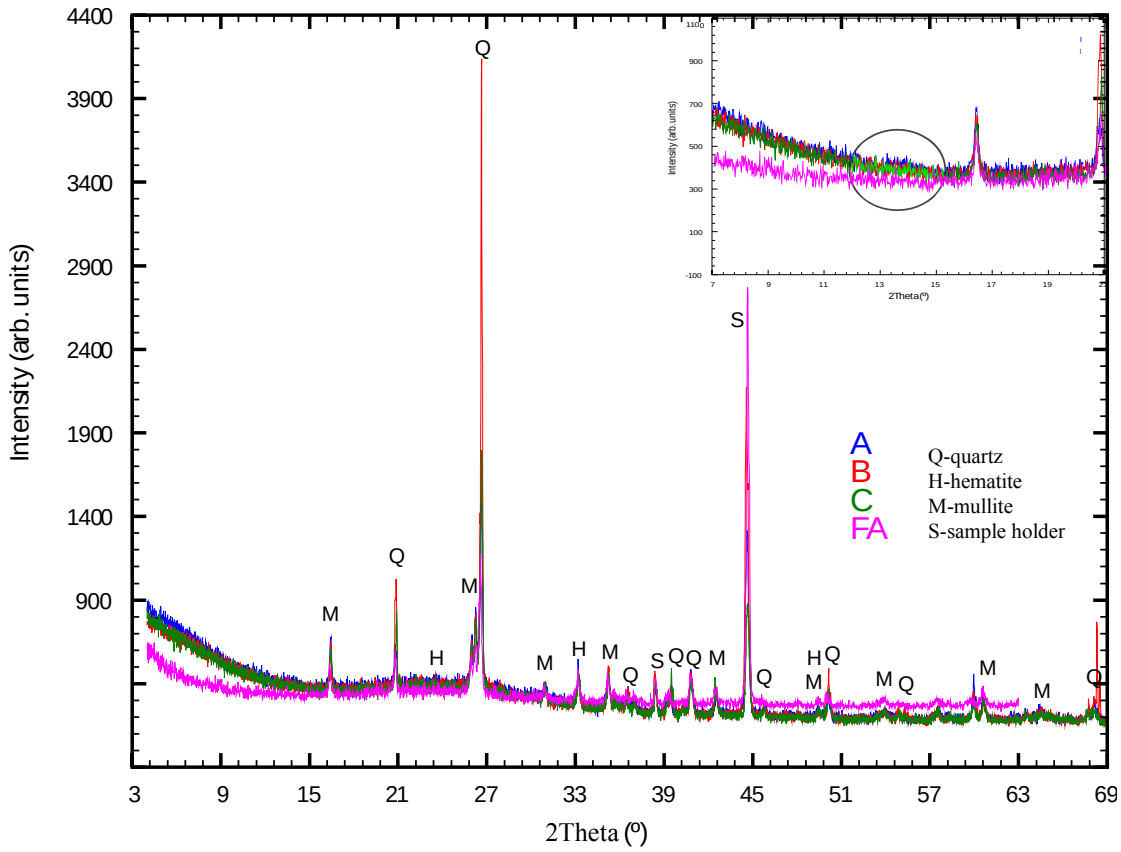
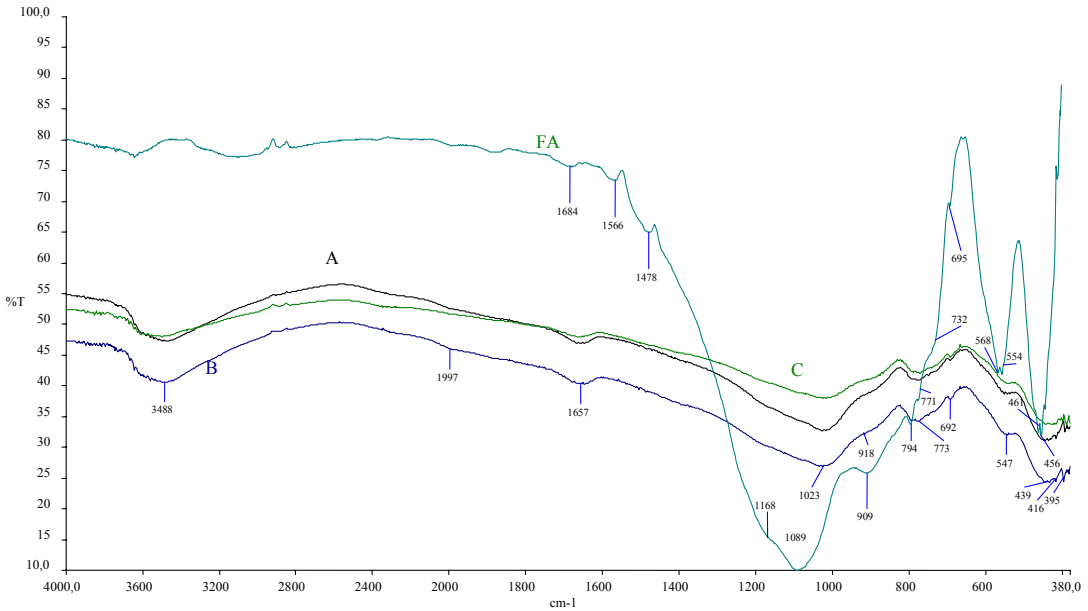


Figure 1.
XRD patterns for the original FA and the AAFA systems (the A, B, C samples).

From the analysis of experimental data a correlation between flexural and compressive strengths of the AAFA mortars at different ages (3, 7, and 28 days) has been estimated by a simple lineal regression model. The lineal equations obtained are of the type of equation: $C_N = BF_N$, where F is the value of flexural strengths at N days and C the values for compressive strengths. The results obtained (Table 2) indicate that a significant relationship exists for all ages studied. It allows the estimation of compressive strengths once the flexural strengths are known and vice versa. It is also observed that the mean value of mechanical strengths increases as reaction time increases

Table 2. Lineal correlation equations among flexural and compressive strengths and their correlation coefficient

Time, days	Lineal equation	Correlation coefficient
3	$C_3 = 2.833F_3$	0.9373
7	$C_7 = 3.734F_7$	0.8900
28	$C_{28} = 5.2807F_{28}$	0.9878



Wave number, cm^{-1}

Figure 2.
FTIR spectra for the original FA and AAFA mortars (the A, B, C samples).

In Fig. 3, the microstructure together with the EDS analysis of the hardened fly ash- based geopolymers thermally cured at 85 ^{o}C for 24 h is presented.

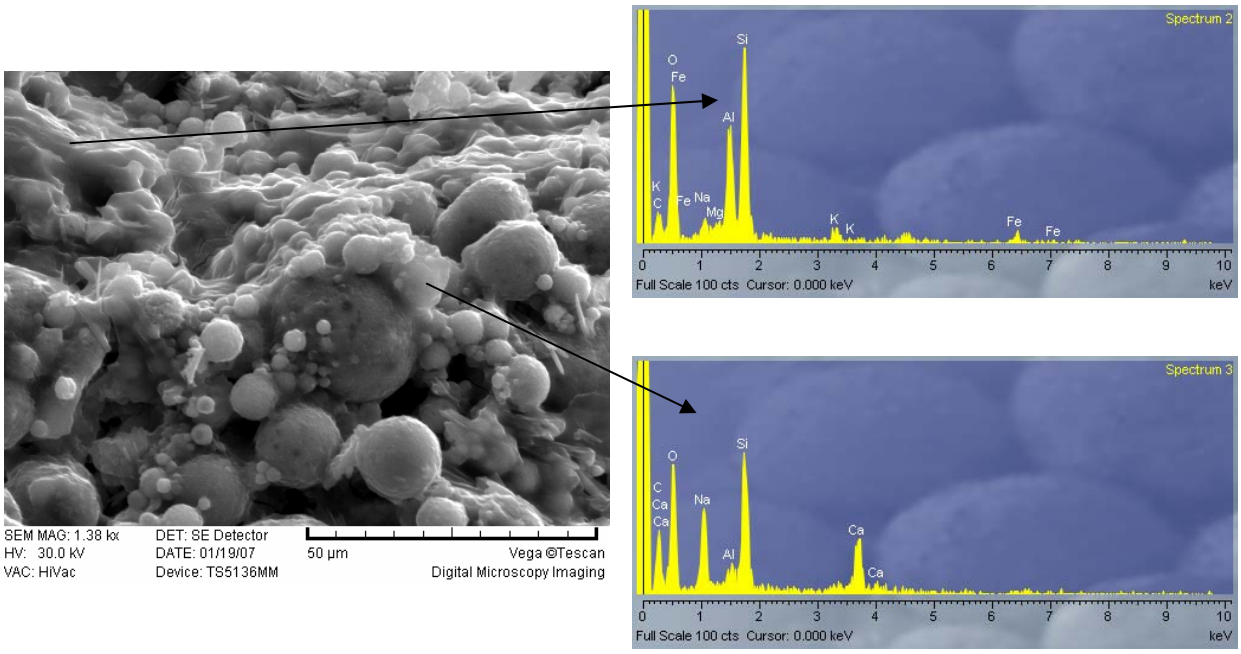


Figure 3.
SEM/EDS analyses of the hardened fly ash-activated (AAFA) mortar samples.

As it can be seen in the figure, together with the unreacted spheres of fly ash, there exists the glass-like matrix of the amorphous aluminosilicate gel. In addition to Al, Si, amount of Fe, Na, Ca, K, Mg were also found by EDS analysis in the geopolymeric materials.

CONCLUSIONS

The method applied for synthesis the AAFA mortars, described in the present work, did not cause complete dissolution of fly ash used as the FTIR spectra confirmed the presence of the 794 cm^{-1} band of quartz, and the 692 and 547 cm^{-1} bands of mullite. XRD analysis also confirms this finding. However, the disappearance of the 500-650 cm^{-1} band, as well as the displacement the main band of the original fly ash used towards lower wavenumber were observed. The appearance of the new band at 1023 cm^{-1}, attributable to three-dimensional structure of the alkaline aluminosilicate gel, suggested the depolymerisation and structural reorganisation of the amorphous phases in the AAFA materials. Mechanical strength development of the AAFA mortars were affected substantially by the curing conditions and by the duration of thermal activation, when the maximum compressive strength have achieved for AAFA mortar cured 24 h at a temperature of 85 ^{o}C . Mathematical models, describing the correlation between flexural and compressive strengths of the mortars as a function of different ages studied were established.

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INFLUENCE OF THE SURFACE CHARACTERISTICS ON QUALITY OF THE OFFSET PRINTING PLATE

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Izvorni znanstveni rad / Original scientific paper

Abstract:
The surface characteristics of the offset printing forms, beside the physical and chemical properties, is a defining factor concerning the functioning of the conventional and CtP printing forms. The quantity of the adsorbed fountain solution as the most important factor in the printing process is directly influenced by the surface characteristics of the non printing areas on the printing form. The micro grained and porous surface adsorbs a much higher quantity of fountain solution then the flat and smooth surfaces.
The research in this papers includes the measuring the factors of roughness, 3D projection and area analysis on four samples of offset plates made by different manufacturer. The results obtained show the differences, and enables to compare and define the influence of different roughness parameters on the printing forms in the printing process, and thus the final print quality on different substrates.

1. INTRODUCTION

In modern printing, offset is the most espoused technique in all parts of the world. Advantages of an offset are quick and simple preparation of the printing plate, large number of impressions per hour, possibility of printing on different substrates, both roll and sheet-fed and high quality of a print.

Differing from other printing techniques, printing plate used in offset has a flat surface elaborated with different mechanical and physical-chemical processes in a way that printing and non-printing areas, as elemental parts of a printing form, has an opponent physical-chemical properties. Printing areas of a form are oleophilic and hydrophobic, thus being able to accept oily printing ink, while non-printing areas are oleophobic and hydrophilic thus ink repellent and water attracted. However, oil attracting of a non-printing areas is not so accentuated, so ink residues on these areas are possible. In order to prevent that, water based solution that contains numerous additives is used (dampening solution).

The main and the most important physical phenomenon, which occurs on the surface of a printing plate, in both areas, is adsorption.

Adsorption is a phenomenon of substances accumulation on the barrier of two phases' surface (surface of a solid surrounded by liquid or gas) in concentration that is higher than the concentrations of both phases. Adsorption mechanism is based on free surface energy of particles on solid's surface. Particles of contiguous phase are moving chaotically and when they approach surface to sufficient distance (10^{-7} cm) under the influence of adsorption powers that attract and hold them, they are being adsorbed to the surface. Higher the free surface energy, higher the adsorption powers will be, consequently if the surface of adsorbent is larger, more substances will be adsorbed. Therefore, coarse surfaces adsorb more particles then the smooth ones. On the salient surface points, such are broaches and peaks of the wrinkles, adsorption is more emphasized due to higher non-compensated energy of surface particles in particular areas.

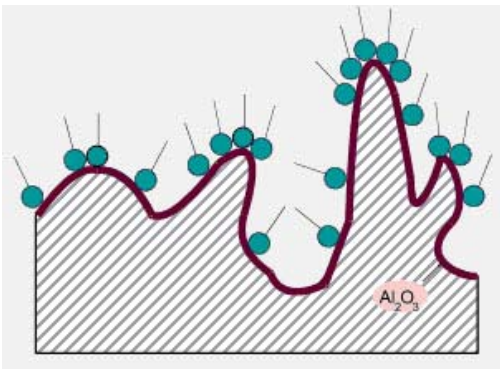

Fig. 1. *Schema of the adsorption on rough surface*

Increasing the concentration and reaction time allows particles to adsorb surface until it is completely covered, thus forming protected adsorbent film, which can be mono or polymolecular.
By the efficacy of electrostatic forces, polar molecules adsorb to the surface in such a way that molecules side which has different charge then the surface is oriented towards it, so it is about oriented adsorption [1,2]. Exactly the oriented adsorption is used in technology of offset printing.
As the most represented material in printing plates' production, aluminium with Al_2O_3 layer is generally used. Because of its polar characteristics, Al_2O_3 layer represents non-printing areas on a printing form, since it adsorbs polar molecules of water to a great extent. Plate making technique itself requires mechanical and chemical pre-processing of aluminium in order to obtain surface with desired mechanical, physical and chemical properties. Hence, aluminium surface is grained both mechanically and electrochemically, and anode coated with porous Al_2O_3 layer.
In printing process, surface roughness of a printing plate has a critical role for obtaining quality print. Important parameters in a process are also specifics of the ink, printing press and the surface characteristics of substrate used. Plates graining is special process operation of a plates manufacturer and it is to be taken into special consideration, since physical-chemical characteristics of a surface and surface phenomena on a printing plate affects printing process itself.
Depending on attributes of a measured surface profile, roughness parameters can be divided into 3 elemental groups:

1. Amplitude or vertical roughness parameters (characteristics of vertical surface deviations apart from horizontal surface inconstancy spacing Rp, Rv, Ra, Rz)
2. Longitudinal or horizontal parameters (parameters completely determined by the horizontal spacing of the surfaces rough inconstancy, apart from amplitudes of peaks and recessions)
3. Hybrid roughness parameters (parameters that depend on peaks and recessions amplitudes and on horizontal spacing i.e. depend on profile form. Cited parameters are determined only for specific control of measured surface consumption Rpk, Rk, Rvk, Mr1, Mr2 [3,4,5.]).

During the plate production, certain degree of surface micro-roughness is obtained by the mechanical, chemical and electrochemical processes. Depending on grained plate characteristics, prints are also impacted by the quality of printing and non-printing areas generation. Different manufacturers use various methods of plate graining and by measuring roughness parameters condition of a surface can be described.
Roughness of a printing plate's surface determines its alteration, friction in contact with some other surface, it defines sensitivity of a surface, appearance, consumption etc. Implementation of roughness parameters in researches, according to the function of printing plate surface and processes of its production, can significantly affect increasing of surface's consistency during printing. In order to describe condition of a measured surface adequately it is necessary to chose corresponding roughness parameters. The most often used parameters for describing surface roughness of a printing plate, in addition to parameter Ra (arithmetic average of profile deviations), are parameters Rms

(root mean squared error), Rt (maximal distance between the highest peak and lowest recession), Rz (average roughness height), Rp (average grain depth), Rk (depth of recessions in a profile), Rpk (reduced height of profile peaks) and others [6].

2. EXPERIMENTAL

As samples for measuring roughness three types of offset printing plates from different manufacturers were used:

Sample 1 aluminium-based silver halide plate
Sample 2. positive chemistry-free thermal plate
Sample 3. negative photopolymer violet plate

Analyses were performed under the same conditions for all printing plates. Offset plates were exposed and developed, so printing and non-printing areas were both on the surface of a plate. Measuring for research was performed only on non-printing areas.
Offset printing plates included into the experiment have rough aluminium base obtained by different graining treatments. Surface roughness, among the rest, affects forming of copying layers on a plate. By using the measuring methods, very clear data can be obtained; these are represented by values of roughness parameters that define basic characteristics of a printing plate.
For measuring of a printing plate's surface roughness digital measuring device **Veeco CP-II,** which allows measuring of the material surface characteristics, graphical presentation and data analysis, was used. Device used allows analysis of a surface due to very angular and precise measuring head, which moves across the sample's surface and gives representation of a sample (3D picture of a surface) with possibility of enlargement to atomic resolutions [6].

3. RESULTS AND DICUSION

Roughness of a printing plate's surface determines its alteration, friction in contact with some other surface; it defines sensitivity of a surface, appearance, consumption and weight toleration. Implementation of roughness parameters in researches, according to the function of printing plate surface and processes of its production, can significantly affect increasing of surface's consistency during printing. In order to describe condition of a measured surface adequately it is necessary to chose right roughness parameters.

Measured surface of sample 1 was 30 x 30 μm, and the results obtained by measuring roughness parameters on non-printing areas shows relatively high values of parameter Ra. Light and dark parts of a sample, which represent recessions and peaks of a printing plate's non-printing areas, can be easily determined at the surface (Fig. 2.). It is obvious that the maximal roughness (Rt) is 3.2 μm.

Roughness parameters of a non-printing areas of sample 1:

Ra = 0.4622 µm
Rms =0.5740 µm
Rt = 3.2570 µm
Rz = 1.4766 µm

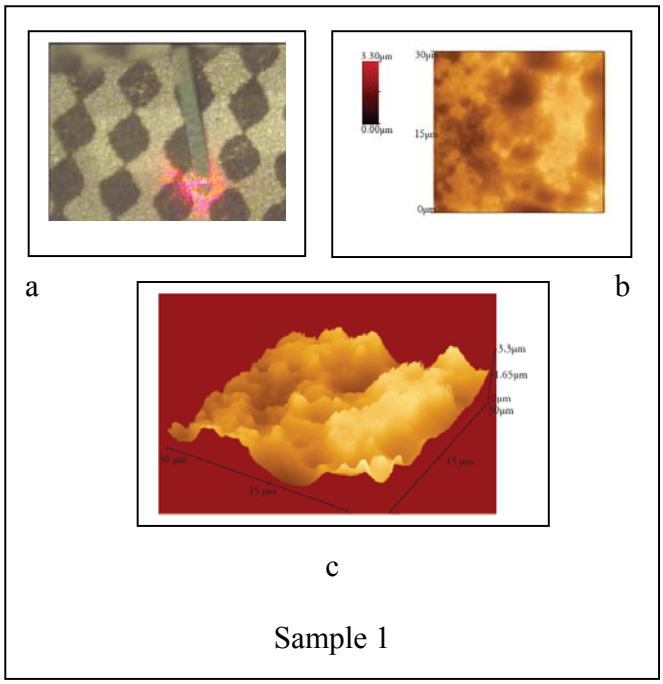

Fig. 2. *Sample 1.: a) measurement position; b) surface appearance;*

Measured surface of a sample 2 was also 30 x 30 µm, and roughness parameters, surface appearance and 3D projection are shown in Figure 3.

Data obtained by measurement show that sample 2 has significantly smaller Ra values then sample 1, which means that his micro-roughness is smaller. That kind of surface absorbs less molecules of water, so in selective wetting conditions in printing process undesired scumming can occur (Fig. 3).

Roughness parameters of a non-printing areas of sample 2:

Ra = 0.1674µm
Rms = 0.2045 µm
Rt = 0.9707µm
Rz = 0.5102µm

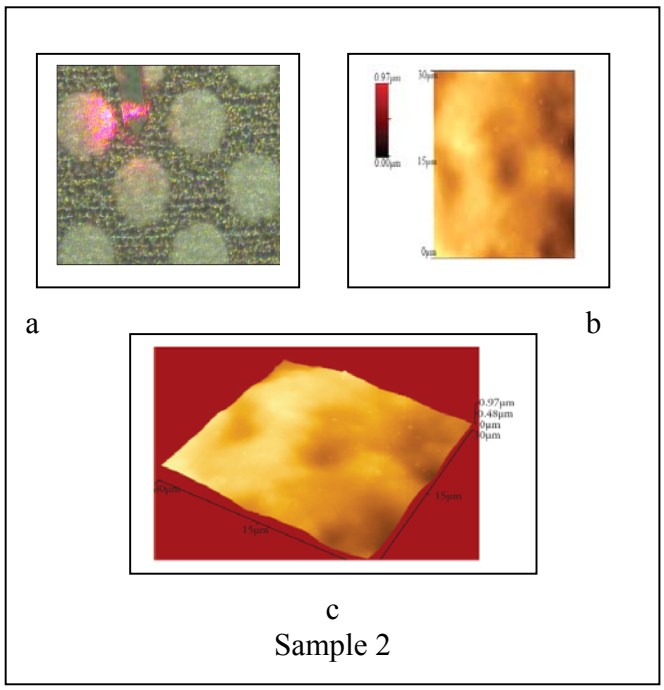

Fig. 3. *Sample 2.: a) measurement position; b) surface appearance; c) 3D projection*

Sample 3 also shows significantly lesser values Ra comparing to sample 1., thus its micro-roughness is smaller than the roughness of sample 1 (fig. 4.).

Roughness parameters of a non-printing area of sample 3:

Ra = 0.1549 µm
Rms = 0.2218 µm
Rt = 3,3168 µm
Rz = 2.1584 µm

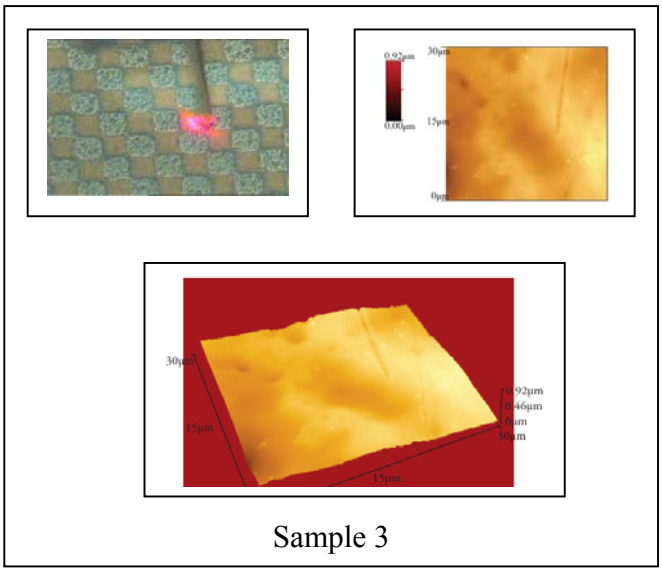

Fig. 4 *Sample 3: a) measurement position; b) surface appearance; c) 3D projection*

During printing process, by consumption of both printing and non-printing areas, some modification at the surface of a printing form occur.
Combination of a data and conditions that characterize process of consumption is expressed by the term tribologycal-system, and there are few classifications, among which are also a part related to abrasion that includes an offset printing.
When it's about offset printing, functional parts of a system are distinguished, such as printing form, blanket and interlayer (ink, water and particles of a paper dust). Consumption phenomenon can be compared with system of functional parts attributes and inter media.
Friction and consumption coefficient are not the real features of a material, but consequences of the strong irreversible and dispersal interactions between parts of a system. Tribologycal-system includes: tribo-element 1 (aluminium plate), tribo-element 2 (blanket) and interlayer (ink, fountain solution and particles of a paper dust).
Observing the originated modifications it is determined that in printing process there are loss of hydrophilic and oleophilic properties of aluminium plate's surface layer. During process of printing mechanically grained and anodized Al_2O_3 layer is being consumed, and on exhausted surface crinkles oriented toward cylinder's axis appear.
The substrate itself, as a carrier of impression, can affect changing of printing plate's roughness. It is shown that the coarser substrates, with stiff inorganic fillers, influence the larger consumption of a printing plate's surface. Although printing plate's surface is not in a direct contact with surface of a paper, paper's particles transferring to offset cylinder, and from blanket to printing plate's surface. Fillers in paper contain stiff particles, and particles detached from surface's anodized aluminium layer and detached copying layer's particles that together have an abrasive impact on the printing plate's surface, thus

decreasing its roughness. Decreasing the surface roughness during printing will affect reducing ink transfer from printing plate to the substrate.

4. CONCLUSION

CtP technology is determined by characteristics of continuous development and very emphasized and quick changes. In order to improve productivity, increase quality and simplify operating, manufacturers focus their activity on modifications existing technologies.

Since there is large number of different CtP technologies in the market, it is important to make a good choice, which, in most cases, represents compromise between quality, price and working speed.

Systematization of CtP technologies, studying basic principles and analyzing characteristics of every technology and its components, ensure quality of a final product – print. Since every component is one of the factors that affect results of a printing process, printing plates have a very important role [7]. Data obtained by measuring samples characteristics allow extremely precise representation of different plate surfaces with roughness parameters, thus enabling analysis of CtP plates surface's characteristics. From three analysed samples, highest specific surface area has sample 1. In oriented adsorption conditions, such high value of specific surface area enables binding of higher quantity of fountain solution, and consequently better printing plate handling during printing process.

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OŠTEĆENJE EKRANSKIH CIJEVI VISOKOTLAČNOG GENERATORA PARE

DEMAGE OF HIGH PRESURE STEAM GENERATING EKONOMIZER

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Izvorni znanstveni rad / Original scientific paper

Abstract: The cause of cracking/ leaking of a high pressure steam generating economizer tube are investigated. For investigation the real samples were used. Pieces of tubes were taken on place of cracking/ leaking tubes served as real sample. From each pieces two 10 x 100 mm strips were cut out. One strip was further cut into 10 x 10 mm plates. From other strip magnetite layer was separated off, ground and homogenized. The prepared samples were measured with Philips counter diffractometer and CoK_{α} radiation, scanning electron microscope atomic absorption spectrometry and optical microscopy.
Before measurement, sample plate was prepared by grinding with rough/ fine abrasive paper and etching and analyses by means of light microscopy and photographic technique know as back reflection method. The concentration of the Fe_3O_4, αFe_2O_3 and FeO phases were determined by the method of external standard. The obtained values were calculated mathematically, by Statistica software.

Key words: damage, cracking, leaking, economizer tube, analysis

Sažetak: Istražen je uzrok pucanja/ curenja ekranske cijevi visoko tlačnog generatora pare. Za istraživanje uporabljeni su realni uzorci, uzeti na mjestu pucanja/ curenja cijevi kao dijelovi cijevi. Iz svakog dijela isječene su dvije trake dim. 10 x 100 mm. Jedna traka je dalje isječena na pločice dim. 10 x 10 mm. S površine druge trake mehanički je skidan magnetitni sloj, usitnjavan i homogeniziran. Pripremljeni uzorci mjereni su na difraktometru s brojačem, tipa Philips uz uporabu CoK_{α} zračenja, pretražnom elektronskom mikroskopijom i mikroanalizom, atomskom apsorpcijom i svjetlosnom mikroskopijom. Prije mjerenja dio uzoraka u obliku pločica pripremljen je metalografski i analiziran svjetlosnom mikroskopijom, te tehnikom filma metoda povratne refleksije. Maseni udio faza Fe_3O_4, αFe_2O_3 i FeO određen je metodom vanjskog standarda. Dobivene vrijednosti obrađene su matematički, uporabom programa Statistica.

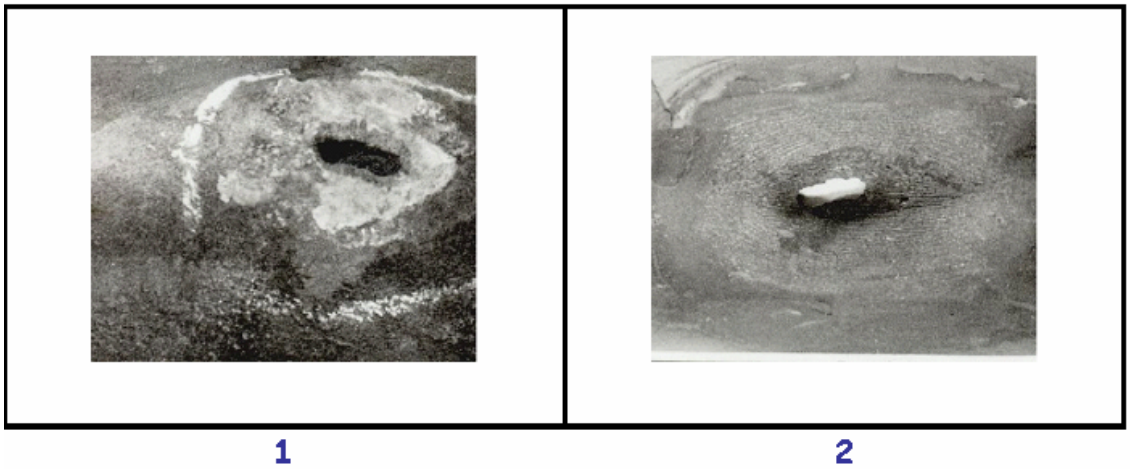
Ključne riječi: oštećenje, pucanje, curenje, ekranska cijev, analiza

UVOD

Unutar sistema visokotlačnog generatora pare, površine ekranskih cijevi su najizloženije djelovanju: visoke temperature, oksidaciji kisika otopljenog u vodi, ubrzanoj koroziji, pojavi pitinga [1], promjeni mehaničkih i tehnoloških svojstava cijevi [2], te nepotpunim uvjetima potrebnima za nastanak zaštićenog magnetitnog filma. Prema Belinecu [3] to može biti uzrokom prestanka rada visokotlačnog generatora pare i potrebitosti sanacije nastalih oštećenja. Za uspješnost njihova provođenja Jakšić [4] preporuča sistematsko praćenje i izučavanje uzroka nastalih oštećenja. Tako u svrhu iznalaženja uzroka curenja/ pucanja ekranskih cijevi visokotlačnog generatora pare uporabljene su različite metode analize. Dobiveni rezultati u cijelosti su dani u ovom radu.

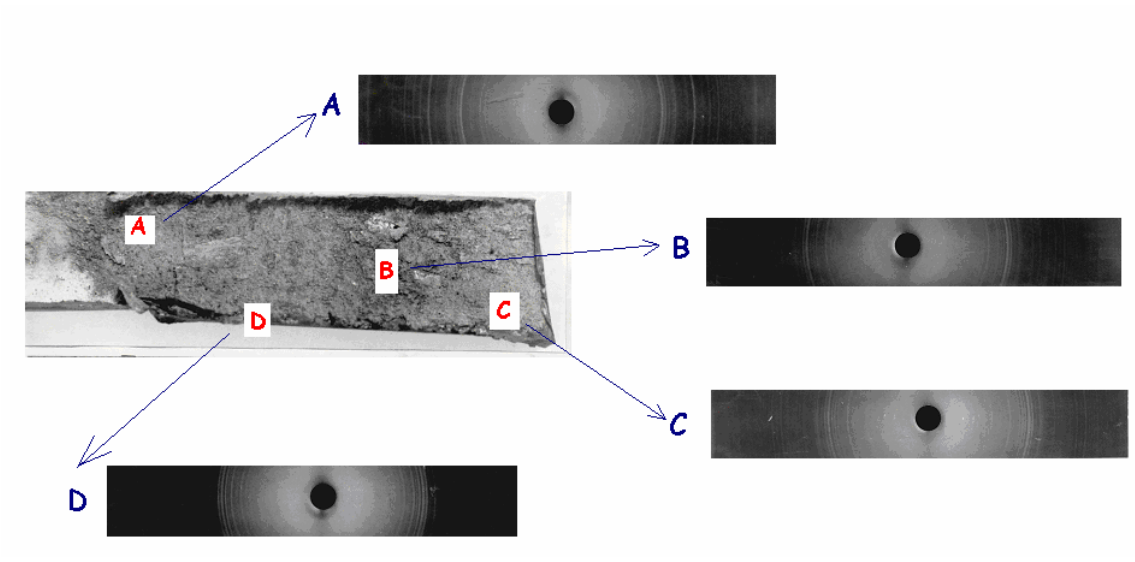
EKSPERIMENT

Za istraživanje uzroka zapaženih oštećenja na snopu ekranskih cijevi u obliku curenja i/ ili njihova pucanja uporabljeni su realni uzorci. Uzorci su uzimani izravno na mjestu zapaženih oštećenja, slika 1. kao dijelovi cijevi. Iz svakog dijela cijevi isječene su trake dim. 10 x 10 mm i/ ili sa cijele površine trake mehanički je strugan magnetitni film.



Slika 1. Prikaz oštečenja na površini ekranske cijevi: 1 – unutrašnoj i 2 – vanjskoj.

S preostalog dijela (uzetog uzorka cijevi) uzimani su uzorci magnetitnog filma ″in situ″ u obliku praha. Mjesto uzimanja uzorka praha određeno je na osnovi boje nakupina različite veličine i oblika raspodijelenih po površini magnetitnog filma, slika 2.

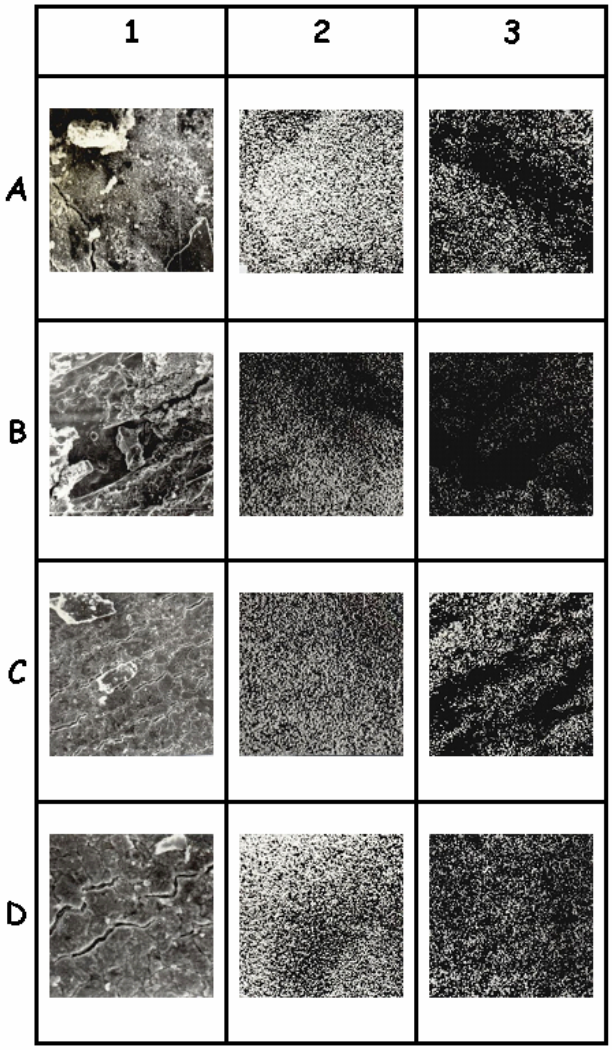


Slika 2. Snimka unutrašnje površine ekranske cijevi: **A**, **B**, **C**, **D** mjesto uzimanja uzorka ″in situ″ i njihove difrakcijske slike.

Uzeti uzorci u obliku pločica mjereni su izravno i/ ili nakon pripreme površine (*brušenjem*, *poliranjem*, *nagrizanjem*). Uzorci uzeti u obliku praha usitnjeni su i homogenizirani ručno (u ahatnom tarioniku) i/ ili mlinu za usitnjavanje i homogenizaciju, tipa Spex. Pripremljeni uzorci istraženi su: rentgenskom difrakcijom, pretražnom elektronskom mikroskopijom, spektrometrijom atomske apsorpcije i svjetlosne mikroskopije. Difrakcijske slike uzoraka snimane su tehnikom filma (Debye Scherrova metoda, metoda povratne refleksije) i/ ili brojanjem na uređaju za difraktometriju, tipa Philips uz uporabu CoK_{α} zračenja. Maseni udio faze: Fe_3O_4, αFe_2O_3 i FeO određen je metodom vanjskog standarda [5, 6]. Dobiveni rezultati obrađeni su matematički uporabom programa *Statistica*. Difrakcijske slike snimane tehnikom filma analizirane su vizualno i metodom komparacije uz uporabu JCPD – FS podataka [7 – 9]. Neki od netretiranih uzoraka u obliku pločica analizirani su na pretražnom elektronskom mikroskopu i mikroanalizatoru, u snopu sekundarnih elektrona. Metalografski pripremljeni uzorci u obliku pločica istraženi su univerzalnom kamerom, mikroskopa MF2, tipa Reichart i metodom povratne refleksije (univerzalna ravna kamera) bilježenjem debyjevskog prstena 310 Fe. Maseni udio elemenata: Zn, Ni, P, Cl, CaO, Al_2O_3 i SiO_2 je određen spektrometrijom atomske apsorpcije na atomskom apsorpcijskom spetrometru, tipa Perkin Elmer [10].

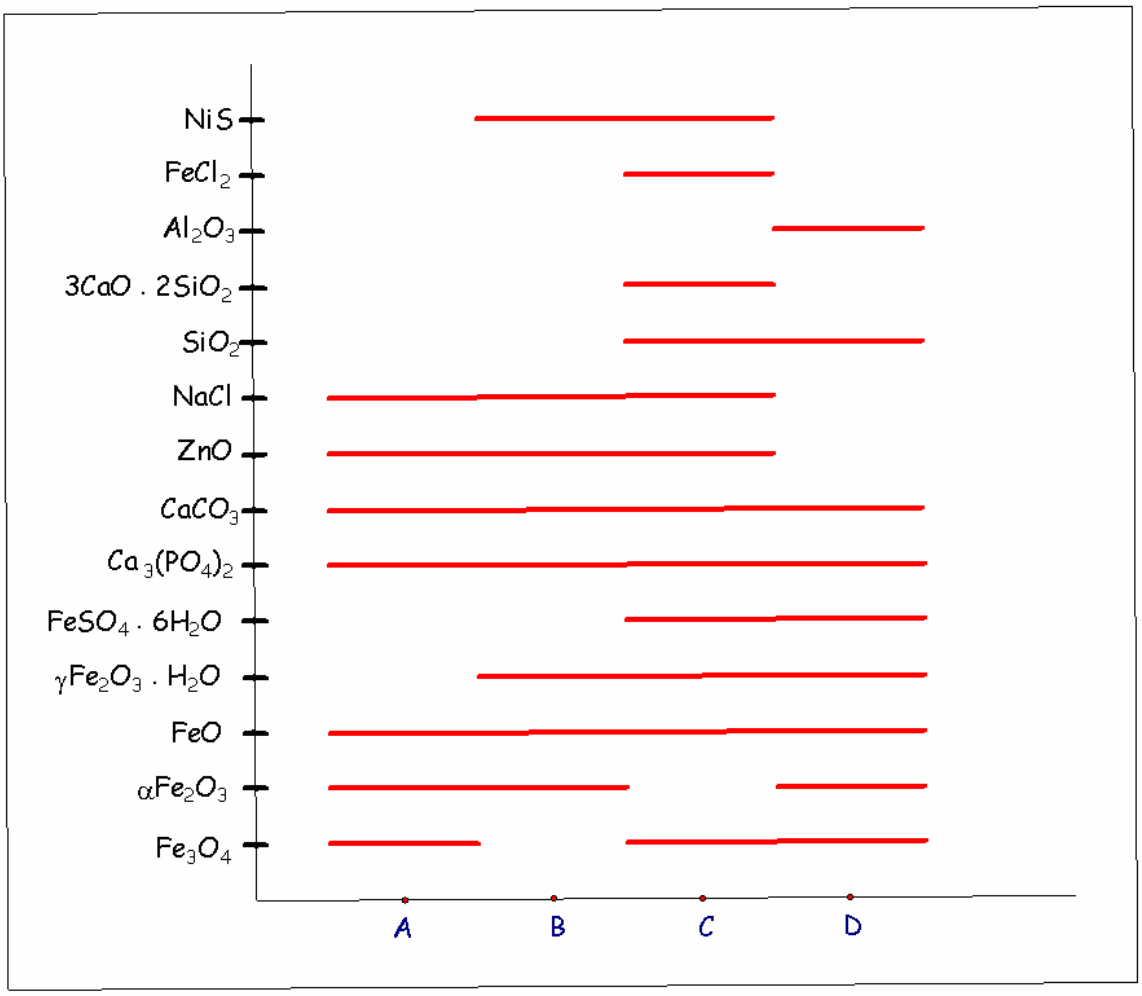
REZULTATI I DISKUSIJA

Tijekom rada generatora pare na snopu ekranskih cijevi zapažena su oštećenja u obliku pucanja i/ ili curenja cijevi. Za iznalaženje njihova uzroka uporabljene su različite metode analize. Tako uporabom metoda analize pretražne elektronske mikroskopije i mikroanalize, slika 3. zapažene su promjene u morfologiji zaštitnog magnetitnog filma u obliku pojave nakupina različite veličine, boje i oblika kao i pucanja magnetitnog filma, slika 3 – **1D**.



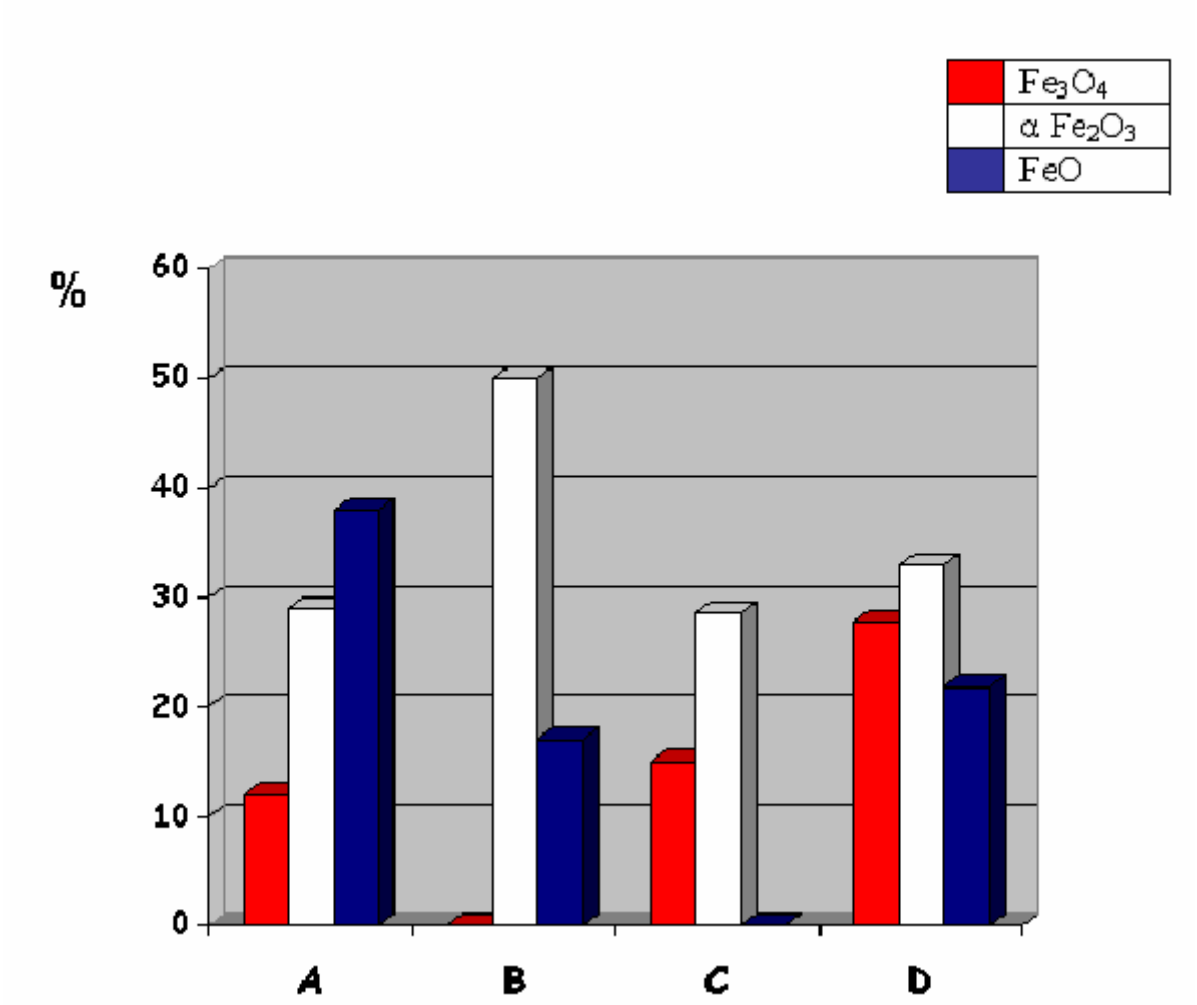
Slika 3. Mikrografija uzoraka zaštitnog magnetitnog filma (uzetih na mjestu **A**, **B**, **C** i **D**) u snopu sekundarnih elektrona pri povečanju 2000:1 i slike emitiranih karakterističnih rentgenskih zraka: 2 - FeK_{α} i 3 - OK_{α}.

Snimke karakterističnog rentgenskog zračenja: FeK_{α} i OK_{α}, slika 3 – 2 i 3 – 3 upućuju na neravnomjernu raspodjelu faza na osnovi Fe - O unutar istraživanih uzoraka zaštitnog magnetinog filma. Na analogne promjene unutar istraživanih uzoraka upućuju i dobivene difrakcijske slike 2. Već njihovo vizualno uspoređivanje upućuje na razliku u broju i intenzitetu zabilježenih debyjevskih prstena. Rezultati fazne analize dobiveni uporabom JCPDS – PDF [7 – 9] podataka, kartica broj: 1 – 1106, 5 – 0490, 5 – 0586, 5 – 0628, 5 – 0664, 6 – 615, 9 – 169, 9 – 327, 10 – 173, 11 – 614, 12 – 41, 12 – 226, 13 – 534, 15 – 393 potvrđuju raznolikost prisutnih faza. U svim istraživanim uzorcima osnovu čine faze: Fe_3O_4, αFe_2O_3, FeO, $Ca_3(PO_4)_3$ i $CaCO_3$, slika 4.



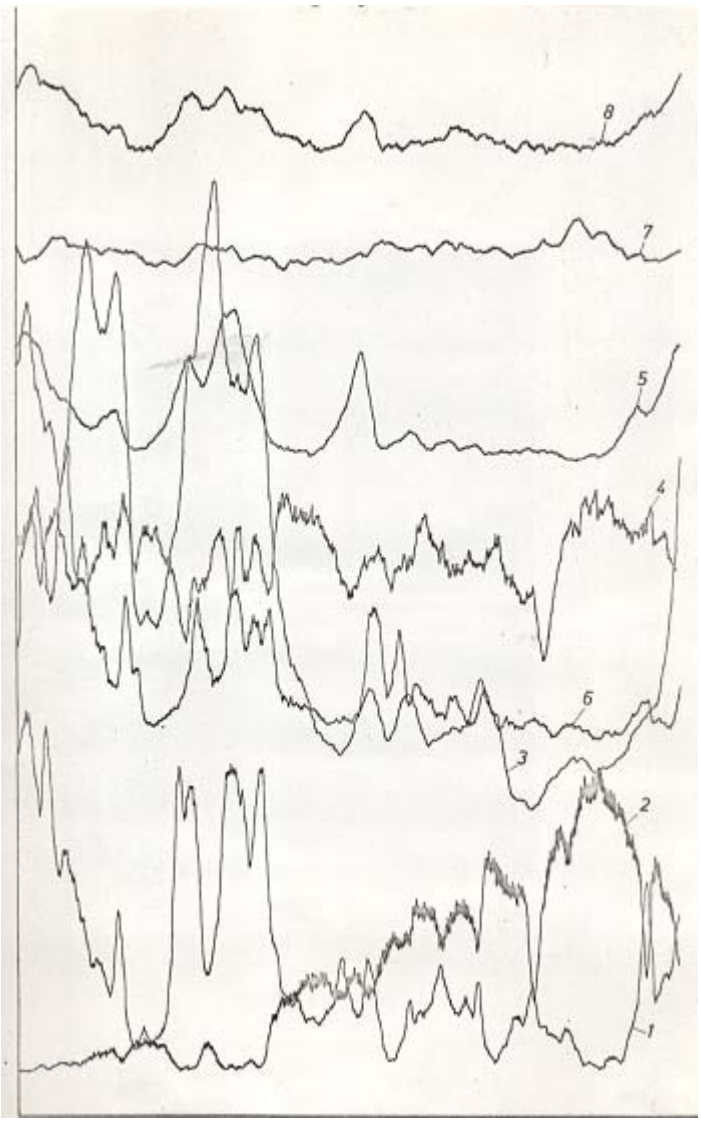
Slika 4. Raspodjela identificiranih faza unutar istraživanih uzoraka magnetitnog filma uzetih na mjestu: **A**, **B**, **C** i **D**.

Ostale faze identificirane su samo u nekim istraživanim uzorcima. Tako faza $FeSO_4 \cdot H_2O$ je identificiran u uzorku **B**, **C** i **D**; NaCl i ZnO u **A**, B i C; $FeSO_4 \cdot 6\ H_2O$ i SiO_2 u **C** i **D**; NiS u **B** i **D**; $3CaO \cdot 2\ SiO_2$ i $FeCl_2$ u **C** te Al_2O_3 u **D**. Zbog njihove prisutnosti u istraživanim uzorcima maseni udio faze Fe_3O_4 se mijenja od 2.5 % (**B**) do 28.8 % (**D**); αFe_2O_3 od 28 % (**A**) do 49.5 % (**B**) i FeO od 1 % (**C**) do 37.5 % (**A**), slika 5.



Slika 5. Promjena masenog udjela faze Fe_3O_4, αFe_2O_3, FeO unutar istraživanih uzoraka magnetitnog filma; **A**, **B**, **C** i **D** mjesta uzimanja uzoraka.

Na prisutnost i drugih faza unutar istraživanih uzoraka upućuju rezultati snimanja profila koncentracije elemenata: Fe, P, Ca, O, Si, Al, Cl i S, slika 6. te njima određeni maseni udjeli spektrometrije atomske absorpcije, tablica 1.

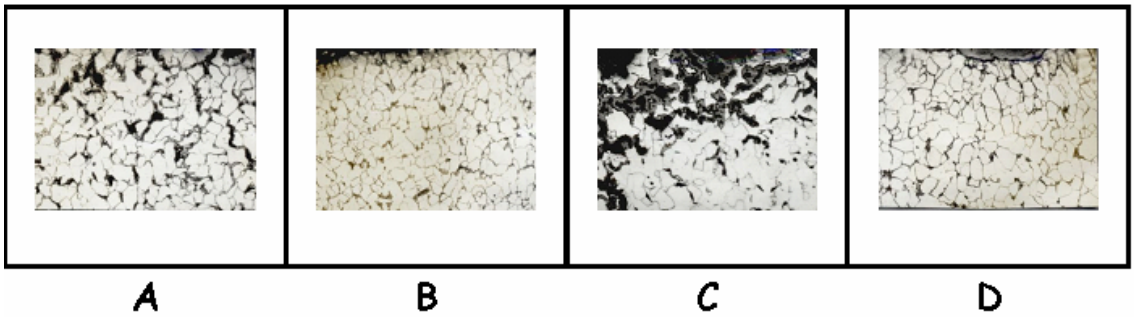


Slika 6. Profil koncentracije elemenata 1- Fe, 2 – P, 3 – S, 4 – O, 5 – Ca, 6 – Si, 7 – Al i 8 – Cl prosječnog uzorka magnetitnog filma.

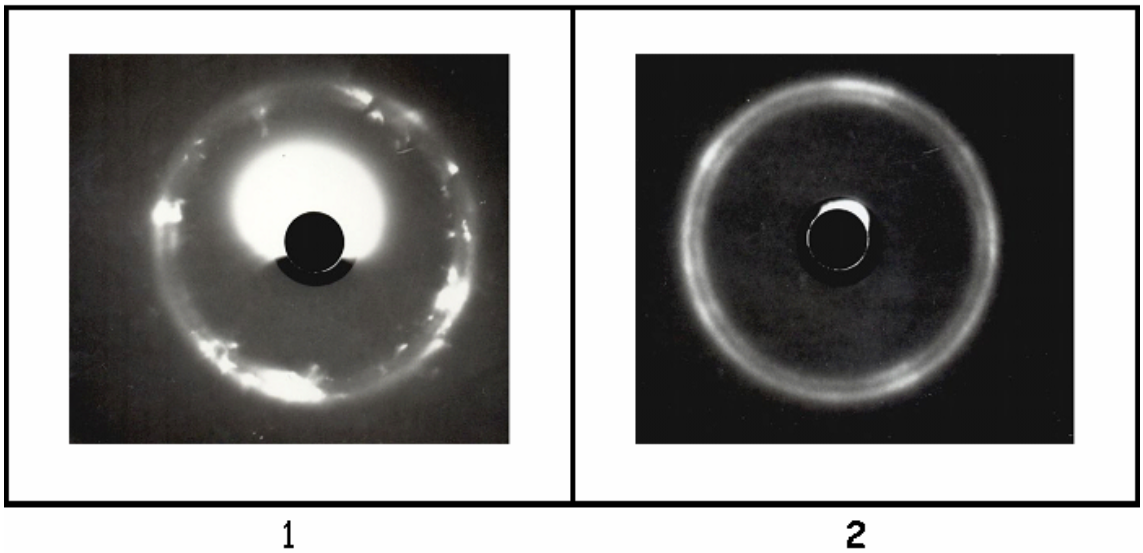
Tablica 1 Maseni udio elemenata istraživanih uzorka zaštitnog magnetignog filma

UZORAK	MASENI UDIO, %						
	Zn	P	Ni	Cl	CaO	Al_2O_3	SiO_2
1	21.697	0.672	0.221	0.055	0.112	2.920	3.940
2	2.361	5.840	0.273	0.297	0.091	0.457	1.883
3	0.642	0.146	0.082	0.068	0.084	0.119	3.026
4	0.020	0.102	0.045	0.032	0.024	0.125	2.895

U idealnom slučaju neovisno o mjestu uzimanja uzoraka magnetinog filma, maseni udio faze Fe_3O_4 je gotovo 100 %, za razliku od istraživanog slučaja. Maseni udio se mijenja od 2.5 % do 28.8 % uslijed prisutnosti novo nastalih faza: αFe_2O_3, FeO, $FeSO_4 \cdot H_2O$, $FeSO_4 \cdot 6H_2O$ i $FeCl_2$ kao produkta nisko temperaturne, odnosno NiS visoko temperaturne korozije [11], produkata nedovoljno demineralizirane vode: $CaCO_3$, $Ca_3(PO_4)_2$ i SiO [12], međuprodukta $3CaO \cdot 2Al_2O_3$ i Al_2O_3 te ZnO nastao korozijom/ erozijom neželjeznih dijelova unutar sistema [13]. Prisutnost novo nastalih produkata ima za posljedicu promjenu stukture, morfologije i debljine zaštitnog magnetitnog filma. Stijenka ekranske cijevi ne zagrijava se jednoliko. Oksidacijsko djelovanje vodene pare je povećano. Nastali atomarni vodik utječe na promjenu mikrostrukture stijenke cijevi [14] u obliku pojave interkristalne korozije, slika 7. ili pojave prenapregnutih zrna različite veličine i unutrašnjih naprezanja, slika 8.



Slika 7. Snimke mikrostrukture istraživanog uzorka ekranske cijevi na mjestima uzimanja uzoraka **A**, **B**, **C** i **D**.



Slika 8. Difrakcijska slika prstena debyjevskog prstena 310 Fe; 1 – na mjesto pucanja ekranske cijevi i 2 – 100 mm dalje od mjesta pucanja.

Naime, na mjestu pucanja ekranske cijevi debyjevski prsten 310 Fe je diskontinuiran i difuzan. Laueove točke su difuzne, neujednačene veličine i ne leže na potencijalnim mjestima debyjevskog prstena, slika 8 – 1. Prema Cullity [15] zapažene promjene u obliku Lauevih točaka posljedica su veličine zrna, a Tayloru [16] prenapregnutih zrna i zaostalih naprezanja. Na difrakcijskoj slici uzroka uzetog 100 mm od mjesta pucanja cijevi promjene su manje

izražene. Difuznost je smanjena i zapaža se razlučivanje 310 Fe debyjevskog prstena na $K_{\alpha_1}K_{\alpha_2}$ dublet uz pojavu kontinuiranosti, slika 8 – 2.

Prema Portu [17] dio nastalog atomskog vodika difundira u metal, reagira s ugljikom i/ ili se uzlučuje u obliku nakupina po granicama zrna i/ ili uključaka. Nastaju mikropukotine koje tijekom eksploatacije međusobno se spajaju u pukotine, nukleuse budućih mjesta pucanja cijevi.

ZAKLJUČAK

Dobiveni rezultati istraživanja uzroka oštećenja ekranske cijevi uporabom metoda pretražne elektronske mikroskopije i mikroanalize, rentgenske difrakcije, svjetlosne mikroskopije i spektrometrije atomske apsorbcije upućuju na promjenu:

- morfologije i strukture zaštitnog magnetintnog filma uslijed pojave nakupina različitog oblika, veličina i boja;
- faznog sastava magnetintog filma uslijed pojave faza: nisko temperatune: αFe_2O_3, FeO, $FeSO_4 \cdot H_2O$, $FeSO_4 \cdot 6H_2O$ i $FeCl_2$ i visoko temperaturne korozije NiS, nedovoljno deminiralizirane vode: $CaCO_3$, $Ca_3(PO_4)_2$ i SiO; međuprodukta: $3CaO \cdot 2Al_2O_3$, Al_2O_3 i ZnO produkta korozije/ erozije neželjeznih dijelova sistema;
- mikrostrukture stijenki cijevi uslijed interkristalne korozije, prisutnosti prenapregnutih zrna različite veličine i oblika te zaostalih naprezanja kao posljedica neujednačenog zagrijavanja stijenke cijevi, povećanog oksidacijskog djelovanja vodene pare i difuzije nastalog atomarnog vodika.

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UTJECAJ VRSTE MATERIJALA NA DIMENZIONIRANJE ALATA ZA IZVLAČENJE SA REDUKCIJOM DEBLJINE ZIDA

INFLUENCE OF MATERIAL TYPE ON DRAWING TOOL DIMENSIONING WITH WALL THICKNESS REDUCTION

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Stručni članak / Professional paper

Abstract: This paper deals with influnce of materials plastic properties on multi-gradiant tools dimensioning with wall thickness reduction.

Conducted analysis was based on designing similar steel and brass elements. Different values of logarithmic deformation rate and drawing ring angles were established for brass and steel capsules under uniform load conditions for all rings in multi-gradiant tool. Although all capsules were of the same size as preparation and output, analysis showed significant dimensional differences for multi-gradiant tools.

Experimental investigation on brass capsule confirmed that this design method fully ensures uniform load of all multi-gradiant tool rings. This method therefore ensures equal wear of all tool rings which results in minimal tool replacement during serial production.

Key words: drawing with wall thickness reduction, multi-gradiant tool dimensioning.

Sažetak: U radu je dana analiza utjecaja plastičnih svojstava materijala na dimenzioniranje višestupanjskih alata kod izvlačenja sa redukcijom debljine zida.

Analiza je načinjena na osnovu projektiranja elementa istih dimenzija od čelika i mjedi. Polazeći od uvjeta jednakog opterećenja svih prstenova u višestupanjskom alatu dolazi se do različitih vrijednosti logaritamskih stupnjeva deformacije i različitih kutova prstenova za izvlačenje za čahure od mjedi i čelika. Iako čahure u oba slučaja imaju iste dimenzije pripremka i izlazne dimenzije, analiza je pokazala da se dimenzije višestupanjskih alata bitno razlikuju.

Eksperimentalno je potvrđeno na primjeru čahure od mjedi da ovaj način projektiranja u potpunosti osigurava jednako opterećenje svih prstenova u višestupanjskom alatu. Na ovaj način osigurava se jednako trošenje svih prstenova u alatu, što dovodi do minimalnog broja zamjena alata u serijskoj proizvodnji.

Ključne riječi: izvlačenje sa redukcijom debljine zida, dimenzioniranje višestupanjskih alata

1. UVOD

Izvlačenjem sa redukcijom debljine zida skoro isključivo se proizvode čahure za sve vrste malokalibarskog oružja. Do sada su se sve čahure proizvodile od mjedi zbog povoljnih mehaničkih svojstava i lakšeg održavanja istih. U posljednje vrijeme čine se značajniji napori da se malokalibarske čahure proizvode od čelika za izvlačenje, prekrivenog tankim slojem bakra. Obzirom da su plastična svojstva čelika za izvlačenje bitno različita od plastičnih svojstava mjedi, javljaju se veliki problemi glede stabilnosti procesa pri izradi velikih serija. Osim mehaničkih svojstava čelika bitna razlika u odnosu na mjed su i tribološka svojstva, koja utječu na stabilnost procesa. U ovom radu za analizu je izabrana čahura 7,62 napravljena od mjedi CuZn28 i čelika W.Nr 1.0338.

2. PLASTIČNA SVOJSTVA IZABRANIH MATERIJALA

Za provedena eksperimentalna istraživanja korištena je mjed CuZn28, koja ima dobra plastična svojstva, tj. mogućnost obradivosti u hladnom stanju i koja je pogodna za toplinsku obradu. U tablicama 2.1 – 2.3 naveden je kemijski sastav i mehanička svojstva izabranih materijala.

Tablica 2.1 Kemijski sastav CuZn28

Kemijski el.	Cu	As	Pb	Fe	Mn	Zn
%	71,91	0,0008	0,005	0,003	0,004	Ostalo

Tablica 2.2 Kemijski sastav čelika 1.0338

Kemijski el.	C	P_{max}	S_{max}
%	0,10	0,03	0,035

Tablica 2.3 Mehaničke osobine CuZn 28 i čelika 1.0338

MEHANIČKE OSOBINE					
Srednja vrijednost	σ_m [daN/ mm^2]	$A_{11,3}$	HB	HB žareno	Veličina zrna [zrno/mm^2]
CuZn28	31,63	76,8	162,2	61,0	455
Č.0148	33,04	42,2	-	-	-

Za dobro poznavanje izabranog materijala u procesu obrade, neophodno je poznavati njegovu krivulju očvršćivanja (tečenja).
Eksperimentalnim putem za izabrane materijale određene su krivulje očvršćivanja trećeg reda. Konačan izraz za krivulju očvršćivanja za CuZn28 [1] ima oblik:

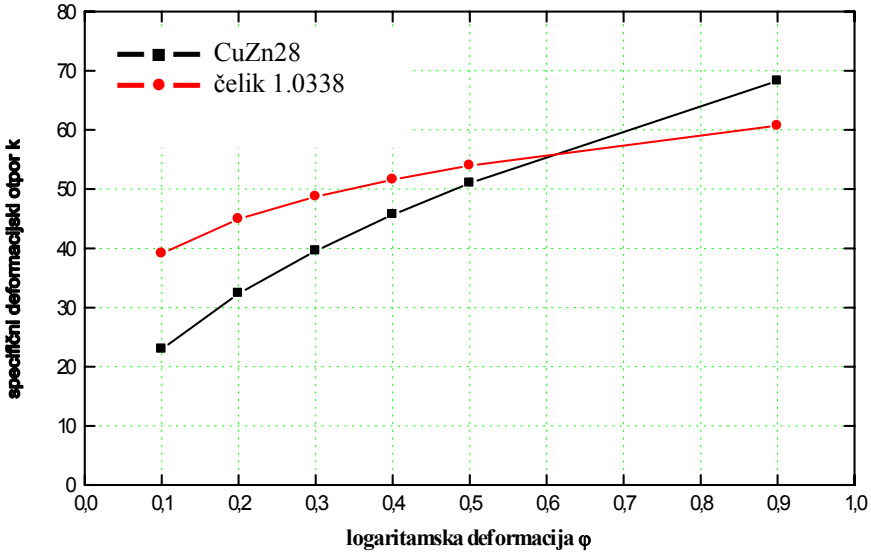
$$k = 71{,}958\varphi^{0{,}496} \qquad \left[daN/mm^2\right] \qquad (2.1)$$

Konačan izraz za krivulju očvršćivanja za čelik 1.0338 [2] ima oblik:

$$k = 62{,}15 \cdot \varphi^{0,2} \qquad \left[daN / mm^2\right], \text{ gdje je} \qquad (2.2)$$

φ = logaritamski stupanj deformacije.

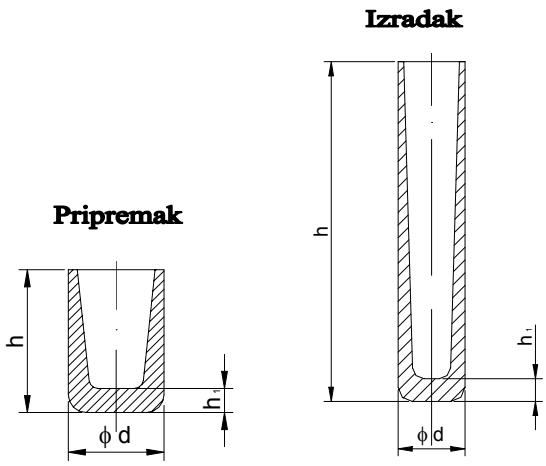
Na osnovu izraza (2.1) i (2.2) konstruirane su krivulje očvršćivanja prikazane na slici 2.1.



Slika 2.1 Krivulje očvršćivanja za CuZn28 i čelik 1.0338

Dimenzije pripremka i izratka

Za eksperimentalna istraživanja kao pripremci su korišteni cilindrični komadi.
Na slici 2.2 dan je izgled pripremka i izratka , a njihove dimenzije navedene su u tablici 2.4.



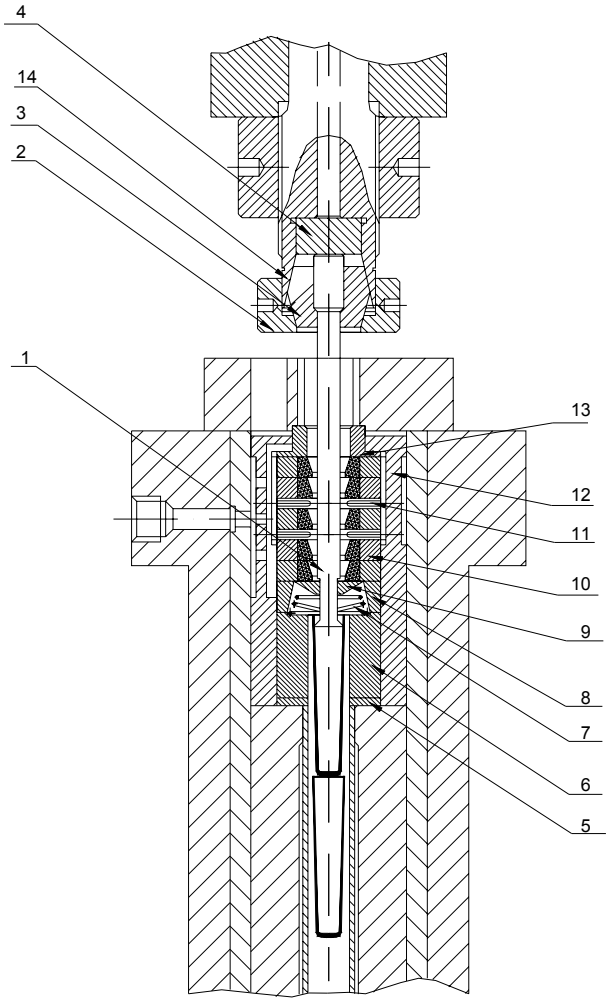
Slika 2.2 Izgled pripremka i izratka

Tablica 2.4 Dimenzije pripremka i izratka

Dimenzije	Pripremak	Izradak
d (mm)	14.2	11.785
h(mm)	21.5	77.40
h_1 *(mm)*	3.5	3.5

2.2 Izbor alata za eksperimentalna istraživanja

Za eksperimentalna istraživanja korišten je petostupanjski alat ugrađen na horizontalnu mehaničku prešu. Za mjerenje sile izvlačenja na poziciji 4 ugrađen je specijalni davač, izrađen od čelika sa nalijepljene četiri mjerne trake, povezane u puni Wheatstoneov most. Mjerni signal sa davača se registrira u uređaju SPIDER 8.



1. Izvlakač
2. Navojna matica izvlakača
3. Stezač izvlakača
4. Podložak izvlakača
5. Podmetač graničnika svl.
6. Graničnik svlakača
7. Opruga svlakača
8. Kućište svlakača
9. Svlakač
10. Prstenovi za izvlačenje
11. Podmetač
12. Nosač prstenova
13. Vodilice
14. Nosač izvlakača

Slika 2.3 Prikaz alata za izvlačenje

3. DIMENZIONIRANJE VIŠESTUPANJSKIH ALATA

Uvjet jednakog trošenja svih prstenova svodi se na jednakost specifičnih deformacijskih radova po svakom prstenu [1], kako slijedi:

$$k_1 \cdot \varphi_1 = k_2 \cdot \varphi_2 = k_3 \cdot \varphi_3 = ... = k_p \cdot \varphi_p \qquad (3.1)$$

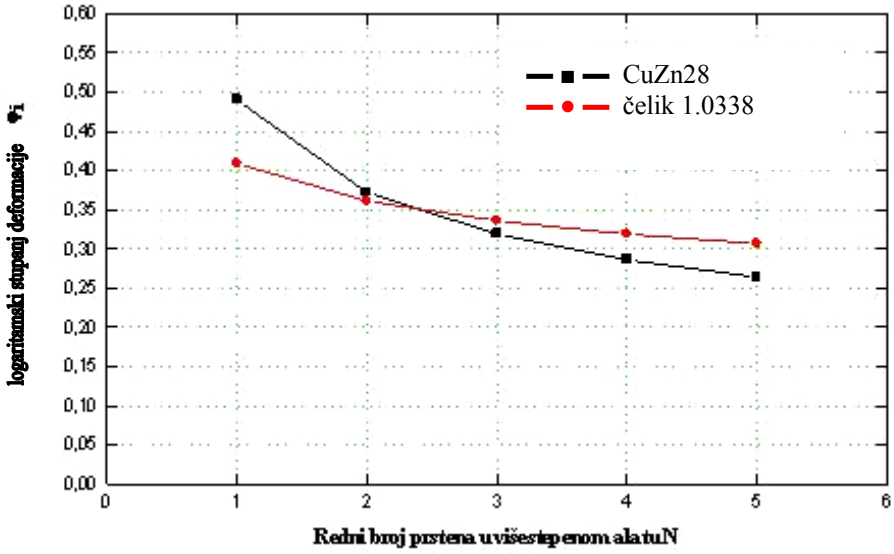
gdje su:

k_1 - k_p specifični deformacijski otpor materijala poslije izvlačenja kroz prvi, odnosno p-ti prsten

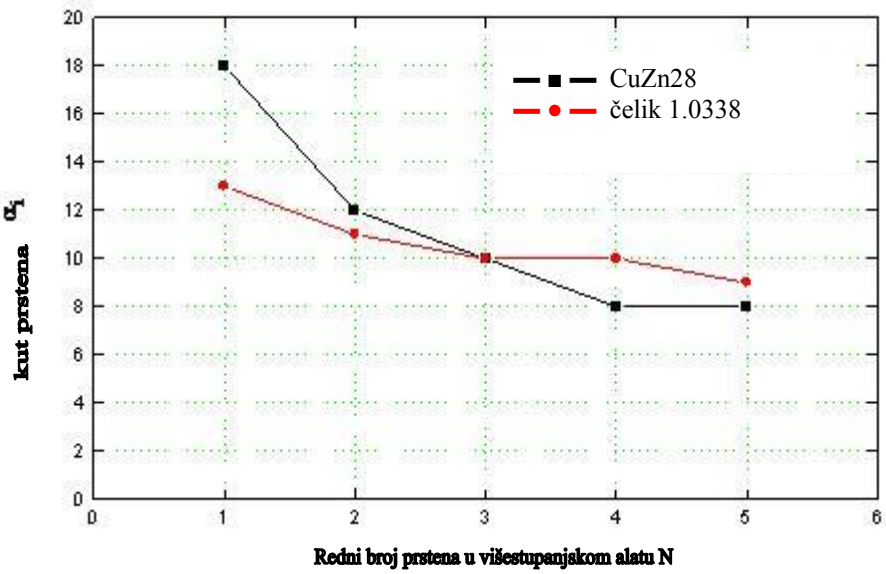
φ_1- φ_p logaritamski stupanj deformacije za prvi, odnosno p-ti prsten

Za rješavanje sistema eksponencijalnih jednadžbi, koji slijedi iz izraza (3.1), napravljen je program pomoću kojega se određuju dimenzije svih prstenova u višestupanjskom alatu.

Koristeći navedeni program [3] izračunate su logaritamske deformacije i kutovi prstenova u petostupanjskom alatu za mjed i čelik. Vrijednosti logaritamskih stupnjeva deformacije su prikazane dijagramom na slici 3.1, a kutova na slici 3.2.



Slika 3.1 Logaritamski stupanj deformacije u petostupanjskom alatu



Slika 3. Kutovi prstenova u petostupanjskom alatu

Na osnovu logaritamskih stupnjeva deformacije danih na slici 3.1 izračunate su dimenzije svih prstenova u petostupanjskom alatu za čahure od mjedi i čelika (tablica 3.1).

Tablica 3.1 Dimenzije petostupanjskog alata

Redni broj prstena	**Čahura od CuZn28**		**Čaura od čelika 1.0338**	
	d_i (mm)	**α_i °**	**d_i (mm)**	**α_i °**
1	13,05	18	13,19	13
2	12,51	12	12,63	11
3	12,18	10	12,25	10
4	11,95	8	11,98	10
5	11,785	8	11,785	9

d_i – promjer prstena

4. ZAKLJUČAK

Na osnovu postavljenog teoretskog modela za dimenzioniranje višestupanjskih alata izračunate su dimenzije svih prstenova u petostupanjskom alatu za izradu čahura od mjedi i čelika.
Eksperimentalnim putem je dokazano da su opterećenja svih prstenova u petostupanjskom alatu na primjeru izvlačenja čahura od mjedi jednaka, što je osnovni uvjet za stabilnost procesa pri izradi velikih serija.
Na osnovu podataka danih u tablici 3.1 vidljivo je da postoji znatna razlika u dimenzijama i vrijednostima kutova prva četiri prstena za čahure rađene od čelika i mjedi.

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EKSPERIMENTALNO ISTRAŽIVANJE VISOKO VISKOZNIH BINARNIH MJEŠAVINA

EXPERIMENTAL STUDY OF HIGHLY VISCOUS BINARY BLENDS

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Prethodno priopćenje / Preliminary note

Abstract: Highly viscous blends are used in process industry as medium for heat transfer. Main goal of this experimental study of highly viscous blends was to design a device for testing the heat convection coefficient α during boiling under forced flow of binary high viscous blends.
The aim was to enable virtual monitoring during boiling and to minimize influence of measuring equipment on test results.
This device could be used in investigations whose main goal is modeling and optimizing industrial processes.

Key words: Convection coefficient, highly viscous binary blends, vaporizer

Sažetak: Visoko viskozne mješavine se primjenjuju u procesnoj industriji kao radni mediji za prijenos topline.
Eksperimentalno istraživanje visoko viskoznih binarnih mješavina ima za cilj dizajniranje uređaja za ispitivanje koeficijenta konvekcije topline α prilikom vrenja pri prisilnom strujanju binarnih mješavina visokog viskoziteta.
Cilj je omogućiti virtualno praćenje fizičkih manifestacija prilikom vrenja i ostvariti ispitivanje sa što manjim utjecajem uređaja na izmjerene rezultate.
Uređaj bi se mogao koristiti u ispitivanjima koja imaju za cilj modeliranje i optimiziranje procesa za industrijske potrebe.

Ključne riječi: Koeficijent konvekcije, visoko viskozne binarne mješavine, isparivač

1. UVOD

Energija odnosno toplina kao energija u prijelazu ima značajan utjecaj na različite tehnološke procese. Kako je tehnološki proces kontrolirana radnja od strane čovjeka, pojavila se potreba za suštinskim sveobuhvatnim poznavanjem utjecaja topline u različitim procesima. Težnja proizvođača je da sa što manje utrošene energije i vremena dobiju kvalitetan proizvod.
Značajan udio u troškovima proizvodnje čine troškovi energije, tako da rješenja sa njenim boljim iskorištenjem predstavljaju izazov i iniciraju proizvođače da financiraju takva istraživanja.
U ovom radu dane su postavke za dizajniranje uređaja za istraživanje koeficijenta konvekcije topline α. Eksperimentalna istraživanja predstavljaju dio industrijskog projekta njemačkog proizvođača Bayer GE iz Leverkusena i ThEt Instituta za termodinamiku i energetiku Sveučilišta u Paderbornu.

2. KOEFICIJENT KONVEKCIJE TOPLINE α

U procesnom inženjerstvu je izražena potreba za određivanjem točne vrijednosti koeficijenta konvekcije topline. Istraživanja su se prvo vodila na najjednostavnijim mješavinama tzv. binarnim (dvokomponentnim) mješavinama nisko viskoznih fluida. Na osnovu spoznaja proizišlih iz tih istraživanja i elementarnih zakonitosti ponašanja mješavina, pristupilo se ispitivanju visoko viskoznih mješavina.
Rezultati preliminarnih ispitivanja, izvršenih na binarnim mješavinama visoko viskoznih fluida, pokazali su razlike u prenosu topline vrenjem u odnosu na binarne mješavine nisko viskoznih fluida. Pokušaji modeliranja procesa sa ustanovljenim odnosima (korelacijom) za vrenje prilikom strujanja fluida, otkrili su velike razlike između izračunatih i izmjerenih vrijednosti koeficijenta konvekcije topline α. Industrija ima potrebe za točnim podacima i empirijskim jednadžbama, koje definiraju fizičke karakteristike i manifestacije vrenja.
Koeficijent konvekcije topline α može se definirati na slijedeći način:

$$\alpha = \frac{\dot{q}}{(T_s - T_{zas})} \quad \left[\frac{W}{m^2 K}\right] \tag{2.1}$$

gdje su:

$\dot{q}$ - toplinski tok;
T_s -temperatura čvrste stijenke i
T_{zas} -temperatura zasićenja kapljevine.

Koeficijent α u mnogome se razlikuje u ovisnosti udaljenosti fluida od grijane površine, pa se uslijed toga uvodi pojam lokalnog koeficijenta konvekcije topline. Uslijed potrebe za pojednostavljenjem u proračunima se koristi srednji koeficijent konvekcije topline, kojeg većina autora definira kao dovoljno udaljeno mijesto od čvrste površine. Koeficijent α je funkcija: faktora oblika površine, veličine tijela, režima strujanja fluida, brzine, tlaka fluida, termofizičke karakteristike fluida itd. Glavni problem u analizi koeficijenta konvekcije je njegovo predviđanje za dizajnerske potrebe. U tablici 2.1 dane su vrijednosti koeficijenta konvekcije u ovisnosti o načinu konvekcije.

Tablica 2.1 Primjer odnosa vrijednosti koeficijenta konvekcije

Sustav konvekcije	Vrijednost α kW/(m^{2}K)
Slobodna konvekcija	0,004-0,05
Prisilna konvekcija (zrak)	0,01-0,55
Prisilna konvekcija (kapljevine)	0,1-5,5
Toplinski prijenos prilikom vrenja (voda)	1,0-110,0
Kondenzacija (para, filmski sloj)	0,55-25,0
Prisilna konvekcija (taljevine metala)	3,0-110,0

3. VISOKO VISKOZNE BINARNE MJEŠAVINE

Poslije ispitivanja mješavina nisko viskoznih fluida uslijedila su ispitivanja koeficijenta α kod binarnih mješavina visoko viskoznih fluida. Visoko viskozne mješavine fluida donose veliki broj nepoznanica i konstruktivnih problema koji se nisu javljali kod nisko viskoznih mješavina (viskozitet dovodi do velikog pada tlaka u cijevima, konstrukcija pumpe je složenija itd).
Za eksperimentalna istraživanja je upotrijebljena binarna mješavina fluida sastavljena od jedne komponente koja je izrazito visoko viskozna (viskoznosti do 1000 Pas) i druge koja je izrazito nisko viskozna.

Tablica 3.1 Fluidi upotrijebljeni u ispitivanjima

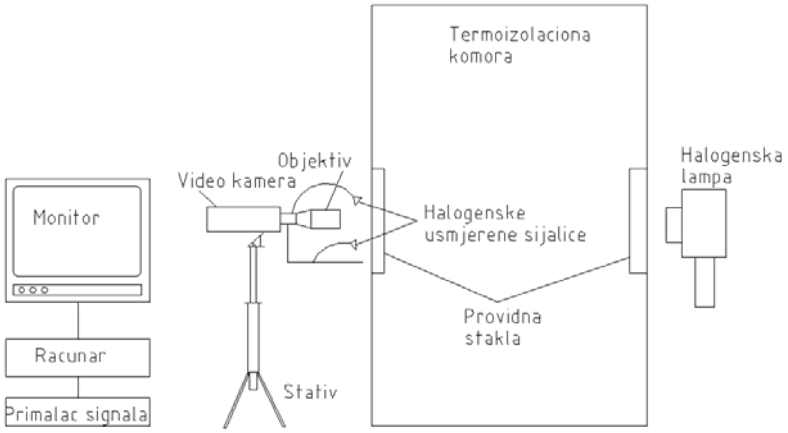
Karakteristika mješavine	**Fluid**	**Temp.Vrenja /viskozitet**	**Fluid**	**Temp.Vrenja /viskozitet**
Fluidi s niskom temperaturom vrenja.	R-22	-40,7 °C 1,256 mPa s		
Mješavine nisko viskoznih fluida s različitom tem. isparavanja	n-Hexan C_6H_{14}	69 °C 2,94 mPa s	n-Pentan C_5H_{12}	36,1 °C 2,40 mPa s
Mješavina visoko viskoznog i nisko viskoznog fluida	Polydimethylsiloxane $(CH_3)_3SiO$ $[SiO(CH_3)_2]_n$ $Si(CH_3)$	>200 °C 130546 mPa s	n-Pentan C_5H_{12}	36,1 °C 2,40 mPa s

Polydimethylsiloxane, poznat pod drugim nazivima **PDMS**, **dimethicone**, **E900**, je najrasprostranjenije korišten organski polimer na silikonskoj bazi. Posebno je prepoznatljiv po neobičnom svojstvu prilikom tečenja, optički je proziran i općenito se uzima da je inertan, neotrovan i nezapaljiv. PDMS je dodijeljen CAS broj 63148-62-9 i često je nazivan dimethicone što je jedna vrsta silikonskog ulja. Kemijska formula mu glasi $(CH_3)_3SiO[SiO(CH_3)_2]_nSi(CH_3)_3$ gdje je n broj ponavljajućih monomernih $[SiO(CH_3)_2]$ jedinica. Tokom polimernog procesa ona proizvodi potencijalno opasan hidro klorofidni gas. Polimer se proizvodi u širokom području viskoziteta, od rijetke tečnosti (kada je n vrlo mali), do plastične mase polučvrstog stanja (kada je n veoma velik). PDMS molekule imaju veoma fleksibilan polimerni kostur (ili lanac), zahvaljujući njihovoj

silikonsko uvjetovanoj vezi. Tako fleksibilan lanac postaje lako veziv kada je molekularna težina velika, što rezultira da PDMS ima neobično veliku vrijednost viskoelastičnosti. Viskoelastičnost znači da na visokim temperaturama, PDMS se ponaša kao viskozna kapljevina, slična medu. Međutim, na niskim temperaturama ponaša se kao elastično tijelo, slično gumi. Drugim riječima ako se ostavi PDMS na površini duže vrijeme, poteći će i prekriti površinu. Međutim, ako se napravi kugla (lopta) od PDMS i baci na površinu, odskočit će od nje kao gumena lopta. Za točnija ispitivanja karakteristika PDMS koristimo dinamičko mehaničku analizu. Ona zahtijeva korištenje specijalnih instrumenata za određivanje karakteristika tečenja materijala za široki raspon temperatura, masenog protoka i deformacija. Zbog PDMS-ove kemijske stabilnosti on se često koristi kao kalibracijski fluid za ovu vrstu ispitivanja. PDMS se upotrebljava mnogo za proizvodnju silikona (akvarijski silikon), u fluidima za prijenos topline, kozmetici (gelovi za kosu)itd. PDMS se koristi u prehambrenoj industriji kao aditiv E900. PDMS može biti ispresjecan u mreže i često se koristi u sistemima za ispitivanje elastičnosti polimernih mreža.
n-Pentan , poznat kao **amyl hydride ili skellysolve** je alkalni ugljikovodik. To je kapljevina, kemijska smijesa, uglavnom upotrebljavana kao gorivo ili razrijeđivač. Oblik n-pentan je linearni kao i kod n-butana samo što je duži ugljikovodik. Kemijska oznaka mu je C_5H_{12}. Kao najisparljiviji ugljikovodik, koji je u tekućem stanju na sobnoj temperaturi, često se koristi u laboratorijima zbog svoje neotrovnosti i manjka funkcionalnosti. Pentan se može u potpunosti miješati s mnogim uobičajenim razrijeđivačima (npr. ugljikoklorid, aromatics, eter) ali se ne može miješati sa kratko lančanim amino ili kratko lančanim alkoholima.

4. POSTAVKA EKSPERIMENTALNIH ISTRAŽIVANJA

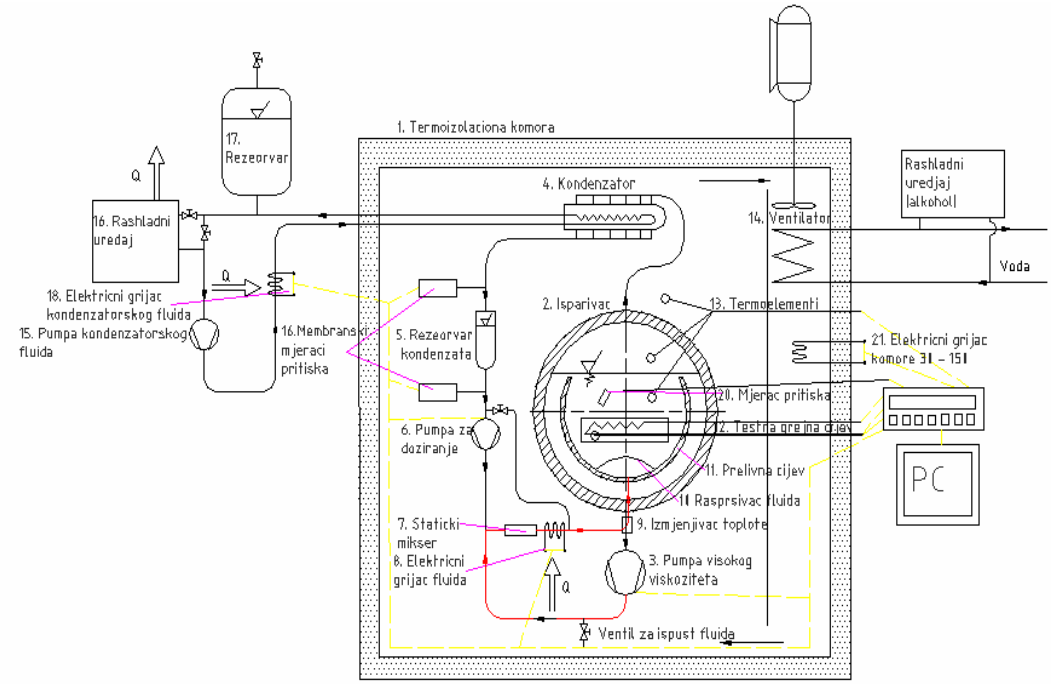
Postav eksperimenta je prikazan na slici 3.1. Visokobrzinska kamera, koja registrira do 4000 slika u sekundi, je postavljena ispred prozirnog otvora termoizolacijske komore. Sa zstražnje strane izolacijske komore postavljena je halogena lampa za stvaranje optimalnog osvijetljenja, kao i dvije male lampe na konzoli objektiva kamere. Podaci s kamere i ostalih mjernih uređaja proslijeđuju se u računalo, gdje se obrađuju.



Slika 3.1 Postav eksperimenta za ispitivanje visoko viskoznih binarnih mješavina

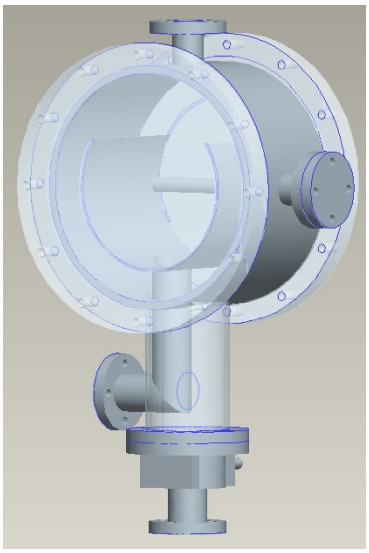
Za nastajanje uvjeta vrenja pri prisilnom strujanju fluida potrebno je imati pregrijanu površinu oko koje će fluid opstrujavati, pumpu ili neki drugi izvor koji će stvarati uvjete strujanja fluida.

Pored nabrojanih elementa potrebni su i dodatni elementi koji će omogućiti potrebne uvjete za eksperiment (mjerni instrumenti za mjerenje podataka stanja mješavine, statička mješalica i pumpa za doziranje kondenzata, koji ostvaruje kemijsku homogenost smjese, kondenzator za vraćanje isparenog n-pentana u kondenzat, kao i električni grijač i izmjenjivač topline, koji regulira temperaturu fluida. Na slici 3.2 prikazana je shema procesa.
U cilju stvaranja što idealnijeg ambijenta za provođenje eksperimenta, ispitna oprema je smještena u termoizolacijsku komoru (1). Zadatak pregrijane površine obavlja testno ispitna cijev (12), koja je postavljena horizontalno u isparivač (2).



Slika 3.2 Shema procesa

Isparivač je centralni i najvažniji predmet cjelokupne konstrukcije, u kojem se odvija proces vrenja pri prisilinom strujanju fluida, te usljed toga i isparavanje razređivača n-pentana od PDMS-a. Zbog toga što se u isparivaču događa proces vrenja, moraju se unutar njega postaviti različiti uređaji koji će obavljati sljedeće funkcije: mjerenje ispitnih podataka, homogeno opstrujavanje fluida oko ispitne cijevi, vizualni kontakt s ispitnom cijevi, omogućavanje kontinuiranog cirkuliranja fluida, brtvljenje konstrukcije.
Na slici 3.3 prikazano je konstrukcijsko rješenje isparivača za ispitivanje visoko viskoznih binarnih mješavina.



Slika 3.3 Konstruktivno rješenje isparivača

5. ZAKLJUČAK

Ponašanje binarnih mješavina je nedovoljno istraženo, dosta fizičkih manifestacija je nepoznato i nema točnih jednadžbi koje opisuju njihovo ponašanje. Koeficijent konvekcije je potrebno pronaći za svaki fluid i miješavinu, što nije lako pošto mnogo faktora utječe na koeficijent.
Istraživanja imaju za cilj ispitivanje fizičkih manifestacija mješavina koja će se upotrijebiti za optimiziranje industrijskih procesa. Visoko viskozne binarne mješavine donose sa sobom veliki broj problema u konstrukcijskom pogledu. Nepostojanje ispitivanja visoko viskoznih mješavina predstavlja veliki problem sam po sebi, jer se koncipiranje opreme ne temelji na isprobanim i uspješnim konstrukcijama nego na logičnim konstrukcijama ali neispitanim u praksi.
Oprema za ispitivanje eksperimentalnih podataka zahtjeva niz preduvjeta (laminarni tok fluida, homogeno opstrujavanje ispitne cijevi, homogeno miješanje mješavine itd.) za postizanje što točnijih ispitnih podataka i za smanjenje utjecaja opreme na mjerene podatke. Prototip opreme će ponuditi rezultate i smjernice za njezin daljni razvoj.

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LOW COST WATER TREATMENT SYSTEM FOR DOMESTIC APPLICATIONS

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Izvorni znanstveni rad / Original scientific paper

Abstract:
The supply of safe drinking water is a major worldwide problem. In the developed world the frequency of water related problems are increasing and the intervals between outbreaks of such problems are decreasing. Two thirds of the earth's surface is covered by water and the human body consists of 75 percent water. The shortage of fresh water supply is as a result of pollution from industrial, agricultural and natural disasters combined with careless or illegal dumping. To make this water suitable for human consumption, it must first be treated. General water treatment is a three-staged process. These stages are, aeration, filtration and disinfection. However, consumers do not always receive potable water even after public treatment. In some cases the consumer must treat the water being supplied to them, or have to source their own water from private wells and treat it prior to use.
This research examines the development of a simple water treatment unit, that may be used for re- treating "mains" supplied water or water abstracted from private wells. In the case of re – treating water, the unit re – disinfects the water. This ensures that all pathogenic bacteria has been neutralised. In the case of treating well water, the main focus is the removal of dissolved iron, followed by disinfection. The main application for this unit is mainly for single house operation under the following parameters,

- That the treatment is carried out without the use of chemicals
- It is simple to maintain
- It can be constructed from readily available components
- It is inexpensive to build and operate
- It is small and compact
- It is universal

While the design of this unit concentrates on single dwelling application, it is possible that the unit could be expanded to treat small groups of dwellings.
Based on results obtained for various treatments undertaken, the water treatment unit developed for this research has proven to be a satisfactory method of producing potable water for domestic drinking and use.

Keywords: Potable water, polluted water, aeration, filtration

Introduction.

This paper is a brief account of the research, design details and construction of the water treatment system. While the idea was initially conceived as a means of treating ferruginous ground water for single housesit soon became clear that it could be adapted for a greater scope. Its design is modular which means that it may be expanded or reduced for treating other water types.

Drinking water is sourced as either ground water or surface water, in either case it must first be treated to render it potable (suitable for human consumption). The treatment processes employed are coagulation, sedimentation, filtration, and disinfection. Depending on the nature of the raw water it may have to be oxidised eg ferruginous water. These treatment processes when carried out on a large scale by a municipal authority involves the use of chemicals. The chemicals used include

- Aluminium sulphate for coagulation,
- Chlorine for disinfection,
- Potassium permanganate for oxidation
- Fluoride for dental health.

All these chemicals carry certain health risks there is an estimated 60,000 tonnes of fifty different chemicals being deliberately added annually to Australia's water.[1] When this treated water is distributed to the consumer they are not guaranteed wholesome drinking water. Several factors can render this treated water unfit for human consumption, such factors include.

- Illegal branching into the main water pipe [2,3].
- Ingress of bacteria through fire hydrants [4].
- Chlorine resistant pathogens [5].

Table 1 outlines such a situation that occurred in Ireland between May to September 2007. The authorities issued "boil water" notices to householders when it was discovered the water being supplied to them was unfit for drinking [6].

Local Authority	***Name of Water Supply.***	***Reason.***	***Population Affected.***	***Date.***
Cork.	Adrigole.	E.coli.	200.	Aug-07.
Cork.	Dromore.	E.coli.	50.	Jul-07.
Fingal.	Leixlip.	E.coli.	500.	Aug-07.
Galway city.	Galway city supply.	Cryptosporidium.	90,000.	Mar-07.
Galway.	Headford.	Cryptosporidium.		Mar-07.
Galway.	Luimneagh	Cryptosporidium.		Mar-07.
Galway.	Mid Galway.	E.coli.	2,083.	Jul-07.
Kerry.	Glenbeigh.	Coliforms.	750.	Aug-07.
Laois.	luggacurran	Coliforms.	20.	May-07.
Laois.	Modubeigh.	Coliforms.	30.	Apr-07
Limerick.	Ballingarry.	Nitrates.	562.	Mar-07.
Mayo.	Swinford.	E.coli.	2000.	Sept-07.
Mayo.	Lough mask.	E.coli.	700.	Sept-07.
Mayo.	Cong.	Cryptosporidium.	500.	Mar-07.
Meath.	Ballivor	E.coli.	1,280.	Aug-07.
Sligo.	North Sligo	E.coli.	N/A	Jul-07.
South Tipperary.	Clonmel.	Cryptosporidium.	11,500.	Jul-07.
Waterford.	Ballinacorty	Turbidity.	1,500.	Jun-07.
Wicklow	Avoca	E.coli.	1,349.	Mar + Jul –07.
Wicklow.	Templecarrig.	E.coli.	300.	Jun-07.

Table 1. Boiling Notices: May to August 2007

There is a need for a system that will treat groundwater as well as water supplied by the municipal authorities. Such a system should,

- Assure the consumer that their water is safe to use.
- Be inexpensive to install.
- Be inexpensive to run.
- Be simple to maintain.
- As far as possible treat the water without using chemicals.

The purpose for this research is to, explore the possibilities of designing and manufacturing such a system. The main emphasis however is to produce a system capable of removing dissolved iron and manganese from groundwater and to neutralise any infectious pathogens.

Concept of the treatment unit.
With a clear set of objectives in mind, a unit was designed that would

- Oxidise ferruginous ground water by natural aeration.
- Filter the water through various graded media
- Remove odour and taste by charcoal filtration.
- Final filtration through a 5-micron disposable element filter prior to disinfection.
- Disinfection through ultra-violet radiation.

Aeration followed by filtration.
This is a natural approach to iron and manganese oxidation. The water being treated is aerated by pumping air through it. This accounts for the fact that there is no dissolved iron or manganese in fast running water, it is self-oxidising. High levels of dissolved iron and manganese can be oxidized by this method. Once the water has been oxidised, it is then passed through various filters, which will remove the precipitated iron and manganese, along with taste and odour where a charcoal filter is used. The maintenance of such a filter requires regular backwashing, the frequency of the backwashing is dependent on the loading of the filter medium [7]

Oxidation of the water.
Natural aeration was achieved by passing the subject water over a series of weirs, thereby inducing turbulence and effectively oxidizing the water.

The results of the precipitation test are shown in Table 2. and Figures 1 and 2.

Time (minutes)	Fe concentration mg/l .	Physical appearance. Visual.
0.	10.0.	Clear.
15.	8.0.	Beginning to cloud.
30.	6.0.	Becoming cloudier.
45.	4.0.	Cloudy.
60.	3.0	Colour deepening.
75.	3.0.	Brown.
90.	2.0.	Colour stable.
105.	1.0	Colour stable.
120.	0.0	Colour stable.

Table 2. Precipitation of Dissolved Iron

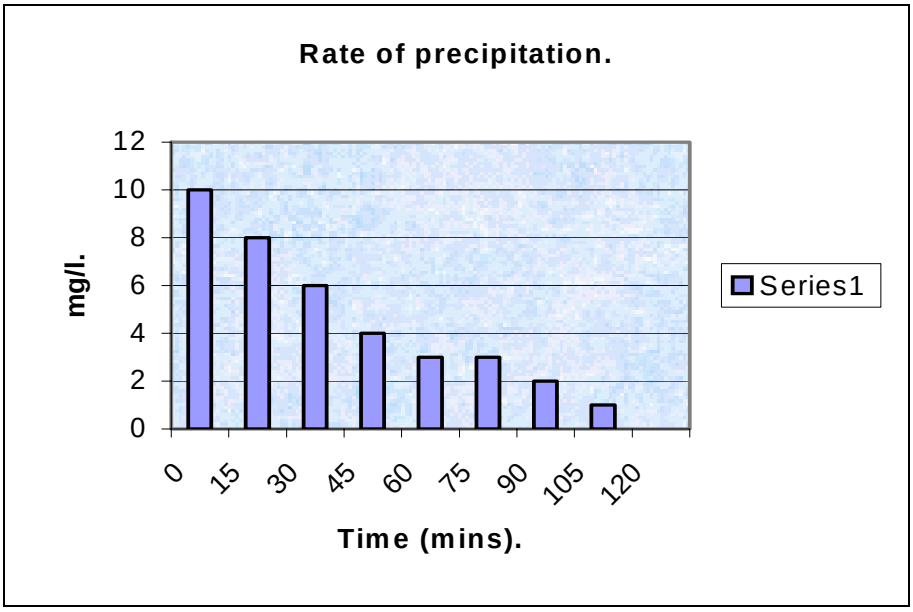


Figure 1 Precipitation Rate of Dissolved Iron unassisted.

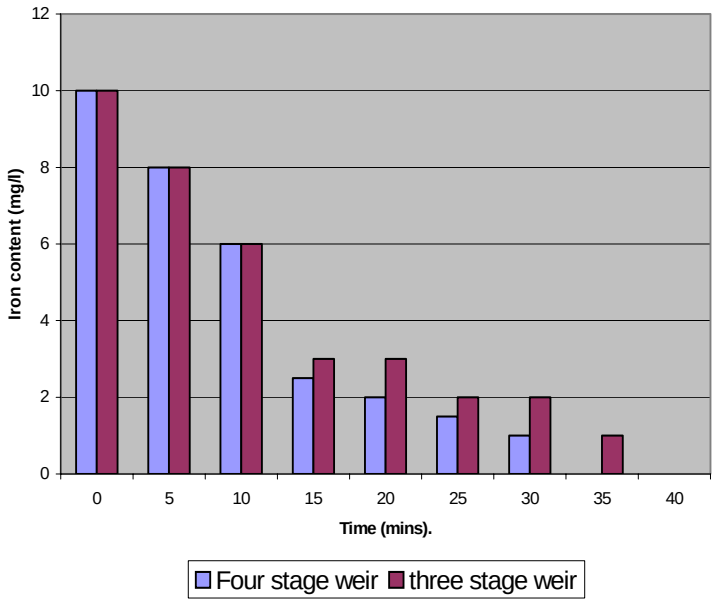


Figure 2. Precipitation Rate of Dissolved Iron using weirs.

Filtration of the Precipitated Iron from water.

Filter Design.
Prior to construction and testing of the prototype unit a series of tests had to be carried out on various filter media in order to ascertain their suitability as filters. These tests involved constructing several filters of different sizes and using different filter media, then measuring their performance rates.

Sand Selection.
The success of an effective water filter is dependent on the selection of a suitable filtering material, such a medium is usually sand. Random samples of sand were selected and tested, the tests were carried out on the samples to determine;

- The uniformity constant of the samples.
- The average grain size.
- The permeability of the various filter media.

Table 3. shows a typical grain distribution chart for a granular filter material in this case garnet. The chart shows 98.4 % of the material is retained at 300µm,thus indicating that this is a 300µm material. Table 4. shows the grain distribution chart of an unspecified grade sand. The percentage retained of this sand is not confined to any particular sieve size. It is therefore useless as a filter medium.

Sample No; 1		**Sand classification.** Garnet		**Total mass of dry sample** 559.02g	
BS Test sieves.	Mass of Sieve	Mass of Sieve / Sample	Mass Retained	Percentage Retained.	Total Cumulative Passing.
	G	g	g	%	%
2.36mm	428.51	428.51	0	0	100
1.18mm	390.68	390.68	0	0	100
600µm	433.31	658.46	2.68	0.48	99.52
300µm	321.82	406.09	550.15	98.4	1.12
150µm	338.37	338.37	6.19	1.2	0
75µm	326.58	326.59	0	0	0
Tray	268.15	268.15	0	0	0
Total.			559.02	100.08	

Table 3 . Grain Distribution garnet

Sample No; 3 Builders		**Sand classification.** Unspecified.		**Total mass of dry sample** 653.18g.	
BS Test sieves.	Mass of Sieve	Mass of Sieve / Sample	Mass Retained	Percentage Retained.	Total Cumulative Passing.
	g	g	g	%	%
2.36mm	428.51	497.23	68.72	10.52	89.48
1.18mm	390.68	540.24	149.56	22.90	66.58
600μm	433.31	611.98	178.67	27.35	39.23
300μm	321.82	479.66	157.84	24.16	15.06
150μm	338.37	411.49	73.12	11.19	3.87
75μm	326.58	348.06	21.58	3.29	0.58
Tray	268.15	271.94	3.79	0.58	0.00
Total.			653.18	99.99	

Table 4. Grain Distribution of an unspecified sand type.

Uniformity Constant.

The Uniformity constant (UC) is determined from a graph of the concentration of particles versus size. The grain size graph is useful when comparing sands and also when determining the UC. Grain size graphs are used to design and select materials for drain systems. The UC of a sand along with the particle size analysis is the most useful tool for estimating a sands performance. see Figure 3.

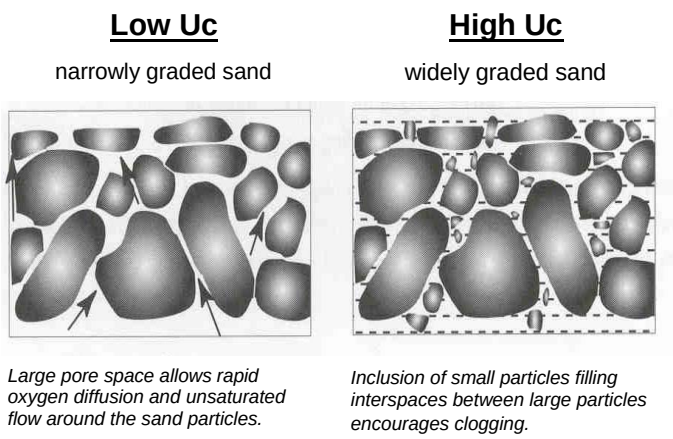


Figure 3. wide and narrow graded sands.

Dual Media Filters,

These filters have proven effective in that, the pre-filter facility increased the service intervals between backwashing. Compared to that of a single medium sand filter. This increase was found to be three times greater, which represented 10% higher water production. However in his article A. Zouboulis et al, [8] omits to state the reason for choosing anthracite. The reason why anthracite is chosen is due to its reduced density compared to sand. This property of anthracite ensures that the stratified nature of the filter is maintained after backwashing, due to the lower settling velocity of the lighter medium. The settling velocity for a 0.6 mm sand with a relative density of 2.65 is, 6.3cm/s, compared to, 1.0mm anthracite with a relative density 1.5 is 4.0 cm/s. [9] Figures 4,5,and 6. show a typical dual media filter in various stages of operation.

Figure 4. multi media filter at rest.

Figure 5. The filter during the backwash cycle,

Figure 6. The filter at rest after backwashing.

Taste and Odour.

The taste and odour of the water is removed by passing it through a carbon filter

Carbon Filters. are normally referred to as activated carbon filters. Activated carbon is available as

(a) Granular activated carbon (GAC) or

(b) Powdered activated carbon (PAC). [10].

Activated carbon is an ideal medium for the removal of the organic materials responsible for tastes and odours. It is also very effective for dechlorination of water.

Disinfection of drinking water.

Ground water that is abstracted from a well-protected aquifer of fine porosity that is naturally free from pathogens would not normally require disinfection. [11] However this not the case in respect of surface water, Treated water in a distribution system is also liable to re-infection through various routes.

Ultra Violet Radiation.

Ultraviolet light is a proven means of addressing microbiologically contaminated water. This simple, safe technology is suitable for both small flow residential applications as well as large flow commercial projects.

Disinfection with UV radiation in the range of 240-290 nm is currently being used as an alternative to conventional chemical disinfectants because by-product formation is negligible. [12] This is the disinfection system used in this project as it is a chemical free process and id is effective in neutralising chlorine resistant pathogens.

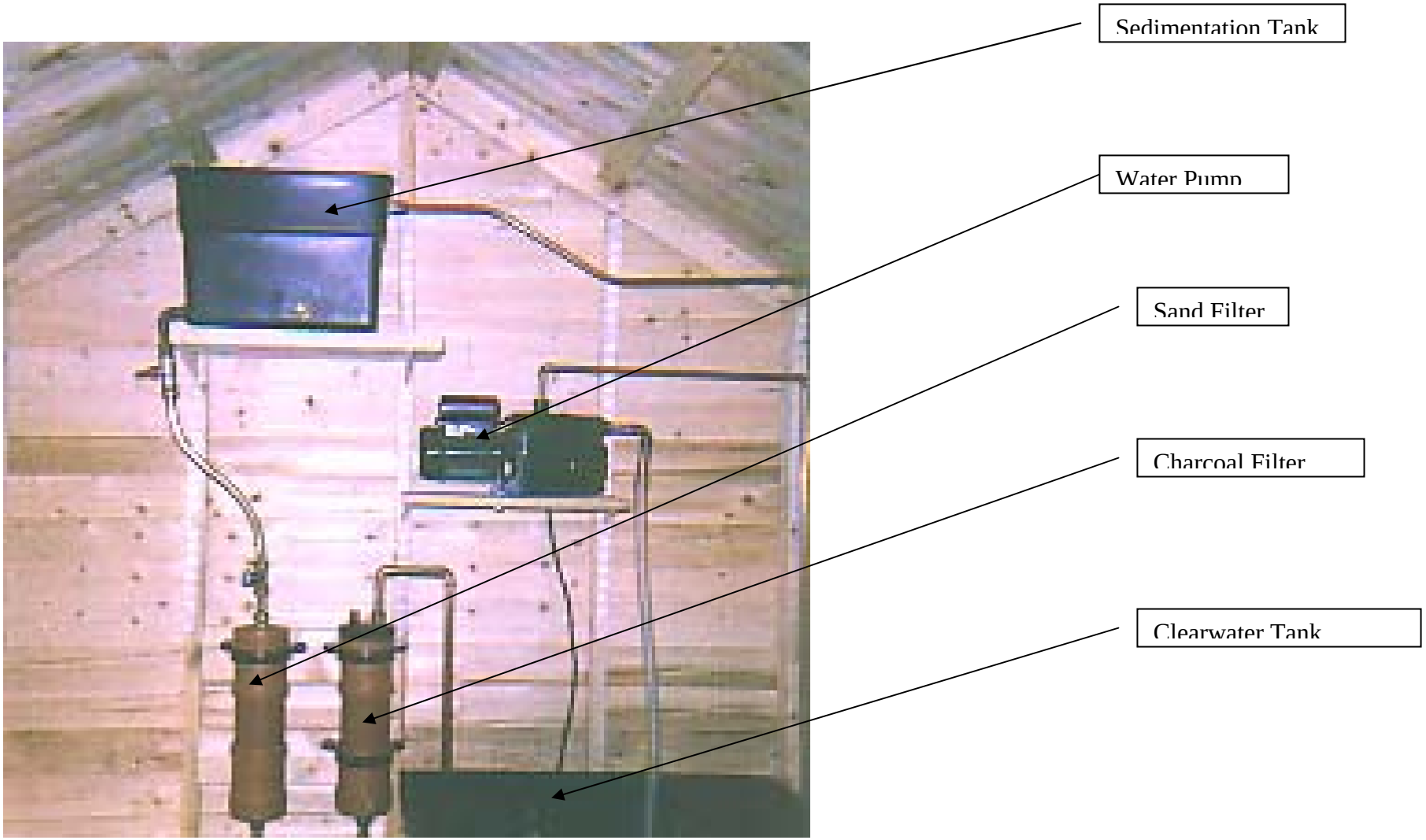
Working models.

Figure 7. shows a photograph of a laboratory test unit with multiple filters and flow control valves. Figure 8. shows a simple working model installed on site, and Figure 9 shows the final filter and UV unit placed near to the point of use.

Conclusions:

The supply of clean drinking water is a major problem in the developed world and the frequency of water related problems are increasing. Addressing the shortage of fresh water supply by removing unwanted and harmful pollutants can be effectively achieved by proper design and technology. This can be achieved by proper aeration, filtration and disinfection prior to use.

Figure 7 Test unit



Filter 8. working model on site

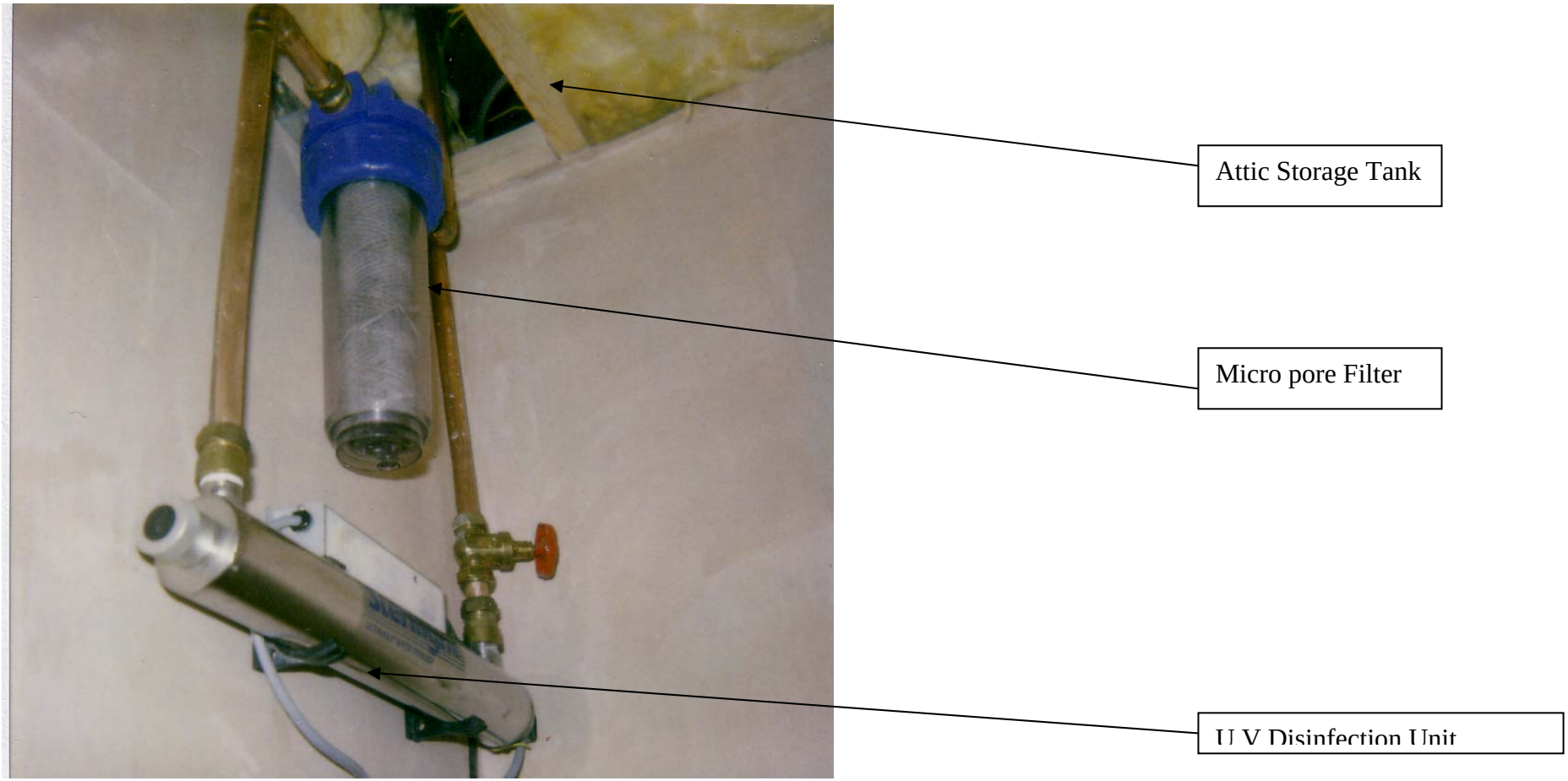


Figure 9. Ultra violet unit near point of use.

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TERMO – MEHANIČKA SVOJSTVA KOČNIH UMETAKA U EKSTREMNIM UVJETIMA PREOPTEREĆENJA

THERMO - MECHANICAL CHARACTERISTICS OF THE BRAKE-PADS IN THE EXTREME OVERLOAD CONDITIONS

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Stručni članak / Professional paper

Sažetak: U uvjetima redovne eksploatacije sintetski kočni umeci imaju karakteristike dosadašnjih kočnih umetaka izrađenih od sivog lijeva, prema UIC-propisima, oznake P 10. Sintetski kočni umetci se razlikuju uglavnom prema koeficijentu trenja. Neke značajke su im povoljnije nego kod kočnih umetaka P-10 i to manja potrošnja, povoljniji utjecaji na kotače kao i stvaranje manje buke pri kočenju.
Ovaj članak obrađuje i prezentira ispitivanja provedena na probnom stolu za sve ove tri vrste kočnih umetaka u ekstremnim uvjetima preopterećenja. Simulirana su termička preopterećenja kočnih umetaka u slučaju pojave kvara ili neispravnosti u sustavu kočnice, jednog ili više vozila, u redovitom prometu ili pri dugotrajnom kočenju na padu.
Obrađena su usporedno termo – mehaničke svojstva kočnih umetaka od sivog lijeva P10, od sinter- materijala i organskih kočnih umetaka.
Provedena ispitivanja su značajna jer obrađuje uvjete koji su najčešće prisutni kod izvanrednih događaja ili neposredno prije udesa zbog takozvanog "otkazivanja kočnice vlaka" na padovima. Iz provedenih ispitivanja je vidljivo da se mogu očekivati različita ponašanja vlaka ovisno o kočnim umetcima koji se primjenjuju na željezničkim vozilima.
Ključne riječi: kočni umetak, mehanička svojstva
Abstract: In regular usage conditions, sinthetic types of the brake pads have most of the characteristics of the former, gray cast brake pads, according to UIC-Regulations, designation P 10. The difference is in the friction coefficient. Results in some areas are better then the results with the P 10 brake pads: lesser consupmtion, better impact on wheels and noise reduction during the breaking process.
This article presents and elaborates the research done on the examination-bench on all three types of brake pads under the same extreme overload conditions. Such conditions are: themic overload of brake pads in the event of malfunction or failure in the brake-system of the one or more vehicles in a regular traffic or during long brake usage on the slopes.
Parallel themo-mechanical characteristics of the P 10 gray cast brake pads, sinter-brake pads and the organic brake pads are analysed.
This research is important because it analysis the conditions during the exceptional situations or the moments prior to the accident induced by «train's brake failure» on the slopes.
Research results show that the different outcomes can be expected in such conditions, depending on the types of the brake pads used.
Key words: Brake pads, Mechanical properties

1. RAZVOJ KOČNIH UMETAKA ZA ŽELJEZNIČKA VOZILA

U posljednje vrijeme se izdvajaju ogromna sredstva od strane EU i UIC-a kako bi se povećala najveća prednost željeznice a to je smanjenje zagađenja u okolišu. Posebno se istražuju mogućnosti smanjenja buke i to buke u željezničkom teretnom prometu.

Prema prethodnim istraživanjima utvrđeno je da se zamjenom kočnih umetaka od sivog ljeva s kočnim umetcima od sintetskih materijala, organskim ili sinter, dobije smanjenje buke u okolišu za oko 10 dB.

Mnogi europski proizvođači se trude proizvesti kočni umetak od raznih neželjeznih materijala kako bi se provela supstitucija dosada najrasprostranjenijih kočnih umetaka od sivog ljeva oznake P - 10. Od 2002. godine na tržištu postoje mnogi organski ili sinter kočni umetci koji su verificirani od strane UIC-a za međunarodni željeznički promet. Proizvođači su pri tome uspjeli u većoj ili manjoj mjeri, za potrebe kočenja vozila u normalnih uvjetima prometa, simulirati eksploatacijske karakteristike sivog ljeva. Ove prilagodbe se odnose najviše na usklađivanje s promjenama koeficijenta trenja kao kod sivog ljeva, na potrošnju kotača i kočnih umetaka, na potrebu zadržavanja adhezijskih karakteristike kotača i tračnice. Sve ovo je bilo neophodno kako bi se zadržali postojeći uvjeti eksploatacije teretnih vagona, prema UIC i RIV propisima.

2. ISPITIVANJA KOČNIH UMETAKA U EKSTREMNIM UVJETIMA

Kako bi se utvrdile razlike u ponašanju kočnih umetaka u ekstremnim uvjetima preopterećenja, na probnom stolu u firmi Becorit u Recklinghausenu 2004. provedena su jedna takva ispitivanja. Ispitivanja je nadzirao Chalmers Universitet.

Ispitivanja su provedena na kočnim umetcima od sivog ljeva P-10, na sinter kočnim umetcima, više tipova, te na kočnim umetcima od organskih materijala, više proizvođača.

Na probnom stolu se obavljala simulacija trajnog kočenja i to:

- određena je brzina vlaka 70 km/h,
- sila na kočni umetak iznosila je 16 KN, odnosno (12 KN),
- trajanje kočenja iznosilo je 60 min,
- postignute temperature su iznosile 900ºC i više.

Ovi uvjeti ispitivanja su izuzetno teški budući se mora računati s uništenjem nekoliko ispitnih monoblok kotača te s mogućim oštećenjima na mjernoj i ispitnoj opremi. Najveće mjerene temperature u eksploataciji kod ekstremnih uvjeta kočenja izmjerene su do ca 700ºC.

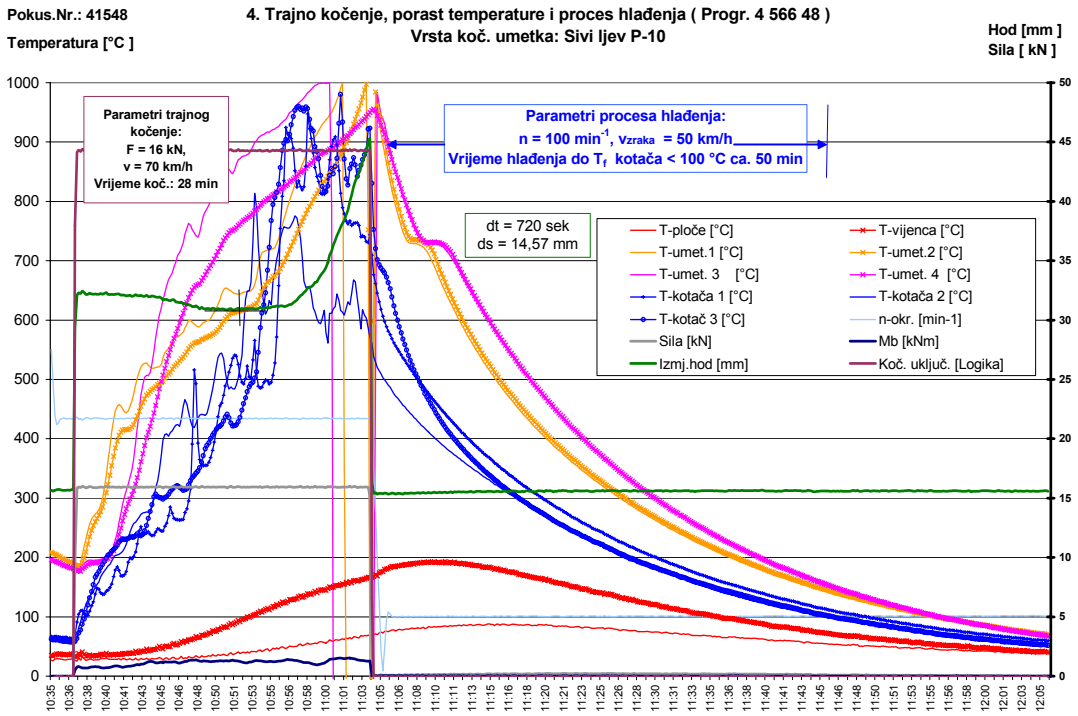
Potrebno je računati da se u uvjetima eksploatacije ne dostižu ovako visoke temperature kao na probnom stolu budući da se jedan dio topline ostvarene kočenjem odvodi putem kontakta kotač tračnica.

Ispitna oprema se sastojala od:

- 3 termoelemta neposredno u tarnoj površini kotača,
- 2 termoelementa u ploči kotača,
- po 2 termoelemta u svakom kočnom umetku,
- mjerač istrošenosti kočnog umetka.

3. MJERENJE TEMPERATURE

Mjerenje temperature je obavljeno termoelementima koji su se nalazili u kotaču i u kočnom umetku.
U kotaču termoelementi su locirani ispod tarne površine, 200 mm iznad glavčine i 110 mm iznad glavčine. U svakom kočnom umetku se termoelement nalazio 10 i 25 mm od leđnog ukrućenja.
Na slici 1 nalazi se primjer dijagrama porasta temperature i hlađenja kočnog umetka od sivog lijeva prilikom ispitivanja.



Slika 1. Raspored temperature u kočnom metku od SL prilikom ispitivanja.

Na slici 2 prikazano je stanje kočnog umetka od sivog lijeva P10 nakon provedenog ispitivanja.

Slika 2. Kočni umeci od sivog lijeva P10 nakon ispitivanja.

4. ANALIZA REZULTATA:

Podatci iz ovih ispitivanja ukazuju na ponašanja kočnih umetaka od različitih materijala u uvjetima mogućih neispravnosti kod kočnica, izvanrednih događaja odnosno u uvjetima dugotrajnih kočenja. Pri tome je utvrđeno slijedeće:

- Kod svakih tipova kočnih umetaka će u relativno kratkom roku 10-15 min. biti dostignuta temperatura na tarnoj površini, kotač-kočni umetak, od 900 º C.
- Najveća postignuta temperatura kočnog umetka, preko 1000 º C, izmjerena je kod kočnog umetka od sivog ljeva P – 10.
- Najuočljiviji vizualni efekti uz stvaranje velikog iskrenja uočeni je kod kočnog umetka od sivog ljeva P - 10
- Najviša temperatura kotača utvrđena je kod kočnih umetaka od sinter materijala.
- Najmanja oštećenja na kotačima vozila nastaju kod kočnih umetaka od organskih sintetskih materijala.
- Kritična temperatura kod koje dolazi do priomjene svojstava umetka je:
  - kod kočnog umetka od sivog ljeva P - 10 700 º C
  - kod kočnog umetka od sinter materijala 650 º C
  - kod kočnog umetka od organskih materijala 450 º C

Zaključak:

Budući da će uskoro novi tipovi kočnih umetaka, sinter i organski kočni umetci, biti u redovitom međunarodnom prometu i to kao obvezni za teretne i putničke vagone, to je potrebno i ovakvim usporednim ispitivanjima s dosadašnjim kočnim umetcima omogućiti uvid u njihovo ponašanja u eksploataciji.

Provedena ispitivanja mogu pomoći utoliko da se odluka o izboru kočnog umetka poveže s mogućim posljedicama koje nastaju kod neispravnosti na kočnici, izvanrednih događaja ili udesa.
Promatrajući nekoliko posljednjih izvanrednih događaja u željezničkom prometu uzrokovanih neispravnostima na kočnici (Plaški, Blata, itd.) gdje je došlo do dugotrajnog kočenja i do takozvanog «bježanja vlaka», kroz rezultate ovih ispitivanja, može se zaključiti slijedeće:

1. Ponašanja kočnih umetaka, odnosno vlaka, kod izvanrednog događaja Plaški 2000., upravo je identično gore navedenim rezultatima ispitivanja.
   - Kočni umetci od sivog ljeva P-10 koji su se nalazili na lokomotivama 2062, lokomotive su uglavnom kočile cijeli vlak, bili su na dionici od oko 25 km potrošene za ca. 40 mm. Normalna potrošnja kočnih umetaka od sivog ljeva iznosi 2 do 3 mm / 1.000 km dok je ovdje u uvjetima trajnog kočenja i visokih temperatura potrošnja bila izuzetno velika a što je utvrđeno i ovim pokusom.
   - Ovako veliku potrošnju kočnih umetaka uvjetuju termo mehanička svojstva sivog ljeva pri visokim temperaturama, 700 °C i više. Kod ovih temperatura dolazi do značajnog pada koeficijenta trenja te do smanjenja funkcije kočenja, a što je također je utvrđeno kod ovog izvanrednog događaja.
     Naime na početku kočenja je utvrđeno smanjenje brzine, dok kočni umetci još nisu bili dostigli svoju kritičnu temperaturu, a nakon toga je došlo do enormnog povećanje brzine vlaka unatoč tome što je pad većim dijelom pruge bio konstantan.
2. U identičnim uvjetima organski kočni umetci bi se ponašali drugačije. Pojavilo bi se također veće trošenja kočnih umetaka, ali ne kao kod sivog ljeva, ali ne bi došlo do velikih oštećenja kotača.
   Prema dobivenim rezultatima već kod temperatura 450 °C dolazi do promjene svojstava a što znači da bi se funkcija kočenja vlaka izgubila i nešto brže nego kod kočnih umetaka od sivog ljeva. Iz ovoga proizlazi da bi mogući udes vlaka nastupio nešto prije nego kod kočnih umetaka od sivog ljeva.
3. Kod kočnih umetaka od sinter materijalatakođer bi došlo do promjene svojstava materijala pri temperaturama iznad 650 °C.
   Potrošnja bi se povećala iznad normale, slično kao kod organskih kočnih umetaka, ali ni približno potrošnji koja je izmjerena kod kočnih umetaka od sivog ljeva.
   Pri tome bi došlo do smanjenja funkcije kočenja zbog pada koeficijenta trenja. Koeficijent trenja opada obrnuto proporcionalno s potrošnjom kočnog umetka a što znači, blaže nego kod organskih materijala odnosno puno blaže nego kod sivog ljeva.
   Ovo bi značilo da će se funkcija kočenja zadržati znatno duže i kod viših temperatura kočnog umetka odnosno kotača, dakle ne bi došlo do tako naglog porasta brzine vlaka.

U uvjetima dugotrajnog kočenja, odnosno "bježanja vlaka" važno je mnogo detalja koji će uvjetovati iskakanje, odnosno udes, ili mogući nastavak vožnje vlaka ali je najvažnije omogućiti što duže vrijeme provođenja funkcije kočenja. Kočenje direktno utječe na brzinu vlaka, a o brzini ovisi stabilnost vlaka, te je zbog toga potrebno procese koji uvjetuju na smanjenje kočenja, odgoditi što duže.
Prema gore navedenim zaključcima a koji su proizašli iz rezultata ispitivanja najpovoljnije rezultate, za slučaj bježanja vlaka, daju kočni umetci od sinter materijala.
Zbog toga je za naše uvjete prometa, brdske pruge, moguće otkazivanja kočnice itd., posebno za vučna vozila, potrebno izabrati kočne umetke od sinter materijala.
Sadašnji ispitivani sinter kočni umetci su izrađeni na bazi bakra odnosno na bazi željeznog sintera.
Sastav materijala za sinter kočne umetke kao i recepti za izradu organskih kočnih umetaka su još uvijek tajna proizvođača.

Napomena

Sva provedena ispitivanja odnose se na jedan ograničeni broj kočnih umetaka koji je neposredno odabran prema mogućnostima i koji se trenutno može naći na vozilima pojedinih UIC - željeznica. Veći dio sinter i organskih kočnih umetaka još uvijek nije verificiran od strane UIC-a, trenutno se praktično na svim značajnijim željeznicama obavljaju ispitivanja ovakvih kočnih umetaka (na HŽ-u se upravo ispituju tri tipa sintetskih kočnih umetaka), tako da se očekuje široka paleta ovih proizvoda na tržištu.

Potrebno je računati i s time da će se pojaviti i drugi tipova, sinter i organskih kočnih umetaka, koji mogu imati potpuno drugačija svojstva od gore navedenih i utvrđenih svojstava, budući da ovakva ispitivanja nisu nužna za verifikaciju u međunarodnom prometu od strane UIC-a.

KARAKTERIZACIJA TEKUĆINE ZA HLAĐENJE, ISPIRANJE I PODMAZIVANJE NAKON OBRADE Si I SiO_2

CHARACTERIZATION OF COOLING LIQUID AFTER MACHINING Si AND SiO_2

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Sažetak: Tijekom grubog i finog brušenja monokristalnog Si i taljenog SiO_2 korištena je 5 %-tna vodena otopina INA-sintetične tekućine. U radu je provedena karakterizacija INA-sintetične tekućine koja se koristila za obradbu Si i SiO_2. U tu svrhu određeni su fizikalno-kemijski parametri, svojstva zaštite od korozije, svojstva pjenjenja, te svojstva hlađenja i podmazivanja. Navedeni parametri su određeni prije strojne obradbe te nakon grubog i finog brušenja. Tekućina nakon grubog i finog brušenja sadrži čestice materijala koji se obrađivao. Prije ponovne uporabe tekućine potrebno je prethodno odijeliti odgovarajućim postupkom (filtracijom ili sedimentacijom) čestice materijala. U tu svrhu određena je i raspodjela veličina čestica u tekućini nakon obradbe. Rezultati ispitivanja pokazuju da se fizikalno-kemijska svojstva INA-sintetične tekućine ne mijenjaju nakon obradbe, te da se ona nakon postupka odjeljivanja čestica Si i SiO_2 može ponovno koristi u procesu obradbe.

Ključne riječi: INA-sintetična tekućina, grubo i fino brušenje, monokristal Si, taljeni SiO_2.

Abstract: INA-synthetic liquid (5 % water solution) was used during the coarse and fine grinding of single crystal Si and fused SiO_2. In order to characterize INA-synthetic liquid, its physical and chemical properties, corrosion protection, foaming, coolant and lubricant properties were determined. These parameters were determined before the machining as well as after coarse and fine grinding. Liquid contains particles of treated material after coarse and fine grinding. Therefore, particle size distribution was determined in order to select method for solid removal prior to liquid reuse. Results of investigation indicated that the physical and chemical properties of INA-synthetic liquid did not change after machining, which means that liquid can be reused after adequate solid-liquid separation method.

Key words: INA-synthetic liquid, coars and fine grinding, single crystal Si, fused SiO_2.

1. UVOD

Taljeni SiO_2 se dobiva taljenjem prirodnog kvarca, koji se nalazi u kvarcnom pijesku, te hlađenjem pri čemu nastaje amorfna tvar poznata kao kvarcno staklo. Temperatura taljenja je oko 1900 °C. Glavna su svojstva taljenog SiO_2 visoka čistoća, odlična optička transmisijska svojstva, dobra otpornost na toplinske šokove, niska vodljivost, dobra kemijska postojanost, visoka toplinska i električna otpornost. Zbog navedenih svojstava taljeni SiO_2 se koristi u poluvodičkoj industriji, te u industriji optičkih vlakana, a predstavlja i odličan materijal za izradu posuda za taljenje i proizvodnju monokristala Si koji ima široku primjenu u poluvodičkoj industriji. Monokristalni silicij se dobiva kristalizacijom iz taline, primjer je Czochralski metoda (metoda izvlačenja monokristala iz taline). Iz takvih se kristala izrađuju procesori, memorijski čipovi, tranzistori, diode i mnogobrojni drugi dijelovi elektroničkih uređaja [1-4]. Na slici 1A prikazan je ingot monokristala Si koji je dobiven postupkom izvlačenja monokristala iz taline. Obradom monokristalnog Si ingota (slika 1A) i taljenog SiO_2 (slika 1B) mogu se dobiti proizvodi različitih oblika prema zahtjevima kupca za poluvodičku industriju (slika 1 C i 1D).

Slika 1. (A) Ingot monokristala Si, (B) taljeni SiO_2, (C) proizvodi od monokristala Si i (D) proizvod od taljenog SiO_2.

Zbog visokih zahtjeva koji se postavljaju na točnost dimenzija, raznovrsnost oblika i stanje površine, tijekom obradbe dijelova od Si i SiO_2 nužna je primjena suvremenih alatnih strojeva kojima se mogu postići uske tolerancije. Visoke tvrdoće navedenih materijala zahtijevaju u obradbi korištenje dijamantnih reznih alata čija se zaštita tijekom postupka brušenja postiže dodatkom odgovarajućeg sredstva za hlađenje te ispiranjem i podmazivanjem (tekućina za hlađenje). Prilikom obradbe navedenih materijala, pomoću tekućine za hlađenje ujedno se odnose čestice obrađenog materijala iz radne zone te se alat i drugi strojni dijelovi zaštićuju

od korozije. U radu je provedena karakterizacija INA-sintetične tekućine koja se koristila za obradbu Si i SiO_2.

2. EKSPERIMENTALNI DIO

2.1. Obrada Si i SiO_2

Grubo i fino brušenje monokristalnog Si i taljenog SiO_2 provedeno je u tvrtki Applied Ceramics, d.o.o., Sisak. Tijekom obradbe korištena je 5 %-tna vodena otopina INA-sintetične tekućine. Gruba obradba provedena je na glodalici tipa Bridgeport series 1 uz korištenje dijamantnih alata za grubu obradu. Dijamantne čestice su povezivane elektro platiranjem u jedan sloj. Alat se koristi sve dok se ne skine sloj dijamantnih čestica. Veličina zrna dijamanta za grubu obradu je grit 80 do 100.
Fino brušenje je obavljeno CNC uređajem Haas tipa V1. Korišteni su alati sa dijamantnim česticama povezani metalom. Veličina zrna dijamanta za finu obradbu je grit 220 do 320.

2.2. Ispitna tekućina i metode ispitivanja tekućine

Tijekom grubog i finog brušenja korištena je INA-sintetična tekućina za hlađenje, ispiranje i podmazivanje. Formulacija INA-sintetične tekućine za obradbu materijala koja se miješa s vodom sadrži površinsko aktivne tvari bez aromatske jezgre, korozijski inhibitor derivat kapronske kiseline, EO/PO blok polimer, vodu i druge potrebne aditive. INA-sintetična tekućina ne sadrži mineralno ulje i stoga ne ostavlja masni sloj na obrađenoj površini što je za ovu primjenu izuzetno važno. Posjeduje Vodopravnu dozvolu i nije štetna za ljude i okoliš jer ne sadrži štetne spojeve, a prema preporukama važnih institucija [5]. Primjenjuje se pomiješana s vodom u koncentracijama od 2 do 7 % ovisno o zahtjevima procesa obradbe ili materijala koji se obrađuje.
Za određivanje svojstava ispitnih tekućina za hlađenje i podmazivanje korištene su uobičajene ili standardizirane fizikalno kemijske metode ispitivanja a zatim i posebne metode za određivanje uporabnih svojstava tekućina [6]. U Tablici 1 prikazana su svojstva koncentrata i otopine INA-sintetične tekućine za hlađenje te odgovarajuće metode ispitivanja. Provedena su sljedeća ispitivanja:

- stabilnost koncentrata i otopina,
- svojstva zaštite od korozije,
- svojstva pjenjenja sintetične tekućine,
- svojstva hlađenja i podmazivanja.

Stabilnost koncentrata i otopina, Interni test 1, određuje se pri različitim temperaturama vizualno. Za ispitivanje svojstava zaštite od korozije primijenjene su dvije metode. Jedna od najpoznatijih metoda za ispitivanje korozijskih svojstava je po Herbertu: DIN 51360-01 odnosno IP 123 a sastoji se u određivanju korozijskih pojava na ispitnoj ploči od lijevanog željeza u prisustvu čeličnih čestica. Na ploču dimenzija 100x100 mm stavi se dva grama čeličnih čestica koje se preliju jednim mililitrom ispitne tekućine i ostave mirovati pri normalnoj temperaturi i definiranoj vlažnosti kroz 24 sata. Nakon toga se uklone metalne čestice i ocjenjuju promjene ispitne ploče na mjestima dodira. Prema DIN 51360-01 rezultat se iznosi u obliku SXRY, gdje je S - jačina obojenja (X = 0 - 6), R - veličina korodirane površine (Y = 0 - 6).
Filtar papir test DIN 51360-02, IP 287, sastoji se u ispitivanju korozijskih pojava na filtar papiru koje ostavljaju čestice od lijevanog željeza. Na papir određenih dimenzija stavlja se

dva grama čestica, prelije s dva mililitra ispitne otopine i ostavi stajati dva sata pri sobnoj temperaturi. Ocjenjuju se korozijske mrlje na filtar papiru ocjenom od 1 do 6 prema intenzitetu korodirane površine.
Svojstva pjenjenja sintetične tekućine određena su Internim testom (IT 2). U ispitni graduirani cilindar od 100 ml stavi se 50 ml ispitne tekućine, a potom se cilindar okreće 20 puta tijekom 15-20 sekundi. Razlika između gornjeg volumena i početnog volumena otopine 50 ml izražava se kao količina pjene u ml. Nakon 5 minuta promatra se količina pjene koja se izražava kao stabilnost pjene ili pad pjene, ako nestane u kraćem vremenu (sekunde). Ispitivanje svojstava hlađenja i podmazivanja (EP svojstva) provedeno je laboratorijskim mehaničko-dinamičkim testovima a to su: stroj s 4 kuglice, ASTM D 4172 i Reichert-ova vaga.

Tablica 1. Svojstva INA-sintetične tekućine za obradbu materijala

SVOJSTVO, Metoda ispitivanja	INA-SINTETIČNA TEKUĆINA ZA OBRADBU MATERIJALA
KONCENTRAT	
Izgled i boja, vizualno	bistra, tamno žuta tekućina
Stabilnost, 4, 20 i 50 °C/24h, Interni test 1	stabilan
Viskoznost, 40 °C, $mm^2 s^{-1}$, ISO 3104	4,5
OTOPINA, 5 % u T.V. (15 °nj),	
Izgled, vizualno	bistra otopina
pH-vrijednost, ASTM D 1287	8,8
Rezerve alkalija, ASTM D 1221	7,76
Pjenjenje, Interni test 2; količina pjene, ml Stabilnost, količina pjene nakon 5 min, ml	20 0
EP-svojstva Promjer istrošenja, mm, ASTM D 4172 Površina istrošenja, mm^2, Reichert vaga	 0,88 31,5
Korozijska svojstva Herbert test, DIN 51360-01; 1,5 % otopina Filtar papir test, DIN 51360-02; 2 % otopina	 R0/S0 0

2.3. Raspodjela veličine čestica

Nakon obrade uzorkovane su četiri suspenzije u svrhu određivanja:
- raspodjele veličina Si čestica nakon grubog brušenja monokristala Si,
- raspodjele veličina Si čestica nakon finog brušenja monokristala Si,
- raspodjele veličina SiO_2 čestica nakon grubog brušenja taljenog SiO_2,
- raspodjele veličina SiO_2 čestica nakon finog brušenja taljenog SiO_2.

Raspodjela veličina čestica određena je metodom osjetljivog električnog polja pomoću uređaja Coulter Counter ZM (Coulter-Electronics Ltd., Luton, UK). Coulter metoda određivanja veličine čestica i brojanja čestica zasniva se na mjerljivim promjenama električnog otpora nastalog od nevodljivih čestica suspendiranih u elektrolitu. U tu svrhu ispitni uzorci su dispergirani u 1 % vodenoj otopini NaCl koja je prethodno profiltrirana kako bi se iz nje uklonile čestice koje predstavljaju pozadinski šum. Za mjerenje su korištene kivete čiji je promjer otvora 200 μm. Rezultati ispitivanja iskazani su u diferencijalnom obliku, a predstavljaju učestalost pojedine veličine čestica, odnosno volumni udjel čestica u intervalu

veličina ($dQ_3/dx = q_3$). Nakon odjeljivanja čestica Si i SiO_2 iz korištene tekućine za hlađenje određeni su fizikalno-kemijski parametri (Tablica 2).

3. REZULTATI I DISKUSIJA

Tijekom grubog i finog brušenja Si i SiO_2 u tvornici Applied Ceramics, Sisak, korištena je 5 %-tna vodena otopina INA-sintetične tekućine. Nakon provedene obradbe na radnim strojevima uzeti su uzorci suspenzije za analizu. Rezultati ispitivanja karakterističnih fizikalno-kemijskih svojstava INA-sintetične tekućine prije uporabe (svježa 5 %-tna vodena otopina), te nakon finog i grubog brušenja Si i SiO_2 prikazani su u Tablici 2. U svim ispitnim uzorcima čestice iz ispitnih uzoraka suspenzija su centrifugiranjem uklonjene prije analize.

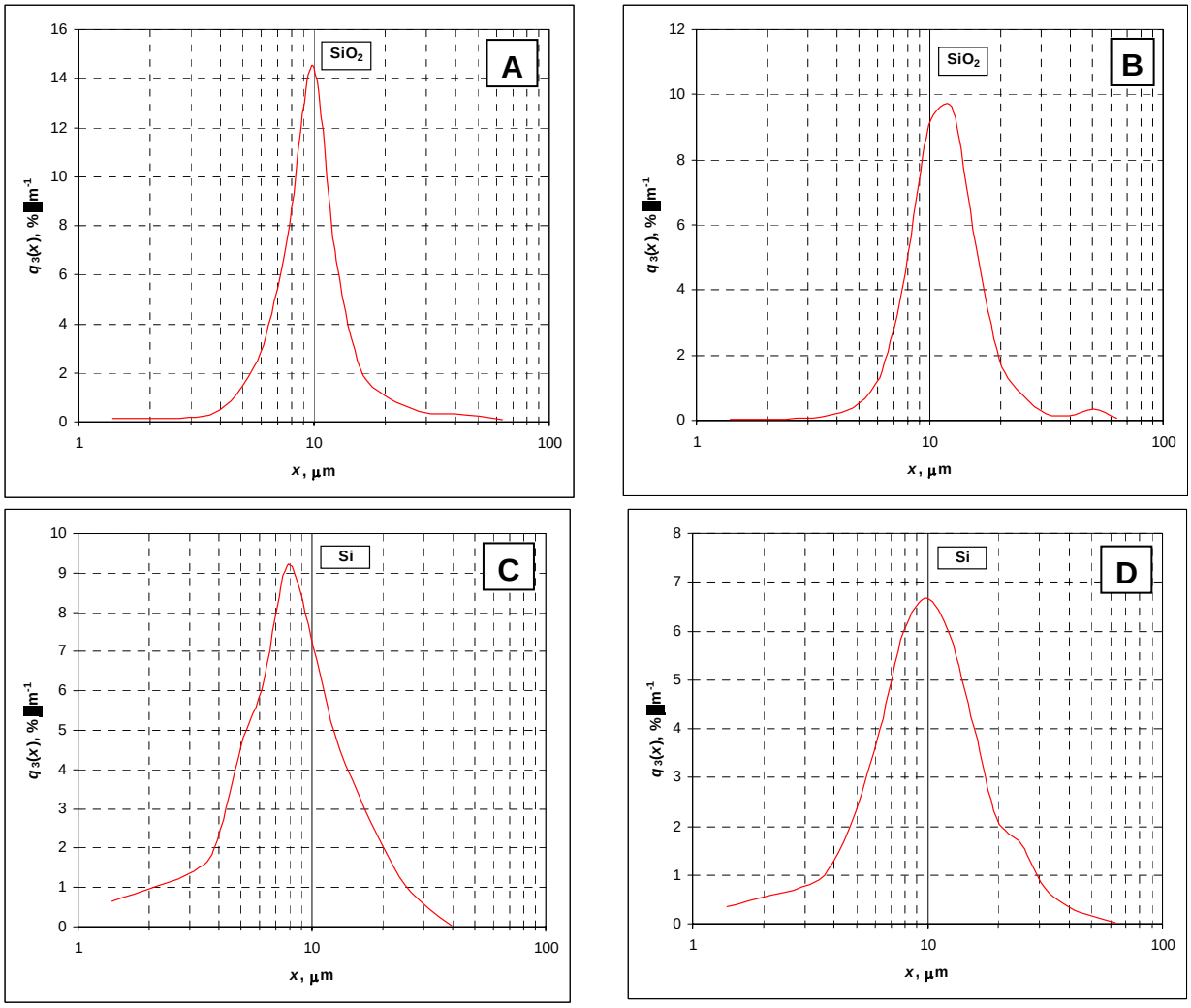
Tablica 2. Rezultati ispitivanja INA-sintetične tekućine nakon upotrebe

UZORAK-DOB:	230/08	231/08	232/08	233/08	INA-norma
materijal, obradba	Si grubo brušenje	Si fino brušenje	SiO_2 fino brušenje	SiO_2 grubo brušenje	svježi uzorak, 5 %-tna otopina
Izgled i boja otopine Vizualno **statički**	bistra otopina, talog bijeli pahuljast	bistra otopina, talog bijelo-sivkast pahuljast najviše	bistra otopina, talog bijeli pahuljast	bistra otopina, talog bijeli pahuljast najmanje	bistra bezbojna otopina
Izgled i boja otopine Vizualno **promiješano**	bistra bezbojna otopina	bistra bezbojna otopina	bistra bezbojna otopina	bistra bezbojna otopina	bistra bezbojna otopina
pH-vrijednost, ASTM D 1287	8,51	8,49	8,56	8,59	8-9
Rezerve alkalija, ml 0,1 NHCl, ASTM D 1121	7,41	9,68	10,80	7,77	6,4-8
Koncentracija, refraktometrom, %*	2,4xf=4,8	3,2xf=6,4	3,6xf=7,2	2,6xf=5,2	2,5xf=5
Korozija Herbert test, DIN 51360/I	nema korozije	nema korozije	nema korozije	nema korozije	nema korozije
Korozija Filter test, DIN 51360/II	nema korozije	nema korozije	nema korozije	nema korozije	nema korozije
OPASKA:	a)	a)	a) filtrirano/ kvantitat. filtar papir: bistra otopina	a)	-

*$\mathbf{f_C}$/refraktometar=2 (faktor korekcije koncentracije za očitanje refraktometrom)
a=otopina je odličnih radnih svojstava, iznad taloga.

Stvarna koncentracija otopine refraktometrom* = očitanje na prizmi refraktometra x f_C

Rezultati ispitivanja svih karakterističnih parametara ukazuju da se uporabljena 5 %-tna vodena otopina INA-sintetične tekućine može ponovno uporabiti u procesu obradbe. Otopina nakon obradbe sadrži i čestice materijala koji se obrađivao pa je, između ostalog, potrebno odrediti i raspodjelu veličina čestica kako bi se odabrao odgovarajući postupak njihove separacije prije ponovne uporabe. Raspodjela veličina čestica nakon grubog i finog brušenja Si i SiO_2 prikazana je na slici 2.



Slika 2. Raspodjela veličina čestica nakon: (A) finog brušenja SiO_2, (B) grubog brušenja SiO_2, (C) finog brušenja Si i (D) grubog brušenja Si.

Rezultati raspodjele veličina čestica nakon grube i fine obrade Si i SiO_2 ukazuju da su dobivene monomodalne raspodjele, te da je prosječna veličina čestica između 8 i 12 µm. Navedene čestice mogu se ukloniti filtracijskim ili sedimentacijskim postupcima, preporučljivo pod djelovanjem centrifugalne sile. Odabir odgovarajuće metode i uređaja moguće je provesti uz dodatne laboratorijske filtracijske testove.

4. ZAKLJUČCI

Pri postupcima finog i grubog brušenja silicijevih materijala primijenjena je INA-sintetična tekućina za hlađenje, ispiranje i podmazivanje koja je manje štetna za ljude i okoliš.
Zbog visokog stupnja odnošenja čestica materijala pri brušenju, koje se ispiru radnom tekućinom i sporo talože, dolazi do brzog zagađenja radnih tekućina. Cilj je bio ispitati mogućnost ponovne primjene korištenih tekućina.
Rezultati fizikalno-kemijskih parametara 5 %-tne vodene otopine INA-sintetične tekućine za hlađenje, ispiranje i podmazivanje prije i nakon obrade (grubo i fino brušenje) ukazuju da se navedena tekućina može koristi u više ciklusa obradbe. Prije ponovne uporabe potrebno je iz korištene tekućine odijeliti čestice Si i SiO_2 odgovarajućom separacijskom metodom.

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UPOTREBA PROGRAMA OTVORENOG KODA U GRAFIČKOM DIZAJNU

OPEN SOURCE PROGRAME USE IN GRAPHIC DESIGN

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Stručni članak / Professional paper

Sažetak: Kvalitetan program nezaobilazan je alat na poslovima grafičkog dizajna u svakom grafičkom studiju ili tiskari (grafička struka koristi računala u gotovo svim segmentima cjelokupne grafičke industrije). Za većinu poslova potrebno je nekoliko specijaliziranih programa čime troškovi nabavke komercijalnih programa značajno opterećuju poslovanje tvrtki. Za razliku od komercijalnih programa, programi otvorenog koda temeljeni na slobodnoj programskoj podršci su besplatni. Međutim, njihova zastupljenost u grafičkim studijima i tiskarama na području Republike Hrvatske u komercijalne svrhe za poslove dizajna grafičkih proizvoda i pripreme za tisak vrlo je mala.

Ključne riječi: linux, otvoreni kod, gimp, inkscape, scribus

Abstract: Unavoidable tool for graphic design businesses in each graphic studio or printing house (graphic industry use PC-s in almost all its segments of process and business) is high-quality program. For majority graphic businesses it is necessary to have several very specialised programs thus supply costs for commercial program purchase makes business more weight. As opposed of commercial programs, open source programs are based on free program assistance but anyhow their representation in croatian graphic studios and printing houses for commercial purposese for product design and editing is very low.

Key words: linux, open code, gimp, inscape, scribus

UVOD

U začecima informatičke tehnologije softver se dijelio i mijenjao među malobrojnim korisnicima računala na sveučilištima, istraživačkim laboratorijima, institutima te vladinim organizacijama budući da je u to vrijeme bio slobodan (lako dostupan i besplatan). Tek krajem 70-ih godina 20. stoljeća pojedine su tvrtke, bojeći se konkurencije, počele zatvarati izvorni kod i licencirati svoj softver ograničavajući slobodu korisnika, a taj model ograničavanja softvera je vrlo brzo bio prihvaćen od strane većine informatičke industrije.

Nasuprot tom modelu, 80-tih godina 20. stoljeća donose zaokret i sve veće zalaganje za ponovno uvođenje slobodnog softvera u svakodnevni rad. Nastali pokret utemeljio je Richard Stallman.

Slobodni softver stvar je slobode, a ne cijene, a isti ukazuje na slobodu korisnika da pokreće, presnimava, distribuira, proučava, mijenja i poboljšava softver. Navedene opcije moguće su samo u slučaju posjedovanja svih sloboda.

Točnije navedene slobode za korisnika softvera su sljedeće:

- sloboda pokretanja programa, u bilo koje svrhe (sloboda 0),
- sloboda proučavanja rada programa, i prilagodbe istog vašim potrebama (sloboda 1), a pristup je moguć samo putem izvornog koda.
- sloboda distribuiranja presnimaka, da biste mogli pomoći svomu bližnjemu (sloboda 2),
- sloboda poboljšavanja programa i ustupanje vaših poboljšanja javnosti, za blagodat cijele zajednice (sloboda 3). (1)

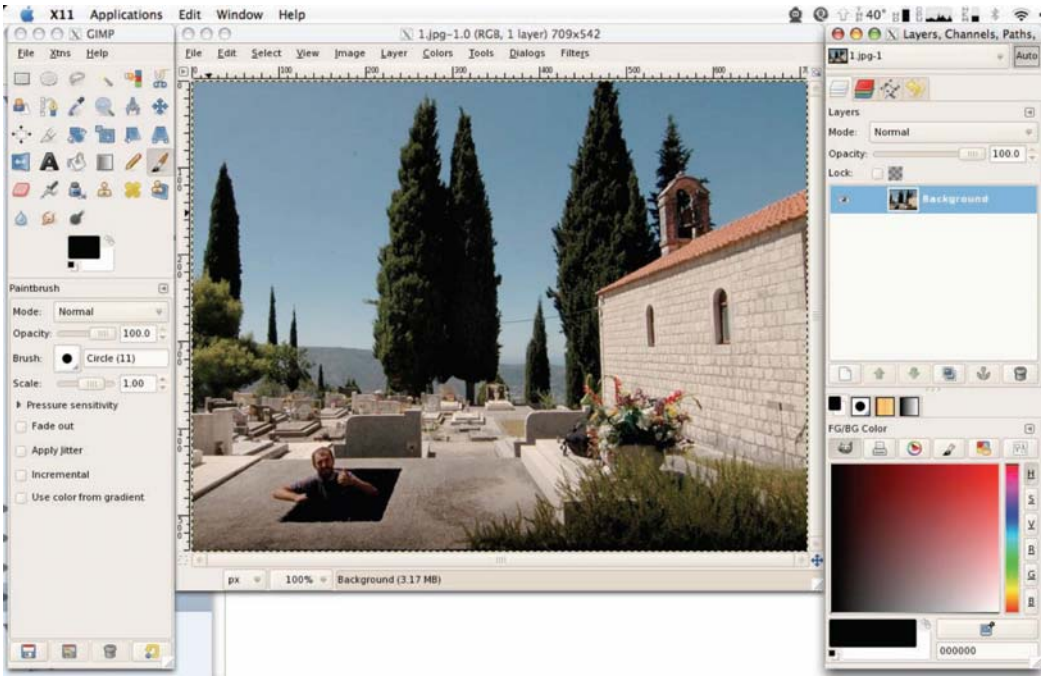
Danas postoji velik broj licenci koje definiraju prava i obveze kako autora, tako i korisnika softvera otvorenog koda (obično autor zadržava pravo da se kod daljnje distribucije njegovog koda mora vidjeti tko je prvi autor, tj. autor prve verzije programa, dok je u tom slučaju obveza korisnika da sačuva informaciju o autoru programa).

Neke od češće korištenih otvorenih licenci su:

- GPL - GNU General Public License GFDL - GNU
- Free Documentation License LGPL - GNU Lesser
- General Public License OPL - Open Content License

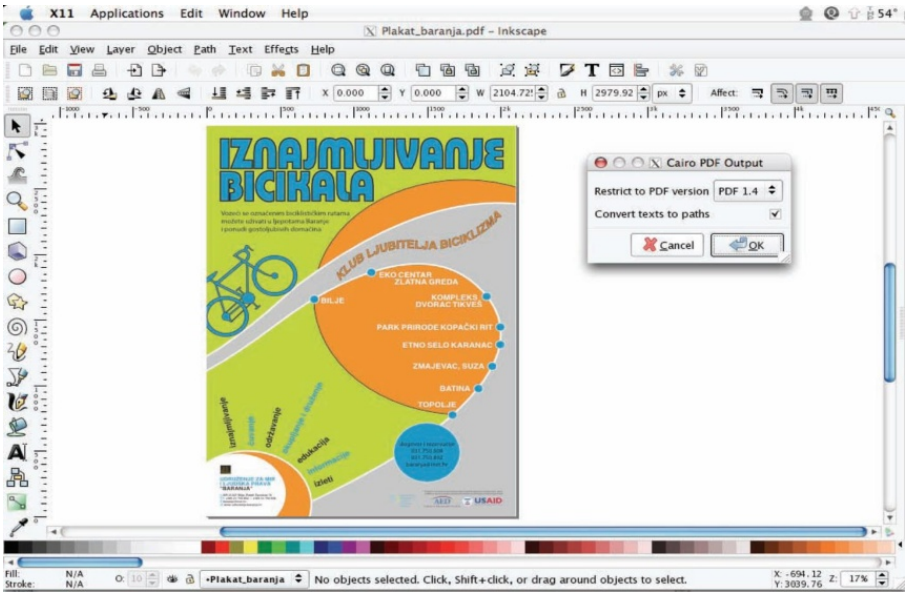
GNU General Public License (kratice GNU GPL i samo GPL) je najšire korištena licenca za besplatni softver, koju je originalno kreirao Richard Stallman za projekt GNU, a koristi ju i jezgra operativnog sustava Linux.(2) Sama uporaba Linux-a u „stolnom izdavaštvu“ i industriji je u porastu. (3,4)

Od programa otvorenog koda navest ćemo GIMP (GNU Image Manipulation Program - u prijevodu program za obradu grafike licenciran otvorenom licencom) koji predstavlja najpopularniji besplatan program za obradu/stvaranje rasterske grafike. Najčešće se koristi za obradu digitalne grafike i fotografija, a kako ima jako dobru podršku za razne filtere koji se koriste pri radu računalnom grafikom, po kvaliteti se uspoređuje čak i s Adobe Photoshopom (iako nije osmišljen da bude Photoshop klon). (5) GIMP je programiran pod X11-a na UNIX-u, ali je dostupan i za Linux, Microsoft Windows i Apple OSX operacijske sustave. Inačica GIMP-a sučeljem prilagođena Photoshopu naziva se Gimpshop (www.gimpshop.com).



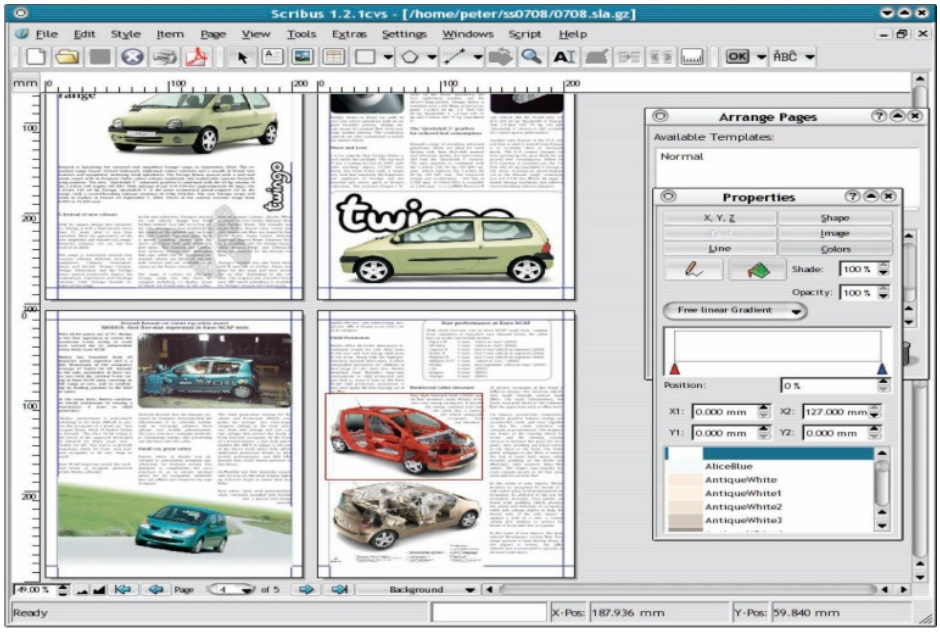
Slika 1. *GIMP 2.4.6, osnovno sučelje i prozori s alatima*

Inkscape je besplatni program otvorenog koda za izradu i manipulaciju vektorskom grafikom. Inkscape svoje dokumente sprema u SVG formatu. Riječ je o odličnom, fleksibilnom standardu koji uvodi značajan red u područje kojem je to već duže vrijeme potrebno - vektorsku grafiku. SVG je baziran na XML-u, što garantira podršku W3C-a i još nekih velikih autoriteta u standardizaciji računalnih tehnologija, ali i veliku fleksibilnost i mogućnost razvoja. Inkscape također potpuno podržava CSS standard stoga nije zanimljiv samo web dizajnerima, već i dizajnerima u grafičkoj i tiskarskoj industriji. (6) Program je namijenjen manipulaciji vektorskom grafikom, kao zamjena ili čak konkurencija za Illustrator i Freehand. Trenutno stabilna verzija je 0.46 i unatoč ranoj fazi razvoja, program je prilično stabilan i upotrebljiv. Inkscape je primarno razvijan za Linux platformu, ali je dostupan i za OS X, UNIX i Microsoft Windows operacijske sustave.



Slika 2. *Inkscape 0.46, malo opcija kod izvoza u PDF*

Sljedeći program, Scribus je jedini besplatni program za stolno izdavaštvo (osim projekta Passepartout, koji je još u ranom stadiju razvoja), objavljen pod GNU GPL licencom. Glavne verzije se mogu pokrenuti na Linux, Unix, Max OS X, OS/2 i Microsoft Windows operativnim sustavima.(7) Navedeni program nudi visoke mogućnosti za izradu stranica koje se mogu usporediti s vlasničkim programima za stolno izdavaštvo - Adobe PageMaker, QuarkXPress i Adobe InDesign, a danas najviše korištena stabilna verzija Scribusa kod pripreme novina, brošura, letaka, plakata i knjiga je 1.3.3.12.



Slika 3. *Izgled sučelja verzije Scribus 1.2*

PRIMJENA PROGRAMA OTVORENOG KODA U HRVATSKIM GRAFIČKIM STUDIJIMA I TISKARAMA

CILJ ISTRAŽIVANJA

Vodeći se hipotezom kako se programi otvorenog koda ne koriste u većoj mjeri u komercijalne svrhe za poslove dizajna grafičkih proizvoda i pripreme za tisak u grafičkim studijima i tiskarama na području Republike Hrvatske, napravljeno je istraživanje koje je za cilj imalo utvrditi u kojoj mjeri se ti isti programi zaista i koriste.

METODOLOGIJA

Ovo istraživanje fokusira se na mapiranje stavova spram korištenja programa otvorenog koda u hrvatskim grafičkim studijima i tiskarama i opisuje specifičan tip istraživanja javnog mnijenja koji se obično naziva "anketiranje". „Metodologija provedbe učinkovite ankete/upitnika zahtijeva nekoliko koraka koje treba poduzeti prema sljedećem kronološkom redu:

1. Odrediti jasnu svrhu/cilj istraživanja.
2. Odlučiti o frekvenciji istraživanja.

3. Zadužiti uvježbano osoblje odgovorno za anketiranje.
4. Odrediti populaciju za istraživanje.
5. Identificirati uzorak istraživanja.
6. Odrediti metodu prikupljanja podataka.
7. Identificirati područja prikupljanja podataka.
8. Izraditi niz standardnih pitanja.
9. Razviti metode maksimalnog povećanja postotka sudionika koji ispunjavaju upitnik.
10. Predtestirati, analizirati i unijeti promjene u anketu.
11. Statistički analizirati i izvesti zaključke.
12. Objasniti rezultate analize.
13. Dokumentirati postupke praćene tijekom istraživanja, obraditi podatke, analizirati i prezentirati rezultate.
14. Objaviti rezultate.“ (8)

Istraživanje je provedeno na uzorku od 988 ispitanika, a podaci o hrvatskim grafičkim studijima i tiskarama dobiveni su od strane Hrvatske obrtničke komore, Hrvatske gospodarske komore te putem javno dostupnih baza poduzetnika na Internetu. Maksimalna pogreška uzorka je +/-1%. Sudjelovanje u istraživanju bilo je dobrovoljno, a svi ispitanici upoznati su da će svi prikupljeni podaci biti prikazani skupno, da će se rezultati istraživanja, kao i sam upitnik koristiti isključivo za potrebe izrade završnog rada te se neće ni na koji način zloupotrijebiti. Od ukupno 988 poslanih upitnika njih 84 dostavilo je ispunjene upitnike što predstavlja 8,5% uzorka.

REZULTATI ISTRAŽIVANJA

Prema rezultatima istraživanja, kada govorimo u kontekstu tvrtki u grafičkoj industriji (tiskarama, grafičkim studijima), tvrtke u prosjeku imaju 8 zaposlenika (od 1 zaposlenika do 30 zaposlenika) što ih svrstava u grupu malih poduzetnika. Većina tvrtki obuhvaćenih istraživanjem prisutna je na tržištu posljednjih desetak godina (najstarija tvrtka u istraživanju započela je s radom 1991. godine, dok je nekolicina mlađih tvrtki svoje djelatnosti registrirala tek prije 2 godine).

Temeljem dostavljenih podataka vidljivo je da se u prosjeku 6 zaposlenika svakodnevno koristi računalom što je 75% zaposlenih djelatnika u tvrtkama obuhvaćenih ovim istraživanjem.

Od 84 tvrtke koje su dostavile ispunjene upitnike njih 24% na računalima ima instaliran Linux operativni sustav, 10% Free/Open BSD, 57% Apple OSX te 95% Microsoft Windows operativni sustav. Kod onih tvrtki koje koriste različite operativne sustave, omjer korištenja na računalima je slijedeći: 9% računala ima instaliran Linux operativni sustav, 3,5% Free/Open BSD, 28% Apple OSX a čak 59,5% Microsoft Windows operativni sustav.
Iako Microsoft Windows, prema rezultatima ovog istraživanja, još uvijek koristi čak 95% hrvatskih grafičkih studija i tiskara, potrebno je uočiti ne tako malen udio hrvatskih grafičkih studija i tiskara koji na svojim računalima imaju instalirane operativne sustave otvorenog koda (Linux i Free/Open BSD).

Rezultat provedenog istraživanja je i taj da 76% tvrtki barem na jednom računalu koristi softver otvorenog koda (Apache, mySQL, Mozilla, OpenOffice.org, GIMP, Inkscape, Scribus,

Blender, Xara, itd.) uz opasku da ne tako malen broj korisnika Microsoft Windows operativnog sustava koristi neke od programa otvorenog koda.

Od tvrtki koje koriste softver otvorenog koda (76% tvrtki odnosno njih 64), 12,5% ga koristi manje od 1 godine, 12,5% u periodu od 3 do 5 godina, 12,5% više od 5 godina, dok najveći broj tvrtki (njih 62,5%) softver otvorenog koristi u razdoblju od 1 do 3 godine. Te tvrtke softver otvorenog koda koriste kao operativne sustave (37,5%), za uredsko poslovanje (kao uredske pakete - 43,5%), za poslove programiranja (31,5%), dok samo 19% tvrtki (odnosno nešto više od 14% tvrtki koje djeluju u sektoru grafičke industrije) softver otvorenog koda koristi za poslove grafičkog oblikovanja i pripremu za tisak.

Nadalje, 12 tvrtki obuhvaćenih istraživanjem koje u potpunosti koriste softver otvorenog koda kod poslova grafičkog oblikovanja i pripreme za tisak koriste GIMP, dok njih 30% (4 tvrtke) koriste i Scribus i Xaru. Svi gore dobiveni rezultati idu u prilog postavljenoj hipotezi da još uvijek mali dio grafičkih studija i tiskara u Hrvatskoj koriste softver otvorenog koda kod poslova grafičkog dizajna i pripreme za tisak.

Tvrtke koje u svom poslovanju koriste softver otvorenog koda, kao najvažnije razloge korištenja navode manje naknade za licence odnosno besplatno korištenje (19%), neovisnost od softverske industrije (15%), funkcionalnost (11,5%), uštedu na instalaciji, prilagodbi i održavanju (10%), dok kao manje bitne razloge navode odnos cijene i performansi, stabilnost, same performanse, velik broj potencijalnih aplikacija i postojećih rješenja, uštedu na edukaciji zaposlenika, te know-how u zajednici i podršku open source zajednici. Na temelju dobivenih rezultata vidljiv je primarni razlog korištenja softvera, a taj je ušteda na troškovima - cijena softvera, održavanja, edukacije zaposlenika, itd.

Od 24% tvrtki obuhvaćenih istraživanjem koje ne koriste softver otvorenog koda, njih 80% isti niti ne planira koristiti u budućnosti dok ga ostali planiraju koristiti jedino u poslovima programiranja (njih 100%). Glavni razlog ovakve odluke je očit, a to je već spomenuta ušteda na troškovima odnosno njegovo besplatno korištenje. Podjednaki udio (22%) tvrtki kao najbitniji razlozi nekorištenja otvorenog softvera u budućnosti navode da jednostavno ne znaju kako ga koristiti niti znaju išta o slobodnom softveru odnosno nemaju odgovarajuću podršku Također 22% anketiranih odgovora da je nekorištenje softvera otvorenog koda pitanje politika tvrtke, dok 12% odgovara da nemaju potrebe za softverom otvorenog koda jer postojeći programi koje koriste zadovoljavaju njihove potrebe.

Iz navedenog može se zaključiti da je potrebna jača promocija softvera otvorenog koda, no jednako tako istovremeno treba raditi i na podizanju kapaciteta i edukaciji tvrtki koje se bave održavanjem softvera, kako bi u svakom trenutku budući korisnici imali odgovarajuću podršku.

Na posljednje pitanje da li koriste legalni ili nelegani softver, svega 33,25% ima instaliran legalan sav softver na svim računalima što je u skladu s recentnim istraživanjima tržišta i posljednjim studijama koje pokazuju razinu korištenja nelegalnog softvera u hrvatskom gospodarstvu. Unatoč dobivenom podatku ipak treba imati na umu da li je dan odgovor iskren.

Dobiveni rezultati korištenja legalnog softvera realna su slika u hrvatskom gospodarstvu što otvara prostor za dodatnu edukaciju vlasnika i zaposlenika, rad tvrtki koje se bave zaštitom

autorskih prava, ali i za dodatnu promociju softvera otvorenog koda koji svojim otvorenim licencama osigurava legalnost korištenja.

ZAKLJUČAK

Open source je kao ideja i pokret daleko odmakao od svojih skromnih početaka i još davno napustio granice Linuxa kao jedinog operativnog sustava na kojem obitava. Isto tako, svaki od spomenutih programa prevalio je dug put od prvih eksperimenata do upotrebljivih alata koji sa svakom slijedećom verziju postaju sve veća konkurencija komercijalnim rješenjima.

Iako je GIMP više nego dovoljan da zamijeni Photoshop u većini situacija, odgovor na pitanje može li se preporučiti profesionalcima koji pripremaju materijale za tisak bio bi: ”Još uvijek ne!”. Programeri GIMP-a su na dobrom putu da jednog dana dostignu upotrebljivost i široku lepezu mogućnosti, ali do tada je potrebno riješiti još podosta problema od kojih nisu svi tehničke prirode. Upotreba npr. procesnih PANTONE boja koje su standard u tiskarskoj industriji se plaća stoga su izuzetno male šanse da će ikada dobiti podršku u bilo kojem programu otvorenog koda, a ne samo u GIMP-u.

Inkscape je brz, kvalitetan, nudi velik broj mogućnosti i predstavlja ozbiljnu alternativu najjačim komercijalnim rješenjima, a svakom svojom novom verzijom se nadograđuje kvalitetnim alatima i jedina prava prepreka profesionalnoj upotrebi leži u slaboj podršci za standardne formate zapisa, potpori CMYK sustavu boja i općenito upravljanju bojama.

Iako su sva 3 programa kvalitetna i dovoljno upotrebljiva za manje više sve moguće zadaće, jedini koji u ovom trenutku ima veće šanse zamijeniti komercijalne aplikacije je Scribus sve dok GIMP i Inkscape ne riješe kvalitetnije upravljanje bojama i druge manje tehničke nedostatke.

Iz provedene usporedbe programa u radu vidljivo je da su programi otvorenog koda upotrebljivi za rad s grafikom. Nekima nedostaju neke ključne funkcije, koje predstavljaju svojevrstan standard za grafički dizajn. Zaobilaženje i pronalazak odgovarajućih rješenja iziskuje dosta vremena stoga je na samim grafičkim dizajnerima donošenje odluke koliko je njihovo vrijeme dragocjeno te da li ga imaju dovoljno da ga odvoje za učenje rada s programima otvorenog koda, koji se mogu koristiti čak i u primjerima gdje bi brža bila upotreba komercijalne aplikacije.

Pogledamo li u budućnost, programima otvorenog koda ide sve bolje, a uz konstantno poboljšavanje i ulaganjem energije u razvoj novih funkcija i otklanjanje nedostataka će zasigurno doseći razinu komercijalnih aplikacija, npr. Adobea, koji iza sebe ipak imaju više od 20 godina teorije i prakse koje su im svakako pomogle da se razviju i otklone sve utvrđene nedostatke. Niti njima u početku nije bilo lagano i jednostavno osvajanje tržište no. open source rješenja s druge strane su još mlada, te je za očekivati im je potrebno još nekoliko godina da dostignu jednaku razinu.

Bitan kriterij mnogima, naročito malim tvrtkama (koje predstavljaju većinu hrvatske grafičke industrije što pokazuju rezultati provedenog istraživanja) je i cijena. Ako su troškovi kupnje softvera veliki, dobro će se razmisliti o tome zadovoljavaju li programi otvorenog koda sigurnost i kvalitetu za obavljanje potrebnih poslova. Ono što se sigurno ne može tvrditi jest

činjenica da samo zbog toga što je riječ o besplatnim programima, isti nisu kvalitetni i nisu u mogućnosti obavljati posao kao i komercijalne aplikacije.

Rezultati istraživanja i usporedbe programa ukazuju na velike mogućnosti upotrebe programa otvorenog koda u grafičkoj industriji, ali je prije iste neophodna edukacija svih sudionika i djelatnika grafičke industrije kako bi se u prvom redu smanjio postotak ilegalnog korištenja softvera koji je trenutno u upotrebi.

U konačnici najbitniji zaključak ostaje da su programi otvorenog koda, kao i vlasničke aplikacije samo alat dizajnera i da je na samim dizajnerima odluka koji će koristiti i kakav će rezultat postići.

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EKOLOŠKI INHIBITORI U ZAŠTITI UGLJIČNOG ČELIKA

ECOLOGICAL INHIBITORS IN THE PROTECTION OF CARBONIC STEEL

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Izvorni znanstveni rad / Original scientific paper

Sažetak: U ovom radu ispitana je djelotvornost isparljivih inhibitora VCI (Volatile corrosion inhibitor) i to: amido soli dikarboksilne kiseline oznake VCI 644 i soli glukonske kiseline oznake VCI 645 na brzinu korozije ugljičnog čelika oznake Č0361 u 3.5 % otopini NaCl. Djelotvornost inhibitora ispitana je elektrokemijskom metodom. Metodom kvazi-potenciostatske polarizacije (Tafelove ekstrapolacije) određen je korozijski potencijal (E_{kor}), gustoća korozijske struje (j_{kor}), pokrivenost površine (Θ), te djelotvornost inhibitora (z). Provedena su i stereomikroskopska ispitivanja različitih stanja površine ugljičnog čelika.
Rezultati provedenih istraživanja ukazuju na mogućnost smanjenja brzine korozije ugljičnog čelika u 3.5 % otopini NaCl (umjetna morska voda) primjenom ekoloških inhibitora. Najveću djelotvornost zaštite pokazao je inhibitor VCI 644 u koncentraciji od 2.0 mg/L.

Ključne riječi: korozija, isparljivi inhibitor, ugljični čelik

Abstract: In this paper were examined the efficiency of VCI volatile corrosion inhibitors using the bicarboxylic acid amides marked VCI 644 and the gluconic acid salt inhibitor marked VCI 645 and their effect on the corrosion rate of carbonic steel marked Č0361 in the 3.5 % solution of NaCl. The efficiency of the inhibitor was tested by the electrochemical method. Using the method of quasi-potentiostatic polarisation (Tafel extrapolation) were determined the corrosion potential (E_{cor}), the density of corrosion current (j_{cor}), the surface coverage (Θ), and the efficiency of the inhibitor (z). Stereomicroscopic testing of different states of the surface of carbonic steel was also examined.
The results shown the possibility of decreasing the corrosion rate of carbonic steel in the 3.5 % solution of NaCl (artificial sea water) by using the ecological inhibitors. The highest efficiency was achieved by the VCI 644 inhibitor in the concentration of 2.0 mg/L.

Key words: corrosion, volatile corrosion inhibitor, carbonic steel

UVOD

Unatoč relativno ograničenoj korozijskoj otpornosti, ugljični čelik je značajan konstrukcijski materijal (85 % ukupne proizvodnje čelika). U velikim količinama se upotrebljava u pomorstvu, nuklearnim elektranama, petrokemijskoj proizvodnji i rafinaciji, cjevovodima, kemijskoj industriji, rudarstvu, te opremi za građevinarstvo i obradu metala. Iako je došlo do značajnog razvoja korozijski otpornih legura u posljednjih par desetljeća, ugljični čelik je najisplativiji, te je čak 3 do 5 puta jeftiniji od nehrđajućeg čelika. Kada je morska voda u kontaktu s ugljičnim čelikom korozija je ubrzana. Da bi usporili brzinu korozije danas se sve više primjenjuju inhibitori. To su anorganske i organske tvari koje više ili manje usporavaju tijek korozijskih procesa [1-3]. Svi ti spojevi, bez obzira da li se upotrebljavaju u otvorenim ili zatvorenim sustavima prema okolišu, prije ili kasnije dolaze u vodene tokove, rijeke, jezera i mora. Inhibitorske specije selektivno djeluju s obzirom na kemijski sastav i pH korozivne otopine, te vrstu metala ili legura. Velike količine inhibitora se primjenjuju u neutralnim otopinama, npr. u rashladnim sustavima, izmjenjivačima topline, te vodi u raznim granama industrije koja općenito sadrži otopljene soli, organske tvari i plinove, te ima pH neutralan ili slabo lužnat. Često prisutan kalcij hidrogenkarbonat stvara teško topive taloge kalcij karbonata koji utječe na djelovanje inhibitora [4]. Inhibitori znatno smanjuju brzinu i učinak korozije na razne konstrukcijske materijale. Uspješno se mogu primijeniti kromati, nitriti i fosfati, međutim u novije vrijeme njihova upotreba je potpuno zabranjena zbog toksičnosti, rezistentnosti u vodenim tokovima ili što uzrokuju eutrofikaciju, tj. nagli rast nižih biljnih organizama, bakterija i alga, te tako onečišćuju velike vodene površine i obale rijeka i mora. U ovom radu istraživanja su usmjerena na ispitivanje učinkovitosti djelovanja kemijskih spojeva niske toksičnosti i velike mogućnosti biorazgradnje. U tu svrhu ispitani su inhibitori VCI (isparljivi inhibitori) na brzinu korozije ugljičnog čelika u umjetnoj morskoj vodi.

INHIBITORI

Inhibitori mogu smanjiti brzinu korozije na jedan ili više načina, ovisno kako utječu na pojedine elementarne reakcije u procesu korozije, što ovisi o vrsti metala i korozivnoj sredini. U približno neutralnoj sredini (pH=5-9) za željezo i ugljični čelik je dominantan katodni proces redukcije kisika, te je prema tome brzina korozije pod utjecajem brzine prijenosa kisika prema površini metala. Inhibitori su općenito klasificirani kao adsorpcijski ili stvaraoci filma; anodni, katodni ili miješani; sigurni ili opasni (dodani u premaloj količini za učinkovitu zaštitu uzrokuju lokalna oštećenja, najčešće rupičastu koroziju), oksidirajući ili neoksidirajući, organski ili anorganski. Navedene podjele jedna drugu ne isključuju. Najčešće se inhibitori ispituju s obzirom da li utječu na anodni ili katodni proces korozije. Stvaranje pasivnog filma na površini željeza i čelika pospješuju anodni inhibitori i tako sprečavaju anodno otapanje metala. Njihovo pasivirajuće djelovanje je popraćeno visokim vrijednostima korozijskog potencijala, reda veličine od 0 do – 250 mV (prema ZKE). Anodni inhibitori mogu biti oksidirajući ili neoksidirajući već prema tome da li zahtjevaju prisutnost kisika u otopini da bi se razvio pasivitet [5-7]. Među najpoznatijim anodnim inhibitorima su kromati i nitrati. Anodni inhibitori omogućuju stvaranje ili pomažu održavanje već stvorenog pasivnog filma na željezu da ne dođe do njegova razaranja putem loma u odsutnosti inhibitora na mjestima defekata rešetke Fe_2O_3 uz katodnu redukciju kisika. Može se zaključiti da se pasivni sloj također održava primjenom inhibitora koji osiguravaju zatvaranje inicijalno nastalih pora u oksidnom sloju bilo putem adsorpcije na ta aktivna mjesta, metala izloženog agresivnoj otopini, bilo netopivih spojeva inhibitorskog aniona i željeznih kationa. Najčešće su to Fe^{3+} ioni. U neutralnim otopinama uz prisutnost kisika brzina korozije je određena brzinom redukciije kisika. Uloga katodnih inhibitora je smanjiti brzinu tog procesa stvaranjem netopivog sloja na površini, mnogo veće debljine od pasivnog, što onemogućava transport kisika prema površini. Netopivi slojevi se mogu stvarati reakcijom tvari iz otopine na površini

metala nakon čega slijedi taloženje. Često se odvija više istovremenih procesa. Među katodnim inhibitorima najčešće se upotrebljavaju cinkove soli koje se talože kao cinkov hidroksid na katodnim mjestima površine metala, te fosfati koji stvaraju talog cink fosfata zaštitnih svojstava [8-10].

Ekološki neprihvatljivi inhibitori

Međunarodna tijela za kontrolu onečišćenja okoliša daju norme za primjenu inhibitora korozije sa naznačenom gornjom granicom koncentracije kemijskih spojeva; npr. na listi SAD USEPA (The United States' Environmetal Protection Agency) među štetnim teškim metalima krom i cink imaju prvenstvo dok je na listi Europske ekonomske zajednice (EEC) iz 1976. godine dodan i molibden kao zagađivač. Anorganski spojevi teških metala su otrovni i ne razgrađuju se biološki te iz otpadnih voda dolaze ne samo u površinske već i u podzemne vode. Potrebno je ipak naglasiti da je njihova opasnost limitirana koncentracijom.

Ekološki prihvatljivi inhibitori

Pri upotrebi inhibitora u prirodnim vodama potrebno je uzeti u obzir sadržaj kationa, naročito kalcija, ali i magnezija i ostalih iona obično prisutnih u manjim količinama od kalcija. Oni uglavnom doprinose činu zaštite, npr. taloženjem kalcija karbonata i uz inhibiciju fosfatima, kalcij fosfata. Stvoreni slabo topljivi talozi su propusni, te dolazi do korozije, naročito one lokalnog tipa. Sastav i struktura taloga su pod utjecajem promjene parametara blizu metalne površine, npr. u izmjenjivačima topline uslijed lokalnog povišenja temperature, što opet utječe na topljivost soli i pH, pa može doći do taloženja. Kontrola procesa korozije i stvaranja netopivih taloga mora se provoditi istovremeno. Osim primarne netoksičnosti od kemikalija koje dolaze u vodene tokove traži se da se brzo biološki razgrađuju. U novije vrijeme razvijeni su isparljivi inhibitori VCI na bazi organskih spojeva koji su manje toksični i ekološki prihvatljivi [11-13].

EKSPERIMENTALNI DIO

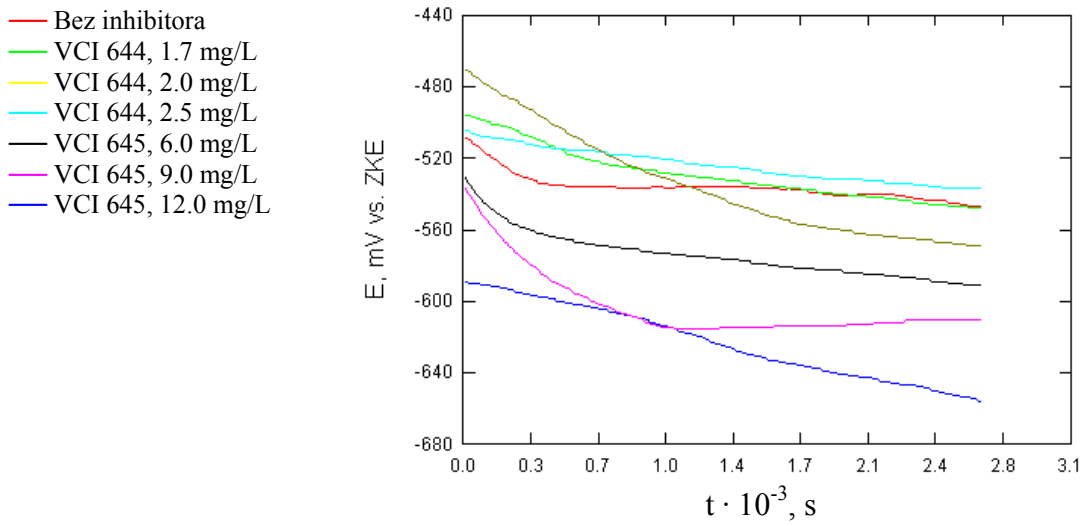
Ispitivano je djelovanje ekoloških isparljivih inhibitora oznaka VCI 644 i VCI 645 različitih koncentracija na brzinu korozije ugljičnog čelika oznake Č0361 (C 0.17 %; P 0.05 %; S 0.05 %; N 0.007%) u 3.5 % otopini NaCl.

Prije svakog mjerenja radna površina uzorka ugljičnog čelika mehanički je obrađena brušenjem brusnim papirima različite finoće, a završno s brusnim papirom SiC granulacije 1200, odmašćena u etanolu i isprana destiliranom vodom. U ovim ispitivanjima korišten je standardni elektrokemijski reaktor s protuelektrodama od grafita te referentnom zasićenom kalomel elektrodom, koja je preko Lugginove kapilare bila u kontaktu s radnom elektrodom. Djelotvornost navedenih inhibitora na ugljičnom čeliku ispitana je elektrokemijskom metodom potencistatičke polarizacije, odnosno metodom Tafelove ekstrapolacije, te mjerenjem promjene korozijskog potencijala (potencijal otvorenog strujnog kruga) u vremenu izlaganja uzoraka 3.5 % otopini NaCl pri 20 ^{o}C sa i bez inhibitora. Metoda potenciostatičke polarizacije provedena je snimanjem polarizacijskih krivulja u području potencijala ± 250 mV od korozijskog potencijala, uz brzinu promjene potencijala 0.5 mVs^{-1}. Primjenom metode Tafelove ekstrapolacije određen je korozijski potencijal (E_{kor}), gustoća korozijske struje (j_{kor}), te djelotvornost inhibitora (z). Na stereomikroskopu su provedena ispitivanja stanja površine ugljičnog čelika sa i bez inhibitora.

REZULTATI I RASPRAVA

Istraživanje inhibitorskog djelovanja na brzinu korozije ugljičnog čelika u 3.5 % otopini NaCl provedeno je elektrokemijskom polarizacijskom metodom uz dodatak inhibitora VCI 644 u koncentracijama od 1.7 mg/L, 2.0 mg/L, 2.5 mg/L i inhibitora VCI 645 u koncentracijima od

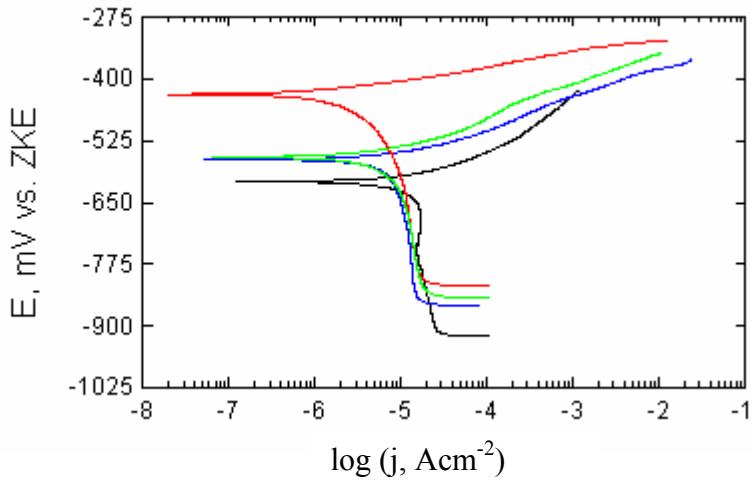
6.0 mg/L, 9.0 mg/L, 12.0 mg/L. Na slici 1. prikazane su krivulje promjene korozijskog potencijala ovisno o vremenu u 3.5 % otopini NaCl sa i bez inhibitora.



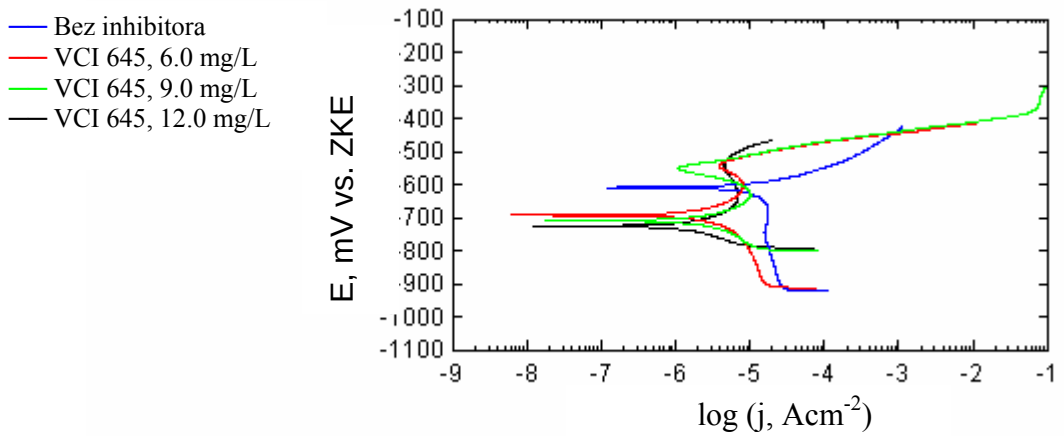
Slika 1. Vremenska ovisnost korozijskog potencijala ugljičnog čelika u 3.5 % otopini NaCl sa i bez inhibitora

Iz prikazanih dijagrama može se vidjeti da pri početku mjerenja dolazi do promjene korozijskog potencijala u negativnom smjeru, a stabilna vrijednost potencijala uspostavlja se za 45 minuta. Isparljivi inhibitor VCI 644 pri svim koncentracijama pomiče vrijednost potencijala prema pozitivnijim vrijednostima, dok dodatak inhibitora VCI 645 kod svih koncentracija pomiče potencijal prema negativnijim vrijednostima u odnosu na korozijski potencijal u 3.5 % otopini NaCl.

Na slici 2. i slici 3. prikazane su polarizacijske krivulje ugljičnog čelika u umjetnoj morskoj vodi sa isparljivim inhibitorima VCI 644 i VCI 645 u različitim koncentracijama i bez inhibitora. U tablici 1. prikazani su kinetički parametri dobiveni Tafelovom metodom ekstrapolacije, prekrivenost površine i stupanj djelovanja inhibitora.



Slika 2. Polarizacijske krivulje ugljičnog čelika u 3.5 % NaCl bez i sa isparljivim inhibitorom VCI 644



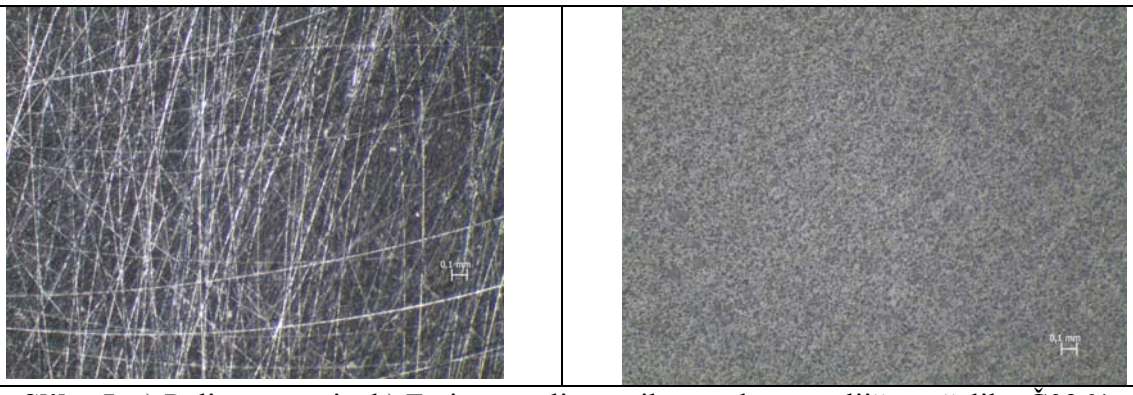
Slika 3. Polarizacijske krivulje ugljičnog čelika u 3.5 % NaCl bez i sa isparljivim inhibitorom VCI 645

Iz dobivenih dijagrama vidi se da dodatak isparljivog inhibitora VCI 644 izaziva značajno smanjenje katodnih gustoća struje, uz neznatan utjecaj na anodni dio krivulje iz čega se može zaključiti da inhibitor VCI 644 djeluje kao katodni inhibitor korozije ugljičnog čelika. Inhibitor VCI 645 jednako djeluje na smanjenje i anodne i katodne gustoće struje, na površini ugljičnog čelika stvara pasivni film što je potvrđeno i stereomikroskopskim ispitivanjem površine ugljičnog čelika.
U tablici 1. prikazani su kinetički parametri dobiveni Tafelovom metodom ekstrapolacije, prekrivenost površine (Θ) i stupanj djelotvornosti inhibitora (z).

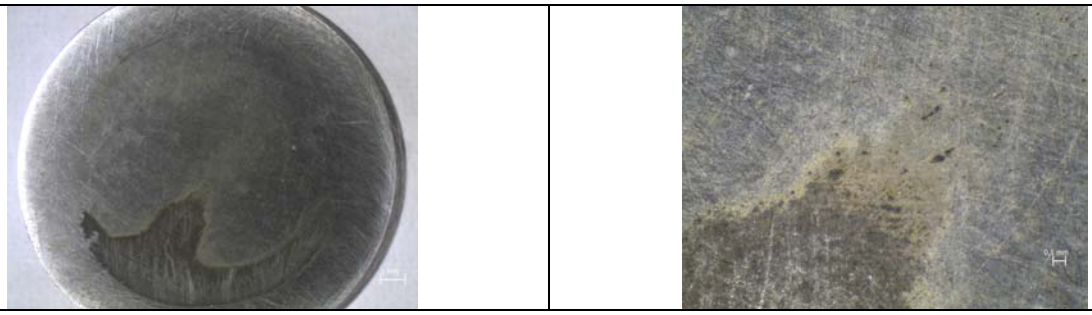
Tablica 1. Usporedni prikaz korozijskih parametara ugljičnog čelika u 3.5 % otopini NaCl sa i bez inhibitora.

Koncentracija inhibitora, mg/L	E_{kor}, mV	j_{kor}, μAcm^{-2}	v_{kor}, $mmgod^{-1}$	Θ	z, %
Bez inhibitora	-608	20.72	0.242	/	/
1.7 VCI 644	-563	10.61	0.124	0.488	48.8
2.0 VCI 644	-431	1.87	0.022	0.910	91.0
2.5 VCI 644	-558	8.88	0.103	0.575	57.5
6.0 VCI 645	-692	5.97	0.069	0.712	71.2
9.0 VCI 645	-709	3.36	0.039	0.838	83.8
12.0 VCI 645	-726	7.45	0.089	0.640	64.0

Analiza površine ugljičnog čelika provedena je pomoću stereomikroskopa prije i poslije potenciostatičke polarizacije uz različita povećanja. Na slici 5a. prikazano je polirano stanje površine ugljičnog čelika, a na slici 5b. mikrostruktura ugljičnog čelika koja je dobivena nagrizanjem u 3 % otopini nitala prije polarizacije. Na slici 6. prikazana su stanja površine nakon polarizacije u 3.5 % otopini NaCl sa i bez inhibitora uz različita povećanja.

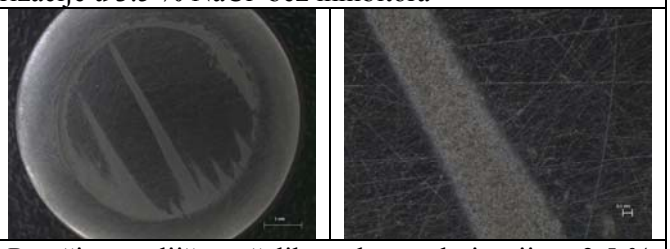


Slika 5. a) Polirano stanje, b) Feritno-perlitna mikrostruktura ugljičnog čelika Č0361

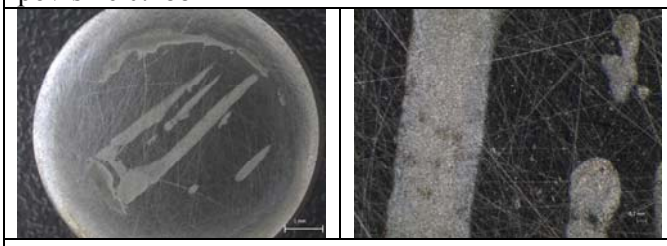


Površina ugljičnog čelika nakon polarizacije u 3.5 % NaCl bez inhibitora

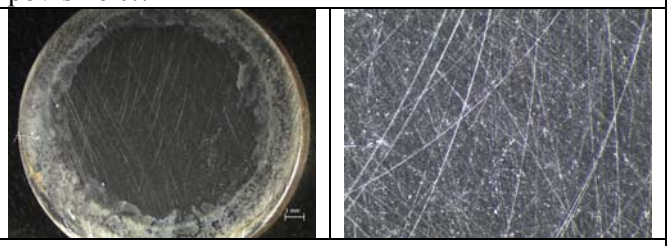
Površina ugljičnog čelika nakon polarizacije u 3.5 % NaCl uz dodatak 1.7 mg/L VCI 644, prekrivenost površine 0.488



Površina ugljičnog čelika nakon polarizacije u 3.5 % NaCl uz dodatak 6.0 mg/L VCI 645, prekrivenost površine 0.712

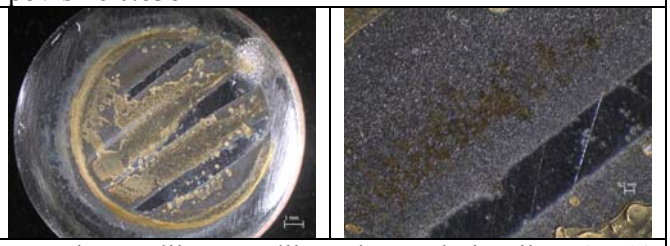


Površina ugljičnog čelika nakon polarizacije u 3.5 % NaCl uz dodatak 2.0 mg/L VCI 644 prekrivenost površine 0.910



Površina ugljičnog čelika nakon polarizacije u 3.5 % NaCl uz dodatak 9.0 mg/L VCI 645, prekrivenost površine 0.838

Površina ugljičnog čelika nakon polarizacije u 3.5 % NaCl uz dodatak 2.5 mg/L VCI 644 prekrivenost površine 0.575



Površina ugljičnog čelika nakon polarizacije u 3.5 % NaCl uz dodatak 12.0 mg/L VCI 645, prekrivenost površine 0.640

Slika 6. Stanja površine nakon polarizacije, različita povećanja

Na osnovu pregleda podataka iz literature i naših mjerenja učinkovitosti inhibicije elektrokemijskim metodama može se konstatirati da se isparljivi inhibitor VCI 644 može uspješno primjenjivati za zaštitu ugljičnog čelika od korozije u maritnim uvjetima samo u koncentraciji od 2.0 mg/L, a inhibitor VCI 645 u koncentraciji od 9.0 mg/L. Ostale koncentracije nisu pokazale djelotvornu inhibiciju ugljičnog čelika.

ZAKLJUČCI

- Cilj ovog rada bio je ispitati djelotvornost isparljivih inhibitora različitih koncentracija na brzinu korozije ugljičnog čelika u 3.5 % otopini NaCl.
- Ispitivanja su provedena s inhibitorom amido soli dikarboksilne kiseline oznake VCI 644 i inhibitorom soli glukonske kiseline oznake VCI 645.
- Dobiveni rezultati polarizacijskih mjerenja (metodom Tafelove ekstrapolacije) pokazuju da inhibitor VCI 644 djeluje kao katodni inhibitor korozije ugljičnog čelika Č0361.
- Rezultati polarizacijskih mjerenja za isparljivi inhibitor VCI 645 pokazuju da djeluje kao mješoviti inhibitor korozije ugljičnog čelika Č0361, te podjednako smanjuje i anodnu i katodnu gustoću struje, odnosno na površini ugljičnog čelika stvara pasivni film.
- Najveća djelotvornost zaštite od korozije (91 %) postignuta je s VCI 644 u optimalnoj koncentraciji od 2.0 mg/L.

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IZLUŽIVANJE UGLJIČNE ANODNE PRAŠINE U VODENOJ OTOPINI

LEACHING OF CARBON ANODE DUST INTO AQUEOUS SOLUTION

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Sažetak:
Svrha rada je bila ispitati izluživanje ugljične anodne prašine u vodenoj otopini. Ugljična anodna prašina nastaje za vrijeme pečenja i transporta anoda u procesu elektrolize aluminija i predstavlja industrijski otpad.
Ispitani su kemijski i mineraloški sastav ugljične anodne prašine. Određeni su anioni i kationi u eluatima kako bi se procijenio utjecaj ugljične anodne prašine na okoliš. Promjene kemijskog sastava, pH vrijednost i provodnost u eluatima praćeni su tijekom 15 dana.
Dobiveni rezultati ukazuju da ugljična anodna prašina nije sasvim inertan materijal.

Ključne riječi: ugljična anodne prašina, izluživanje, vodena otopina

Abstract:
The purpose of this work was to examine the leaching of carbon anode dust into aqueous solution. Carbon anode dust originates from the baking process and transport of anode in aluminium electrolysis and presents the waste material.
The chemical and mineralogical composition of carbon anode dust were established. The anions and cations in water eluates were determined in order to define the influence of carbon anode dust on environment. Changes in chemical composition, pH values and conductivity of water eluates were measured during 15 days.
Results obtained indicate that carbon anode dust is not quite chemically inert material.

Key words: carbon anode dust, leaching, aqueous solution

UVOD

Aluminij se dobiva elektrolizom taline glinice uz dodatak kriolita-elektrolitičkim postupkom. Ćelija je načinjena od čeličnih limova koji su u unutrašnjosti obloženi debelim grafitnim pločama-katodama, a u elektrolitičku talinu glinice i kriolita uronjena je ugljična anoda.
Osnovne sirovine za proizvodnju ugljičnih anoda su naftni koks kao punilo i katranska smola kao vezivo. Za izradu anoda naftni koks se uzima u količinama od 60-70 %, a udjel katranske smole iznosi 14-17 %. Pored ovih sirovina, koriste se još i pečeni i sirovi ostatak (otpadak) anoda koji su neizbježni u procesu proizvodnje anoda i u procesu elektrolize. Pečeni anodni ostatak nastaje kod rabljenja anode u procesu dobivanja aluminija gdje se cijela anoda ne potroši, a sirovi anodni ostatak nastaje za vrijeme pripreme anode za pečenje. Oba ostatka se recikliraju u količinama od 15-20 % [1].
Osim navedenih, u procesu elektrolize aluminija nastaje još jedan ostatak, a to je anodna prašina. Ugljična anodna prašina (UAP) nastaje za vrijeme pečenja i transporta anoda u procesu elektrolize aluminija. Zbog prisutnih nečistoća, ne vraća se u tehnološki proces proizvodnje anoda i predstavlja industrijski otpad.
U radu su ispitani kemijski i mineraloški sastav UAP i praćeno njezino izluživanje u vodenoj otopini tijekom ukupno 15 dana.

EKSPERIMENTALNI DIO

Uzorci ugljične anodne prašine su osušeni na 105 °C u vremenu od 2 sata. Kemijski sastav UAP određen je metodom atomske apsorpcijske spektrofotometrije uređajem AA-6800 Shimadzu. Mineraloški sastav određen je metodom difrakcije rendgenskog zračenja (XRD) na difraktometru Philips PW 1830 uz upotrebu CuK_{α} zračenja.
Izluživanje je provedeno miješanjem 0,75 g uzorka UAP sa 100 ml deionizirane vode. Nakon potresivanja tresilicom CHIRANA PTE III u vremenu od 2 sata, pripravljene smjese su stavljene u kontakt 3, 7 i 15 dana. Odjeljivanje otopine iz suspenzije uzorka UAP u deioniziranoj vodi provedeno je filtriranjem kroz filtar papir Whatman 40. Za mjerenje pH vrijednosti i električne provodnosti upotrijebljen je pH/konduktometar LeV 1.
Sadržaj kationa i aniona u eluatima određen je ionskom kromatografijom upotrebom Methrom Ion Chromatographa 690.
Ispitivanja su provedena na uzorcima različite veličine čestica (0,08; 0,125; 0,2 mm) pri sobnoj temperaturi.

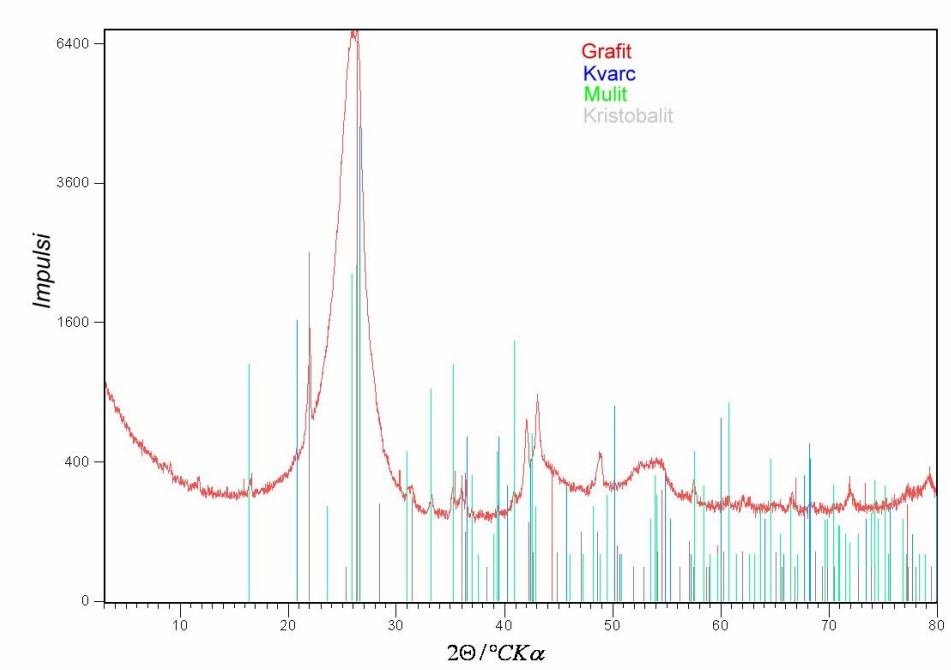
REZULTATI I DISKUSIJA

U tablici 1 prikazani su rezultati kemijske analize ispitane UAP.

Tablica 1. Kemijski sastav UAP

Element	Sadržaj, mas. %
C	94,49
Si	1,73
Al	1,69
S	1,50
Fe	0,34
Na	0,089
V	0,072
Ca	0,044
Ni	0,043

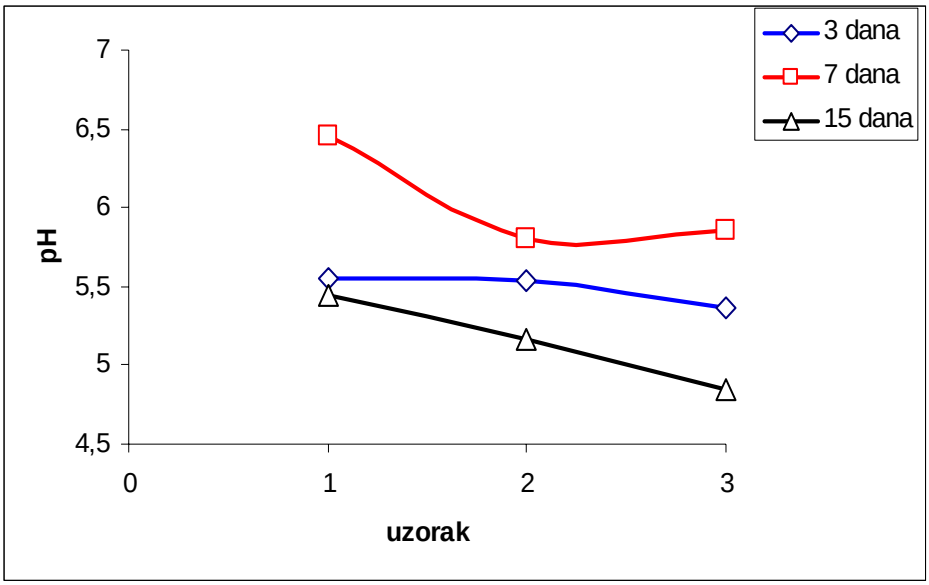
Kao što je vidljivo, najveći je udjel ugljika (94,49 %), a zatim silicija (1,73 %), aluminija (1,69 %) i sumpora (1,5 %).
Sadržaj željeza, natrija, vanadija, kalcija i nikla je od 0,34-0,043 %.
Rezultate XRD analize UAP s karakterističnim dijelovima difraktograma prikazuje slika 1.



Slika 1. Rezultati XRD analize UAP s karakterističnim dijelovima difraktograma

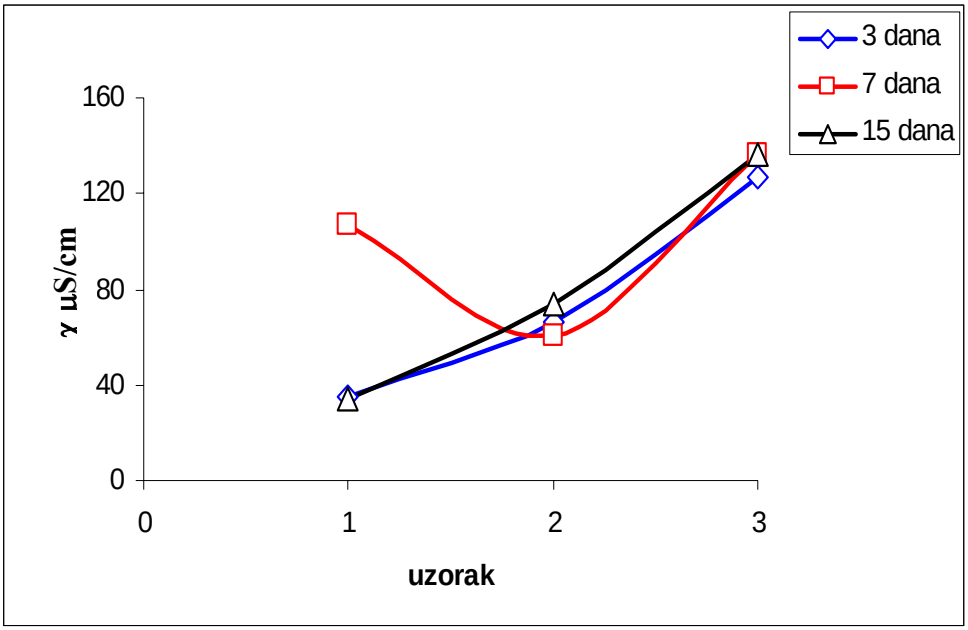
Grafit, kristobalit, kvarc i mulit su glavne faze identificirane u ispitanoj anodnoj prašini. Dobiveni rezultati kemijskog i mineraloškog sastava su u skladu sa sastavom ugljičnih anoda i reakcijama elektrolitičkog postupka proizvodnje aluminija [2, 3]. Naftni koks kao glavna komponenta mase za proizvodnju anoda, treba imati što manje metalnih i nemetalnih primjesa u odnosu na osnovni element ugljik, dobru električnu provodnost i odgovarajuću morfologiju površine. Sve su to pretpostavke za zadovoljavajuća mehanička svojstva i manju reaktivnost anoda [4]. Najvažniji parametri koji definiraju kvalitetu vezivne katranske smole su točka

mekšanja, gustoća i aromatičnost. Pored toga, smola zadovoljavajuće kvalitete treba imati ograničavajući sadržaj pepela i sumpora (< 0,5%), a fiksnog ugljika iznad 52 %.
Prisutni elementi i njihova topljivost u vodi, važan su pokazatelj mobilnosti tvari iz otpada i njihovog utjecaja na ekosustav, a posebno na tlo i vodu. Zbog toga su ispitivane pH vrijednosti, električna provodnost te sadržaj aniona i kationa u eluatima nakon određenog vremena. Rezultati mjerenja pH vrijednosti u eluatu prikazani su na slici 2.



Slika 2. Rezultati mjerenja pH vrijednosti eluata ugljične anodne prašine različite veličine čestica (1-0,2 mm; 2-0,125 mm; 3-0,08 mm)

Dobiveni rezultati su pokazali da nema velike promjene u pH vrijednosti eluata i deionizirane vode (pH vode = 5,5-5,7) koja je korištena za izluživanje.
Također je vidljivo da nema značajnijih promjena pH vrijednosti eluata za uzorke različitih veličina čestica. Izmjerene pH vrijednosti eluata za ispitane uzorke UAP nakon 15 dana kreću se od 4,85-6,46, ovisno o veličini čestica. Ipak, neznatno niže vrijednosti su dobivene za uzorke s najmanjom veličinom čestica (0,08 mm) bez obzira na vrijeme izluživanja.
Sve izmjerene pH vrijednosti kretale su se između 4,85 i 6,46 i zadovoljavale su dozvoljene vrijednosti pH eluata koje su propisane Uredbom o uvjetima za postupanje s opasnim otpadom [5].
Rezultati mjerenja električne provodnosti eluata prikazani su na slici 3.



Slika 3. Rezultati mjerenja električne vodljivosti eluata ugljične anodne prašine različite veličine čestica (1-0,2 mm; 2-0,125 mm; 3-0,08 mm)

Vrijednosti električne provodnosti kreću se od 33,9 do 136,6 µS/cm u odnosu na električnu provodnost vode koja je iznosila od 1,7 do 2,5 µS/cm. Iz slike 3 je također vidljivo da su najveće vrijednosti dobivene za električnu provodnost eluata uzorka UAP s najmanjom veličinom čestica. Prema Pravilniku o uvjetima za postupanje otpadom, maksimalno dopuštene vrijednosti električne provodnosti iznose 50 mS/cm za odlagališta I. kategorije i 10 mS/cm za odlagališta II. kategorije. Iz dobivenih rezultata se vidi da su izmjerene vrijednosti za električnu provodnost ispod maksimalno dopuštenih [6].

Sorpcijska sposobnost jedna je od važnijih karakteristika tla kao podloge za odlaganje otpada, posebno ako se koristi za odlaganje industrijskog otpada. Mogući utjecaj kationa i aniona prisutnih u otpadnoj ugljičnoj anodnoj prašini ispitan je određivanjem njihovih koncentracija nakon izluživanja. U tablicama 2 i 3 prikazani su rezultati određivanja sadržaja Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, F^-, Cl^- i SO_4^{2-} u eluatima ugljične anodne prašine.

Tablica 2. Rezultati određivanja sadržaja kationa (mg/L) u eluatu ugljične anodne prašine

UZORAK	VELIČINA ČESTICA, mm	VRIJEME KONTAKTA, dani	Li^+	Na^+	K^+	Mg^{2+}	Ca^{2+}
1	0,2	3	0,03	2,41	3,22	0,38	5,27
2	0,125	3	0,05	2,25	2,81	0,37	4,87
3	0,08	3	0,07	4,06	3,68	0,57	11,76
4	0,2	7	0,05	4,72	5,67	0,36	8,34
5	0,125	7	0,04	2,28	4,81	0,34	4,15
6	0,08	7	0,07	4,01	7,16	0,61	15,35
7	0,2	15	0,08	4,35	4,98	0,61	11,85
8	0,125	15	0,05	2,29	4,18	0,35	5,85
9	0,08	15	0,03	0,75	3,31	0,12	2,12

Tablica 3.Rezultati određivanja sadržaja aniona (mg/L) u eluatu ugljične anodne prašine

UZORAK	VELIČINA ČESTICA, mm	VRIJEME KONTAKTA, dani	F^-	Cl^-	SO_4^{2-}
1	0,2	3	20,8	23,5	36,1
2	0,125	3	46,2	15,1	85,0
3	0,08	3	98,2	13,3	184,9
4	0,2	7	71,6	5,14	136,4
5	0,125	7	42,3	6,19	76,6
6	0,08	7	209,5	8,4	186,6
7	0,2	15	0,916	1,2	11,86
8	0,125	15	1,46	1,19	21,68
9	0,08	15	3,57	1,25	47,76

Od ispitanih kationa najveći je sadržaj Ca^{2+} (od 2,12 do 15,35 mg/L), a najmanji Li^+ (od 0,03 do 0,08 mg/L). Od ispitanih aniona izmjerena je najveća koncentracija SO_4^{2-} (od 11,86 do 186,6 mg/L), a najmanja Cl^- (od 1,19 do 23,5 mg/L). Nakon ukupno 15 dana izluživanja promijenila se koncentracija aniona i kationa u eluatima neovisno o veličini čestica UAP. Vrijeme kontakta (3, 7 i 15 dana) ima manji utjecaj na promjenu koncentracije aniona i kationa nakon izluživanja nego veličina čestica UAP.

Prisutnost iona u eluatima je povezana s kemijskim i mineraloškim sastavom uzorka, što je direktna posljedica sastava anoda i procesa elektrolize glinice. Glavne mineralne faze identificirane u anodnoj prašini su kvarc i kristobalit (SiO_2) te mulit ($3Al_2O_3 \cdot 2SiO_2$). Obzirom na tehnološki proces, moguća je prisutnost glinice i kriolita (Na_3AlF_6) [1]. Osnovne sirovine za proizvodnju anoda – katranska smola i, posebno, naftni koks sadrže metale (Ca, Mg, Na, K, Fe, Ni, V itd.) i sumpor [7].

Reakcije otapanja, hidrolize i taloženja su najčešće reakcije iona u vodenim otopinama [8]. Obzirom na prisutnost kationa alkalijskih (Na^+, K^+) i zemnoalkalijskih metala (Ca^{2+} i Mg^{2+}), moguće su reakcije hidrolize povezane s promjenama pH vrijednosti. Smanjenje koncentracije aniona u eluatima s vremenom ukazuju na njihovo taloženje.

Promjena koncentracije iona, pH i električne provodnosti nakon izluživanja u vodenoj otopini ukazuje da UAP nije kemijski inertan materijal. Plinovi HF, SO_2, CO, CO_2, Cl_2 i policiklički aromatski ugljikovodici (PAH) doprinose ozbiljnom onečišćenju zraka u aluminijskoj industriji za što je pokazano veće zanimanje nego za anodnu prašinu kao otpadni materijal [9].

ZAKLJUČAK

Rezultati provedenih ispitivanja su pokazali da je kemijski i mineraloški sastav ugljične anodne prašine u skladu sa sastavom sirovina za proizvodnju ugljičnih anoda i procesom elektrolize aluminija.

Nakon izluživanja ugljične anodne prašine u vodenoj otopini ustanovljene su promjene pH vrijednosti, električne provodnosti i sadržaja ispitanih aniona i kationa u eluatima.

Na ispitane parametre nešto je veći utjecaj veličine čestica ugljične anodne prašine nego vremena izluživanja. Može se zaključiti da ugljična anodna prašina nije sasvim kemijski stabilna.

Acknowledgement

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KARAKTERISTIKE Al-In ANODE "AKALPRO-III" U MORSKOJ VODI

CHARACTERISTICS OF Al-In ANODE "AKALPRO-III" IN SEAWATER

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Izvorni znanstveni rad / Original scientific paper

Sažetak: Aluminijske slitine zauzimaju značajno mjesto kao anodni materijal u protektorskoj zaštiti. Protektorske anode od cinka su sklone pasivaciji, a one od magnezija izražavaju samokoroziju koja uvjetuje nizak stupanj djelotvornosti anodnog materijala (≈50%) uslijed čega se smanjuje njihovo protektorsko djelovanje. Pokušalo se pronaći anodni materijal u kojem je pasivno stanje protektora narušeno. Takve mogućnosti pružio je aluminij tehničke čistoće (99.8%) koji je legiran s malim količinama indija. Uslijed toga uvijek prisutni zaštitni oksidni film postaje porozan i ne predstavlja veliki otpor anodnom otapanju aluminija. Energetski kapacitet aluminija legiranjem se smanjuje, pa se nastoji da udio legirajućih komponenata u ukupnoj masi slitine bude što manji.
U ovom radu određivanjem anodne polarizacije uočen je presudan utjecaj indija na negativiranje potencijala. Ispitivanoj slitini dali smo komercijalni naziv AKALPRO-III. Ispitivanja su se provodila u laboratorijskim i realnim uvjetima. Sve tehničke karakteristike ove žrtvovane anode biti će navedene u radu.
Ključne riječi: aktivacija aluminija, slitina Al-In, žrtvovane anode.

Abstract: The aluminum alloys take an important place as anodic material in sacrificial protection. The zinc sacrificial anodes have very high tendency to passivation, likewise the magnesium anodes show self-corrosion which results in low efficiency of the anodic material (approx. to 50%) so protective function is considerable reduced. So an effort has been made to find the anodic material which has disrupted the passive state. Such capability has been found in the technical purity aluminum (99.8%) that has been alloyed with small quantity of indium. Owing to those alloying elements the aluminum oxide film, that is always present, has become porous so it does not represent a barrier to anodic dissolution of aluminum anymore. The contents of the alloying elements must be as small as possible so as not to reduce the aluminum energetic capacity.
In this paper during determination of the anodic polarization, it is noticed that indium have crucial influence to get potential more negative. This tested alloy has been named AKALPRO-III. The investigation has been performed in laboratory and realistic conditions. All technical characteristics of this sacrificed anode will be presented in this paper.
Key words: aluminium activation, Al-In alloys, sacrificial anodes.

Uvod

Većina konstrukcijskih materijala podložna je procesu korozije. U tu svrhu želi se pronaći što djelotvornija mjera zaštite od korozije. Uz klasične metode zaštite pomoću prevlaka i premaza sve više se primjenjuje elektrokemijska zaštita, bilo vanjskim izvorom struje ili katodnom zaštitom upotrebom topivih anoda – protektora.

Katodna zaštita topivim anodama osniva se na tome da se konstrukcija, objekt (npr. čelik – brod) koje se želi zaštititi, spoji direktno ili preko otpora s topivim anodama. Velik interes istraživanja elektrokemijskog ponašanja aluminija i njegovih slitina vjerojatno leži u tome što aluminij pored niza dobrih osobina za razliku od mnogih drugih metala istovremeno posjeduje i dvije dijametralno različite osobine. S jedne strane, termodinamički gledano, aluminij je izrazito neplemenit metal, pa prema tome i vrlo reaktivan. Standardni reverzibilni potencijal $E^0_{Al/Al^{3+}}$ iznosi čak -1.66 V vs. ZKE[1] i ima visoko teoretsko težinsko iskorištenje od 2980 A h kg^{-1} što su privlačne karakteristike s aspekta primjene aluminija kao aktivnog materijala.

Od aktivnog anodnog materijala traži se da se u danom elektrolitu ne inaktivira (pasivira), da zauzme što niže mjesto u ljestvici napona, da ima dobro volumno i težinsko iskorištenje. Dobru korozijsku otpornost aluminij postiže vrlo stabilnim zaštitnim oksidnim slojem koji je gotovo uvijek prisutan na njegovoj površini[2-5].

Modifikacija osobina samog aluminija, odnosno njegovog oksidnog filma u svrhu kontroliranog aktivnog otapanja postiže se legiranjem s malim količinama elemenata kao što su Zn, Hg, Sn, In, Ga i drugih[6-12]. Ovim legiranjem aluminij se aktivira, tj. smanjuje se otpornost oksidnog filma, negativira potencijal i smanjuje negativni diferencijalni efekt.

Efekt aktivacije aluminija može se također postići ako se metalni kationi kao na primjer Hg^{2+}, In^{3+}, Ga^{3+}, Sn^{4+} ili Sn^{2+} dodaju u elektrolit[13].

Eksperimentalni uvjeti

Za izradu aluminijske anode – protektora AKALPRO-III izlivena je aluminijska slitina Al (99.8%) - In (0.1%).

Tehnički aluminij zagrijavao se u čeličnom lončiću oko 15 minuta na temperaturi od 800-850°C. Lončić je bio premazan PROLAN-om 45 (da bi se s njega uklonili tragovi nečistoća). Nakon što je uzorak istaljen dobro je promiješan (čeličnim štapićem) i dodana mu je određena količina legirnog elementa. Metal je ponovno promiješan i vraćen u peć u vremenu 2-3 minute. Zatim je lončić s uzorkom izvađen iz peći, s površine metala skinuta je zgura, metal je još jednom dobro promiješan i izliven u cilindrični rasklopljeni kalup i brzo ohlađen mlazom hladne vode da bi se dobila što homogenija struktura po cijeloj debljini slitine. Za kontrolu homogenosti slitine izvršena su mikrostrukturna ispitivanja primjenom optičkog emisijskog spektrometra (XRF-D).

Za laboratorijska elektrokemijska ispitivanja izrađena je elektroda u obliku kockice brida 1 cm, a elektrodni kontakt je ostvaren pomoću izolirane bakrene žice. Elektroda je sa svih strana, osim s jedne zaštićena epoksi smolom. Slobodna površina iznosila je cca 1 cm^2. Površina radne elektrode prije mjerenja je mehanički i kemijski obrađena. Elektroda je brušena brusnim papirima različite finoće: 360, 600 i 800. Završna glatkoća i zrcalni sjaj dobiveni su naknadnim poliranjem s brusnim papirom finoće 1000. Da bi se odstranio površinski oksidni sloj elektroda je držana 1 minutu u 0.1 M otopini NaOH, zagrijanoj na 40°C. Zatim je elektroda ispirana s destiliranom vodom i postavljena u elektrokemijsku ćeliju

s protuelektrodom od platine i zasićenom kalomel elektrodom kao referentnom elektrodom, koja je preko Luginove kapilare bila u kontaktu s radnom elektrodom. Ispitivanja su provedena u morskoj vodi pri temperaturi $25\pm0.1^{o}C$ i pri pH vrijednosti 7.

Potenciodinamičke polarizacijske krivulje dobivene su mjerenjem pomoću potenciostata (PAR M273A) uz brzinu promjene potencijala od 2 mV s^{-1} vođenog računalom. Mjerenja su izvođena nakon uspostavljanja stabilne vrijednosti potencijala otvorenog strujnog kruga (E_{OCP}) u potencijalnom području $E=E_{OCP}\pm250$ mV u smjeru od katodne do anodne strane.

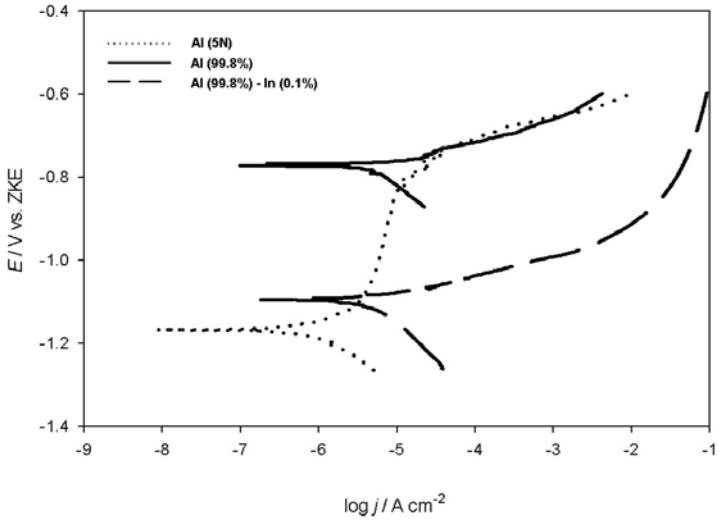
Nakon laboratorijskih ispitivanja i dobivenih rezultata dimenzionirale su se anode - protektori koji bi trebali učinkovito štititi čeličnu konstrukciju. Prethodno su u anode zavareni čelični nosači. U svrhu daljnjeg ispitivanja pripremljene su čelične ploče – oplate koje su pjeskarene do kvalitete Sa2.5 po standardu HRN EN ISO 8501-1. Zatim su obrađene s dvokomponentnim poliamidnim premazom Hempadur 1513/1999 i Hempatexom 4633/5063, a potom 2x s premazom protiv obraštanja AF Classic 7655/5050. Površina oplate iznosila je $2m^2$. Preko čeličnih nosača anode su zavarene na čeličnu ploču (Slika 1.). Prije samog zavarivanja anoda na oplatu izmjereni su potencijali oplate prema referentnoj $Cu/CuSO_4$ elektrodi i aluminijske anode – protektora prema $Cu/CuSO_4$ elektrodi u moru (Slika 2.). Zaštitni potencijal (E_{CCP}) praćen je kroz vremenski period od godinu dana.

Slika 1. Zavarene anode – protektori na čeličnoj ploči.

Slika 2. Čelične ploče s protektorom uronjene u more.

Rezultati i rasprava

Slika 3. prikazuje potenciodinamičke polarizacijske krivulje za superčisti aluminij (5N), tehnički aluminij (99.8%) i protektor AKALPRO-III Al (99.8%) - In (0.1%).



Tablica 1. Elektrokemijski parametri određeni iz polarizacijskih krivulja.

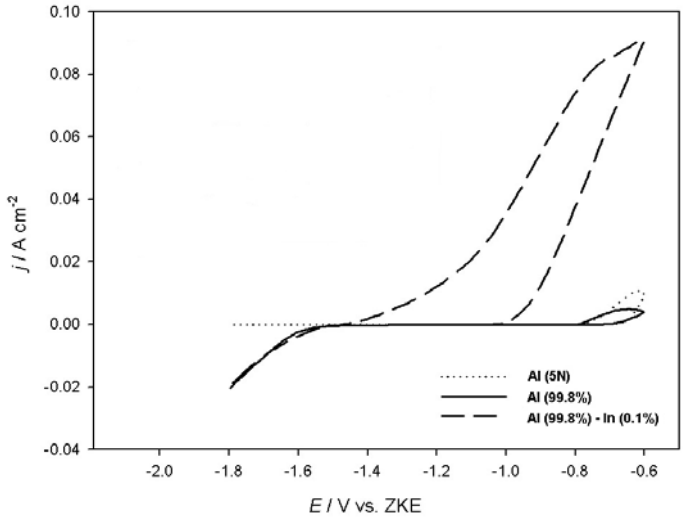
	E_{corr} V	j_{corr} μA cm^{-2}
Al (5N)	-1.158	1.0
Al (99.8%)	-0.776	5.2
Al (99.8%) – In (0.1%)	-1.103	5.5

Slika 3. Potenciodinamičke polarizacijske krivulje za Al (5N), Al (99.8%), Al (99.8%) – In (0.1%).

Dobivene polarizacijske krivulje ukazuju na aktivno ponašanje slitine AKALPRO-III u odnosu na tehnički aluminij. Korozijski potencijal je negativniji za ≈ 0.33 V u odnosu na tehnički aluminij. Slitina ne ispoljava pasivno područje koja je jako izraženo kod superčistog aluminija

Značajan je utjecaj Cl^- iona. Cl^- ioni prodiru kroz oksidni film aluminija uslijed čega dolazi do promjene električnog polja unutar filma i njegove vodljivosti, što pak omogućava aktivno otapanje, tj. dovodi do veće anodne aktivnosti aluminija.

Snimanjem cikličkih voltamograma moguće je odrediti pasivno i aktivno područje potencijala, tj. potencijal depasivacije E_{dp} i potencijal repasivacije E_{rp}. Tipični voltamogrami prikazani su na slici 4.

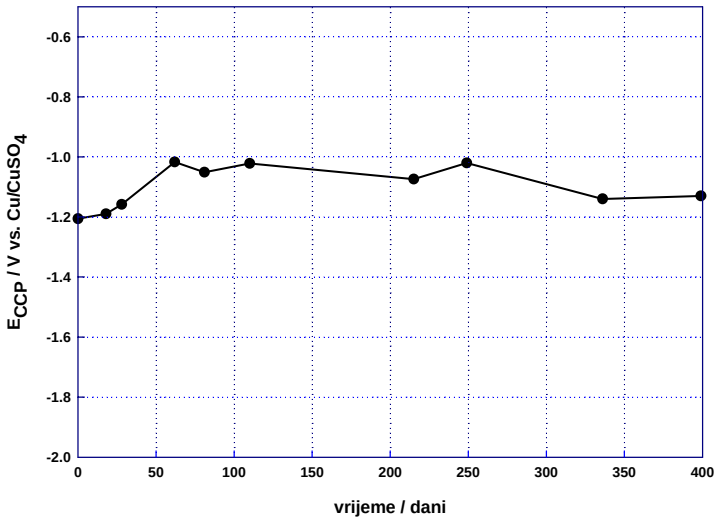


Tablica 2. Elektrokemijski parametri određeni iz cikličkih voltamograma.

	E_{dp} V	E_{rp} V
Al (5N)	-0.654	-0.755
Al (99.8%)	-0.672	-0.789
Al (99.8%) – In (0.1%)	-0.934	-1.192

Slika 4. Ciklički voltamogrami za Al (5N), Al (99.8%), Al (99.8%) – In (0.1%).

Zaštitni potencijal protektora zavarenog na čeličnu ploču prema $Cu/CuSO_4$ elektrodi za vrijeme od godinu dana promatranja prikazan je na slici 5.



Slika 5. Zaštitni potencijal protektora zavarenog na čeličnu ploču uronjenog u morsku vodu prema $Cu/CuSO_4$ elektrodi u vremenskom periodu od godinu dana.

Kao što je prikazano na slici 5. početna vrijednost potencijala je iznosila –1.206 V vs. $Cu/CuSO_4$, a nakon godine dana izlaganja morskoj vodi zaštitni potencijal iznosio je –1.130 V vs. $Cu/CuSO_4$.

Čelične ploče vizualno su pregledane i nije na njima bilo nikakvih destrukcija kao posljedica korozijskih procesa. Nakon toga bili smo u mogućnosti kao i u prethodnim radovima[14,15] definirati tehničke karakteristike anode - protektora AKALPRO-III.

Tablica 3. Tehničke karakteristike anode - protektora AKALPRO-III.

AKALPRO-III	
energetski kapacitet	**2829 A h kg^{-1}**
iskorištenost anode	**94.90 %**
potrošnja anode	**3.096 kg A^{-1} god^{-1}**
zaštitni potencijal	**-1.130 V vs. $Cu/CuSO_4$**
specifična težina	**2.701 g cm^{-3}**

Protektor AKALPRO-III zbog svojih dobrih karakteristika učinkovito će štititi metalne konstrukcije koje se nalaze u morskom okruženju, tj. svih stacionarnih i plovnih objekata, Nadalje, otporan je pri udaru na iskrenje i ne oslobađa značajne količine vodika, te se bez opasnosti može koristiti kao zaštitna anoda u balastnim tankovima, za transport nafte i zapaljivih tekućina.

Zaključci

Istraživanjem elektrokemijskih i zaštitnih svojstava aluminijske slitine snimanjem potenciodinamičkih polarizacijskih krivulja utvrđeno je da se potencijal slitine Al (99.8 %) - In (0.1%) negativira u odnosnu na tehnički aluminij, tj. aluminij se aktivira legiranjem, odnosno smanjuje se otpornost oksidnog filma.

Predloženi protektor AKALPRO-III praćenjem vrijednosti zaštitnog potencijala u vremenskom periodu od godine dana iskazao je nisku potrošnju, visoki izlazni energetski kapacitet i iskorištenje anode od 94.9%.

Napomena:

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APPLICATION OF ELECTRIC ARC FURNACE SLAG

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Abstract:
Steel making process in electric arc furnaces generates up to 15 % of slag, which is, based on its properties, classified as non-hazardous waste. Disposal of such material requires large surfaces and it is rather unfavourable in economical terms. Therefore, researches have been conducted to establish the potential use of slag in different activities.
Slag samples were taken from the non-hazardous land fill run by the Tube Rolling Mill Sisak and the analyses conducted in cooperation with the Faculty of Agronomy and the Croatian Institute of Civil Engineering, both in Zagreb, have shown that slag can be used for agricultural purposes as inorganic soil enhance, in construction industry as an additive to cement and in civil engineering as an additive for road construction.

Key words: electric arc furnace slag, soil enhance, cement, road construction

1. INTRODUCTION

Steel making process in electric arc furnaces generates up to 15 % of slag per ton of steel. Major components of steel mill slag include Ca-silicates, Ca-Al-ferrites, and molten oxides of calcium, iron, magnesium, and manganese. The composition of slag varies upon the type of furnace and charge, the desired grade of steel purity and the furnace operation conditions. Materials to be added to the steel melt directly before the end of the reheating process are not fully embedded in the slag structure, so they can be found in the slag as "free" oxides (CaO, MgO). Compared to blast furnace slag, steelmaking slag shows a considerably higher content of iron, manganese, and magnesium along with the lower silicon content i.e. higher CaO/ SiO_2 ratio, and, finally, it contains almost no sulphur at all. Steel mill slag has more weight, higher hardness and density, it is less porous and highly resistant to polishing and wear and as such is very suitable for road building. [1-4]

On the ground of its properties, slag is classified as non-hazardous waste and it can be disposed off to appropriate landfills. This procedure is rarely applied because it is expensive and requires large surface. Furthermore, there is always the risk that different components of slag might eluate. Therefore it is necessary to examine this metallurgical waste material in detail and apply it in appropriate way i.e. in line with the obtained results, as a valuable secondary raw material for purposes in other branches of economy. [5,6]

In the past, the application of steel mill slag was not attractive because vast volumes of blast furnace slag were available. Slag from the steel mills was used as artificial fertilizer only if it came from the processes that used phosphorous pig iron as raw material to produce steel (so called Thomas slag). The increase of steel mill slag was slow due to the high iron content as only iron (steel) was recycled from the slag and the rest of it was mainly disposed of to landfills. Today, due to the ever increasing share of steel production in electric arc furnaces in the world, the steel mill slag becomes more and more important and it replaces blast furnace slag in many fields of application. [7] For example, portion of the separated slag, that does not have an increased content of metallic components, with regard to its properties, can be applied in the construction industry. [8-10] Furthermore, it was observed that electric arc furnace (EAF) slag can be used as inexpensive absorbing agent in the treatment process for waste waters burdened with metallic ions. [11]

2. EXPERIMENTAL

The steel mill at the Tube Rolling Mill Sisak generates approximately 15% of slag per tonne of steel produced in the electric arc furnace. The slag is disposed to a landfill next to the facility. The landfill covers a surface of 25 ha and in some places it is up to 4 meters high. The slag is mostly crushed, but it it's also partly agglomerated in lumps up to 2.5 meters in diameter. Its macroscopic features indicate the difference in colour (brown, greenish-grey, grey to black), porosity (different size and distribution of pores) and its characteristics are distinctly heterogeneous. The landfill is polluted because, apart from slag, other large waste types (constructional waste, refractory waste, various iron or plastic objects) are disposed there, too. Bearing in mind the different bonding degree of the conglomerated slag as well as the fact that the land is covered with short plants and waste materials, samples were taken from 5 locations and a representative sample with grain size 4 to 85 mm was produced.

In order to establish the possibility to use electric arc furnace slag for road construction, standard examination methods were applied at the Road Construction Laboratory with the Croatian Civil Engineering Institute in Zagreb.

The Department of Plant Nutrition of the Agriculture Faculty, University of Zagreb, conducted the chemical analysis of the electric arc furnace slag from the steel mill. They

examined the parameters relevant for classifying this material to the inorganic soil enhancer group.

The Croatian Civil Engineering Institute in Zagreb investigated the possibility to use slag as a cement additive.

3. RESULTS AND DISCUSSION

Road Constructions

Table 1 shows the test results to establish whether slag is suitable for construction of dams, beds, and mechanically comprised layers (tampons) out of granular material, without bonding agents, in compliance with the general technical conditions for road works. [12]

Table 1: Test results to establish whether slag is suitable for construction of dams, beds, and mechanically comprised layers out of granular material, without bonding agents

Property	Test Method	Unit of Measure	Result	Evaluation Criteria
Density	HRN U.B1.014	g/cm^3	3.831	-
Coefficient of nonuniformity, U= d60/ d10	HRN U.B1.018	-	6.58	>4
Share of particles bellow 0.1 mm	HRN U.B1.018	mass %	0	-
Largest grain diameter	HRN U.B1.018	mm	350	<400 (where 15% are allowed to be up to the size 500)
Optimal moisture, W_{opt}	HRN U.B1.038	%	2.2	-
Maximal dry spatial mass	HRN U.B1.038	g/cm^3	2.794	-
Optimal moisture, W_{opt}	HRN U.B1.038	%	2.7	-
Maximal dry spatial mass	HRN U.B1.038	g/cm^3	2.460	-
Maximal dry spatial mass	HRN U.B1.042	g/cm^3	2.780	-
95% value of maximum spatial mass	HRN U.B1.042	g/cm^3	2.641	-
California Bearing Ratio, CBR	HRN U.B1.042	%	198	min. 80
Grain shape	HRN B.B8.048	mass %	6.2	max. 40
Water absorption	HRN B.B8.031	mass %	0.8	max. 1,6
Frost stability, by the Na_2SO_4-method	HRN B.B8.044	mass %	0.05	max. 7
Share of worn, low quality grains	HRN B.B8.037	mass %	0.4	max. 12
Wear and impact resistance, by the Los Angeles method	HRN B.B8.045	mass %	17.4	max. 45

The density is 3.831 g/cm^3. By defining the granular-metrical composition it was found out that the sample represented a mixture in size from 0 to 350 mm. The non-uniformity coefficient U is 6.58, thus fulfilling the requirement of at least 4 for the construction of dams of stone materials. Re-crushing of slag can result in coefficient 15, because the grain size would decrease and such material could be integrated in the bearing layer. The diameter of the largest grain in the sample is 350 mm and maximal grain size is allowed to be equal to, but not bigger than half of the thickness layer, and not bigger than 400 mm (where 15 % of grains may be the size of up to 500 mm).

In the process of identifying the optimal water content during sample compression using energy from the standard Proctor procedure (0.66 MNm/m^2), with different water dosage, the following parameters were determined:

- optimal moisture, W_{opt} 2.7 %
- maximal dry spatial mass 2.460 g/cm^3.

By identifying optimal water content during sample compression using energy from the modified Proctor procedure (2.66 MNm/m^2), with different water dosage, the following parameters were determined:

- optimal moisture, W_{opt} 2.2 %
- maximal dry spatial mass 2.794 g/cm^3.

Approximation of the pollution with organic substances (colour-metrical method) was conducted by treating samples with the NaOH solution, and the resulting colour of the solution is brighter than the standard colour and it was thus established that the sample contained no organic substances.

The carrying capacity of the material was assessed on the grounds of the lab-determined California Bearing Ratio (CBR):

- on the sample, with compressed energy 2.66 MNm/m^2 (56/5 impacts per layer), with optimal moisture, the CBR was 331 % with dry spatial mass of 2.780 g/cm^3,
- the sample was also compressed with lower energy (28/5 impacts per layer), with optimal moisture, where the CBR was 147 % with dry spatial mass of 2.575 g/cm^3,
- the CBR for the compression energy 0.6 MNm/m^2 (13/5 impacts per layer) was 99 % with dry spatial mass of 2.511 g/cm^3.

The CBR- spatial mass relationship shows that the material was compressed to the spatial mass of 2.641 g/cm^3 (65 % of 2.780 is 198 and it meets the condition that CBR for the crushed stone material must be at least 80%).

Table 2 shows the results of the examination of physical-mechanical properties of slag, in compliance with the general technical conditions for road works, for road pavements. [13] In the laboratory, the sampled slag was dispersed to fractions, on which the physical-mechanical properties were tested.

Table 2: Physical-mechanical properties of laboratory-dispersed EAF slag fractions

GRAIN SHAPE	
FRACTION (mm)	**UNSUITABLY SHAPED GRAINS** mass %
4/8	14.86
8/16	3.87
16/32	0.00

WATER ABSORPTION	
FRACTION (mm)	**WATER ABSORPTION** mass %
4/8	0.99
8/16	0.70
16/32	0.87

FROST STABILITY, Na_2SO_4 METHOD	
FRACTION (mm)	**LOSS OF MASS AFTER 5 CYCLES** mass %
2/4	0.127
4/8	0.076
8/16	0.000
16/32	0.000

SHARE OF WORN, LOW-QUALITY GRAINS	
FRACTION (mm)	**WATER ABSORPTION** mass %
4/8	1.13
8/16	0.00
16/32	0.00

WEAR AND IMPACT RESISTANCE, BY LOS ANGELES METHOD	
GRADATION (mm)	**WEAR-loss** mass %
B(12.5-25.0)	17.4

The shape of the grains is satisfactory as the unsuitably shaped grains account for 6.2 %, and the maximum allowed level is 40 %. The wear and impact resistance of the grains, established with the Los Angeles method, is 17.4 %, which is also acceptable as the loss of mass does not exceed the maximum allowed level of 45 %. The share of worn grains is also acceptable as they account for 0.4 %, which is significantly below the allowed 7 %. Water absorption is 0.8 %, far less than the allowed 1.6 %. The resistance of grains to Na_2SO_4 solution, expressed as the loss of mass, is 0.05 %, whereas up to 12 % is tolerable. Results of physical-mechanical testing of the laboratory-dispersed fractions of slag indicate that water absorption, shape of some worn (low-quality) grains, and the resistance to the Na_2SO_4 solution fully meet all requirements of the stated norms. The wear and impact resistance defined by the "Los Angeles" method meets the criteria set out in HRN U.E9.021 (for all traffic load groups) and HRN U. E4.014 norm (for heavy, medium, light and ultra light traffic load).

Soil Enhancer

The analysed slag samples release neither temperature nor gases in reaction with water, and their water solubility is rather poor. Reaction (pH) of the observed materials is alkalic (pH = 11.09-12.27). The annealing loss at 550 °C is rather low (1.38-1.42 %) and with the temperature increase (1100 °C) the annealing loss is only lightly increased as well (2.86-2.91 %), indicating the inertness of the material at high temperatures. The heating of samples did not result in inflammation.

The results of the chemical analysis (Table 3) clearly show the observed slag to be rich in iron compounds, whereas manganese compounds were accounted for in much lesser quantity. The samples contain approximately 8 % $CaCO_3$, which will, should the slag be used as soil enhancer, have a favourable effect on the improvement of the pH-value of acid soils. Since the slag has very little biogene elements, this material will have no significant impact on plant nutrition.

Table 3: Results of the chemical analysis of EAF slag

Analysed Component	**Unit of Measure**	**Sample 1**	**Sample 2**
		Result / Limit Value	
Dry substance	%	99.68/-	99.82/-
H_2O	%	0.32/-	0.18/-
pH (water)	-	12.27/-	12.09/-
Annealed residue (550 °C)	%	98.58/-	98.68/-
Annealing loss (550 °C)	%	1.42/-	1.38/-
Annealing loss (1100°C)	%	8.73/-	8.30/-
Total P_2O_5	%	0.0123/-	0.0126/-
Total K_2O	%	0.034/-	0.033/-
Total Na	%	0.069/-	0.070/-
Fe_2O_3	%	34.34/-	34.32/-
$CaCO_3$	%	8.34/-	8.34/-
Mg CO_3	%	2.52/-	2.72/-
MnO_2	%	0.496/-	0.476/-
Zn	mg/kg	82.50/150.0	82.50/150.0
Cu	mg/kg	59.06/50.0	62.50/50.0
Ni	mg/kg	75.0/30.0	75.0/30.0
Cd	mg/kg	0.85/0.80	0.85/0.80
Pb	mg/kg	25.20/50.0	25.20/50.0
Cr	mg/kg	30.30/50.0	35.10/50.0
Hg	mg/kg	<0.1/0.8	<0.1/0.8
Mo	mg/kg	1.13/10.0	1.10/10.0
Co	mg/kg	11.52/30.0	11.52/30.0
As	mg/kg	1.23/10.0	1.23/10.0

In line with the Croatian Regulation on protection of agricultural soil from pollution with harmful substances, the limits of the harmful substances extracted in the royal water (aqua regia) are below the maximum allowed levels. Since the analysed materials contain no substances that may be harmful to agricultural production, their use will certainly improve some physical-chemical properties of soil, and they can therefore be categorized as soil enhancers. Should the stated materials really be used for improvement of agricultural soil, the quantities to be applied will have to be adjusted to soil analysis results first.

Cement

The cement mixtures with the addition of 15 % and 50 % slag were tested. The cement was made of clinker from the "*Našicecement*" factory and plaster from "*Ciglana Sinj*". The respective chemical composition of the two materials is shown in Table 4.

Table 4: Chemical composition of clinker and plaster

	Clinker	**Plaster**
Annealing loss	0.32	-
SO_3	0.50	36.57
Insoluble residue/ HCl	0.1	-
MgO	1.38	0.60
CaO	66.53	27.26
SiO_2	21.29	9.83
Fe_2O_3	3.23	Total R_2O_3 0.85
Al_2O_3	5.94	
Na_2O	0.59	
K_2O	0.93	
NaCl	-	0.23
Bonded water	-	13.40
The NORM	HRN EN 196-2121	HRN B. C 8.032

Table 5 shows the test results for cement and two cements with the addition of s 15 % and 50 % foundry EAF slag, respectively. The obtained results indicate that potential to use foundry EAF slag as a cement additive (15%).

Table 5: Properties of pure cement and cement with 15 % i.e.50 % foundry EAF slag

	CEM I 52.5	**Test Sample I**	**Test Sample II**
Reference cement share (mass %)	100	85	50
Slag share (mass %)	0	15	50
Chemical properties (mass %) Annealing loss SO_3 Insoluble in HCl and Na_2CO_3 Insoluble in HCl and KOH S^{2-} Mn SiO_2 Fe_2O_3 Al_2O_3 Cao MgO Cl^- Na_2O K_2O	 1.89 3.59 0.85 0.60 0.01 0.07 20.29 2.36 5.3 61.66 2.46 0.008 0.36 0.89		
Physical and mechanical properties			
Standard consistency	27.4	27.0	26.8

Bonding start (min)	115	120	210
Stability (mm)	0.25	0.25	0.25
Compression strength after 2 days (MPa)	25.7	24.86	-
Compression strength after 7 days (MPa)	-	-	10.8
Compression strength after 28 days (MPa)	56.9	44.9	21.4

4. CONCLUSION

On the grounds of the conducted laboratory testing of steel mill EAF slag stored at the land fill for non-hazardous industrial waste of Tube Rolling Mill Sisak, we can conclude that the physical-mechanical properties of the observed slag indicate its potential use in road building for the following purposes:

- construction of dams and beds,
- non-bonded layers of road pavements (bearing and buffering layers),
- bonded bearing layers of granular stone material,
- asphalt layers of road pavement, either completely or as an additive to stone and/or earthy material (for dams and beds).

For a complete assessment of the suitability of slag to make certain types of asphalt mixtures and non-bonded layers of road pavements, it is necessary to re-crush slag, to separate it in line with the intended use, and to perform full examinations relevant for the intended use. It is additionally important to analyse and identify the content of the components having an impact on the slag volume stability (share of magnesium oxide, presence of di-calcium-silicates and iron).

Furthermore, the examined steel mill EAF slag improves physical-chemical properties of soil and can be categorized as inorganic soil enhancer. Besides that, it can be used as a 15%-additive to cement.

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MONITORING OF CORROSION PROCESS IN ARTIFICIAL SWEAT SOLUTION OF METAL WIRES

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Izvorni znanstveni rad / Original scientific paper

Abstract:
In this paper corrosion process on three different metal wires from electric guitar strings were monitored by scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDX). The coating thickness on wires was measured and monitored before and after 28 days immersion in artificial sweat solution. The changes of the wrap Ni coating thickness before and after the corrosion process were used for monitoring corrosion process. It was observed that thickness of all coatings on all tested samples decreased due to the corrosion process occurred.

Keywords: SEM-EDX, electric guitar string, corrosion in artificial sweat

1. Introduction

Scanning electron microscopy (SEM) is today one of the best known and most widely used of all surface analytical techniques. Energy dispersive X-ray spectroscopy (EDX or EDS) is a chemical microanalysis technique often used together with a scanning electron microscope (SEM). Their combination provides rapid and non-destructive method of surface analysis. In addition to low energy secondary electrons and backscattered electrons, X-rays are generated by primary electron bombardment. The analysis of characteristic X-rays emitted from the sample gives quantitative information of elements investigated. Therefore the EDX technique detects X-rays that are emitted from samples during bombardment by an electron beam to characterize the elemental composition of the surface volume analyzed. When the sample is bombarded by the SEM's electron beam, inner shell electrons of sample atoms can be ejected. When this occurs, electrons from higher energy levels go to the inner shells causing the emission of high energy photons in the X-ray range (Figure 1).

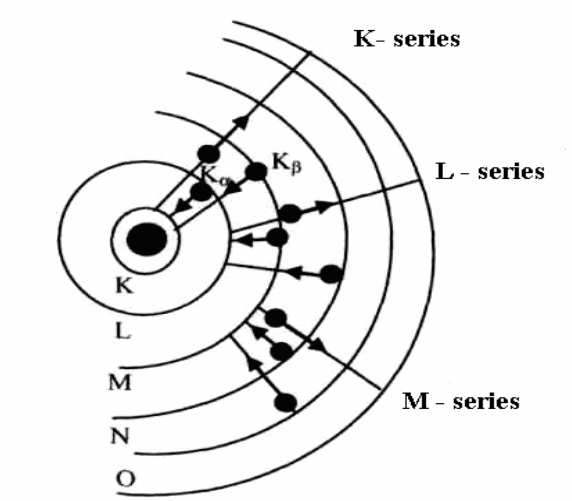

Figure 1: Origin of characteristic line spectra in an atom.

EDX analysis allows different performances: q*ualitative analysis* in which the sample′s X-ray energy values are compared to the known elemental characteristic X-ray energy values in order to identify the unknown elements in the sample; q*uantitative analysis* that shows the amount of each identified element in the sample, *elemental mapping* and *line profile analysis*. Typical applications of EDX allow corrosion evaluation, rapid material alloy identification, small component material analysis and coating composition analysis. The aim of our work was to monitor corrosion process in the artificial sweat solution of metal wires because such investigations are very important for musicians, for materials properties determination and for human health [1-7]. As model samples, three different guitar string were subjected to the corrosion for 28 days.

2. Experimental procedure

Investigated samples were three electric guitar strings produced by D′Addario Company, USA which are used as the E6, A5 and D4 strings for the electrical guitar. Electric guitar strings were

characterized by optical (OM) and scanning electron microscopy (SEM). Chemical compositions of coatings on electric guitar strings were determined by means of SEM equipped with EDX detector.

Thickness of wrap Ni coatings on E6, A5 and D4 strings were measured before and after the corrosion process in the artificial sweat solution. The strings (E6, A5 and D4) were simultaneously put into a sealed polypropylene (PP) tube with 10 ml of artificial sweat solution. The static corrosion tests were carried out at the temperature of 37 °C for 28 days (672 h). After the planned exposure time, the specimens were removed from tubes, rinsed with distilled water and dried in the warm oven preheated at 100 ^{o}C. Afterwards the thicknesses of the wrap Ni coatings of tested E6, A5 and D4 strings were measured. The changes of the Ni coatings thickness before and after the corrosion process were used for monitoring the corrosion process.

3. Results and discussion

Electric guitar strings E6, A5 and D4 consist of two separate parts: steel cores with thin layer of Sn whose thickness is about 1 μm and steel wraps with Ni coatings of different thicknesses (Figures 2 and 3). The shapes of cross sections of all strings (E6, A5 and D4) are the same having the only essential difference in their diameters. Diameters measured by optical (OM) and scanning electron microscopy (SEM) of E6, A5 and D4 strings are 1.07 mm, 0.81 mm, and 0.61 mm, respectively.

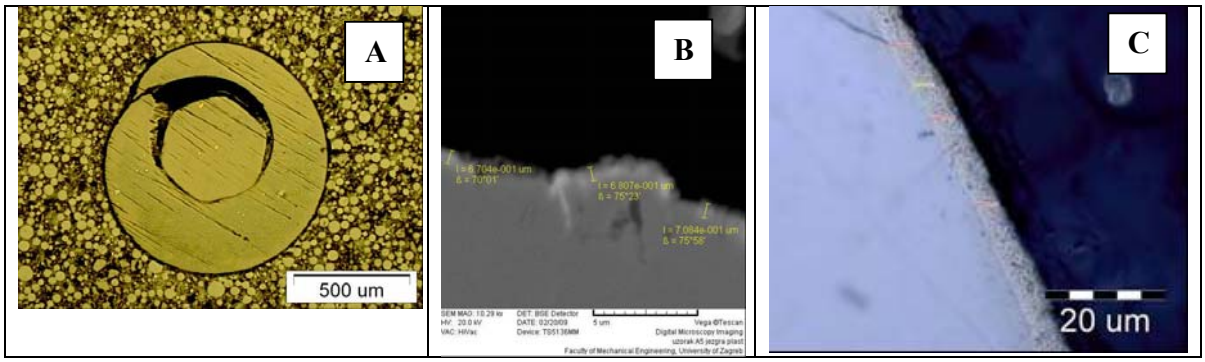

Figure 2: **(A)** Optical micrograph of polished cross-section of electric guitar string E6. **(B)** SEM micrograph of the cross-section of the Sn-coated core for determination thickness of Sn coating. Magnification X10290. **(C)** Optical micrograph of the cross-section of the Ni-coated wrap for determination thickness of Ni coating.

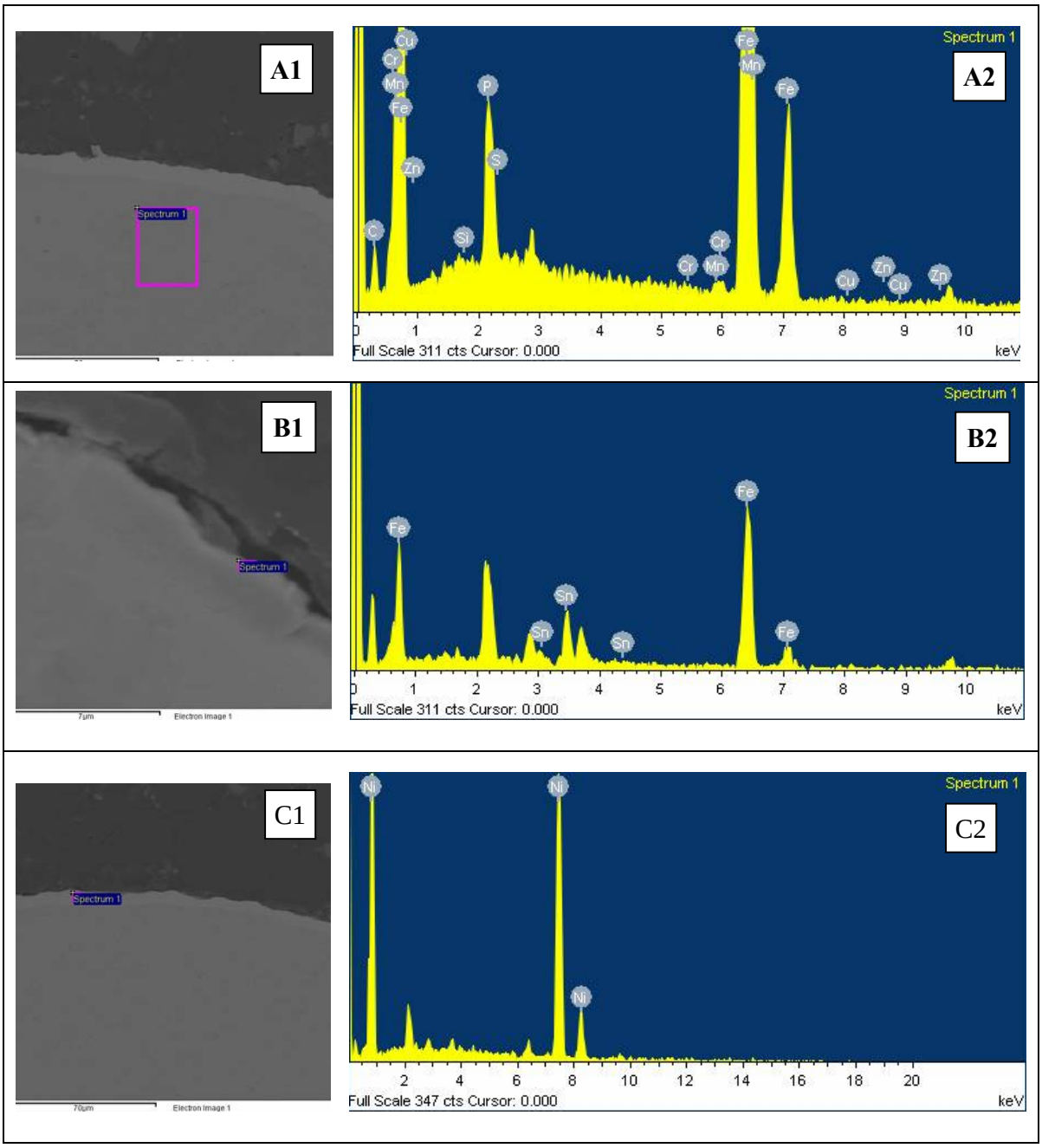

Figure 3: (A2, B2, C2) SEM-EDX spectra results of (A1) core and wrap bulk composition (B1) composition of core coating and (C1) composition of wrap coating, respectively.

Corrosion process was evaluated by measuring the changes of the thickness of wrap Ni coatings on E6, A5 and D4 strings before and after the immersion in the artificial sweet solution for 28 days. Obtained results (Table 2) indicate that thicknesses of all wrap Ni coatings of investigated guitar strings (E6, A5 and D4) decreased for 2.02 μm, 1.42 μm and 2.23 μm, respectively.

Table 2. Values of thickness of wrap Ni coatings of E6, A5 and D4 strings before and after the corrosion process in the artificial sweat solution.

Sample	**Thickness of Ni coating on wrap (d), μm**		**Δd, μm**	**Δd, %**
	before corrosion	after corrosion		
E6	7.65 ± 0.55	5.63 ± 0.67	2.02	26.4
A5	5.00 ± 0.2	3.58 ±0.42	1.42	28.4
D4	5.16 ± 0.66	2.93 ± 0.34	2.23	43.2

4. Conclusions

Investigated E6, A5 and D4 strings consisted of two separate parts: steel core wire with Sn coating which is hexagonal in the cross section and the steel wrap with Ni coating which is round in the cross section. The corrosion of electric guitar strings in the artificial sweat solution was determined by the solubility of Ni coating on the wrap. The thickness of Ni coating on E6, A5 and D4 strings decreased for 2.02 μm, 1.42 μm and 2.23 μm (for 26 – 43 %) on E6, A5 and D4 strings, respectively. These results indicate that corrosion of the investigated metal wires can be monitored by measuring the thickness of the Ni coating on the wraps of investigated E6, A5 and D4 strings.

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CHARACTERIZATION OF ELECTRIC GUITAR STRING A5 BY MEANS OF DIFFERENT TECHNIQUES

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Izvorni znanstveni rad / Original scientific paper

Abstract:
In order to characterization of electric guitar string different following analytical techniques were used: inductively coupled plasma optical emission spectroscopy (ICP-OES), atomic absorption spectrophotometry (AAS), optical microscopy (OM) and a scanning electron microscopy with an energy dispersive X-Ray spectrometer (SEM-EDS). The microhardness of electric guitar string A5 is determined by means of Vickers method.

Keywords: ICP-OES, AAS, OM, SEM-EDS, Vickers microhardness, electric guitar string.

1. Introduction

ICP-OES is method for the determination of simultaneous multi-element analysis metals and some non-metals in liquid samples with high precision, high sensitivity and low detection limits. ICP-OES offers the potential of determining the trace elements and bulk elements in one sample during one run. Plasma OES is safe because only inert gases are used, but spectral interference (direct coincidence of lines, overlapping of nearby lines, overlapping of broadened lines, and continuous radiation) are common in ICP-OES. AAS method possess some advantages, such as, low detection limits (better detection limit posesses ICP-OES, some metal ions have very poor detection limits), interferences and methods for their elimination are well documented. However, AAS is a single element method. AAS has several diadvantages, such as, one element is determined in a series of samples and the instrumental parameters are optimized for the next element. Futhermore, qualitative analysis is impractical and often dangereous gas mixtures must be used. Sample preparation is one of the important parth in the analysis by ICP-OES and AAS techniques. SEM-EDS is a surface analysis method and it is non-desctructive method for analysis of different solids. EDS is capable of determination most metals and non-metals, but for small concentrations this system is not very precise and the detection limit is dependent on the matrix and its surface. SEM-EDS is used for analysis topography, morphology, composition and some crystalographic information [1-5]. In comparison OM and SEM, SEM has higher resolution, magnification and depth of field (Figure 1, [6]).

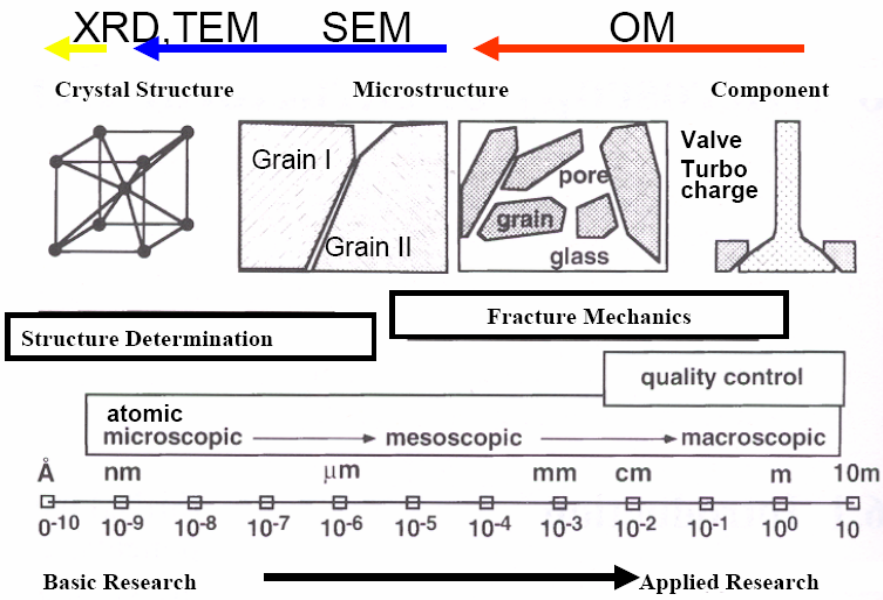

Figure 1. Microstructure ranging from crystal structure to engine components (Si_3N_4). [6]

In this paper different different analytical techniques were used for characterization of electric guitar string A5: inductively coupled plasma optical emission spectroscopy (ICP-OES), atomic absorption spectrophotometry (AAS), optical microscopy (OM) and a scanning electron microscopy with an energy dispersive X-Ray spectrometer (SEM-EDS).

2. Experimental procedure

Investigated sample was electric guitar string marked as A5 which is consist of two wires: a core and wrap. Both wires have coating. String is produced by D′Addario Company, USA and is used as the A5 string for the electrical guitar.

Chemical composition of core and wrap are determined by means of inductively coupled plasma optical emission spectroscopy (ICP-OES), an axially viewed Thermo Elemental "IRIS Intrepid II" XSP, Duo, (Thermo Electron Corporation). The instrument was equipped with a standard one piece extended torch with a quartz injector tube, a cyclone spray chamber and an concentric nebulizer. Major and minor components from different sample parts were checked by flame atomic absorption spectrometer (AAS), AA-6800, Shimadzu. Chemical composition of coatings on core and wrap were confirmed by means of scanning electron microscope (SEM) equipped with energy dispersive X-Ray spectrometer (EDX). Thickness of coatings on core and wrep are determined by means of optical microscopy (OM) and a scanning electron microscopy (SEM). Vickers hardness measurements HV0.1 was performed using indentation load of 0.9807 N for 15 s. Indentation tests were carried out under laboratory conditions on an Instron, Wilson-Wolpert Tukon 2100B, a micro Vickers tester. Before carrying out hardness measurements, all strings were prepared by the standard metallographic technique. The samples were cut, embedded in resin DuroFix-2 Kit, ground and then polished up to 1 μm with a diamond paste until a mirror-like surface was achieved. After chemically etched by immersion in Nital (2 wt % HNO_3 in ethanol) microstructure of strings were analyzed by optical microscope Olympus GX 51.

3. Results and discussion

Electric guitar string A5 consists of two parts: steel core with thin layer of Sn, thickness is about 1 μm (Figures 1A and 1C) and steel wrap with Ni coating (thickness is 5 μm), as was confirmed by SEM-EDS micro analysis. The microstructure of wrap of A5 string includes typical ferrite

crystals of low carbon steel (Figure 1C). Results of microstructure (Figure 1C) as well as chemical composition (Table 1) indicated that wrap of A5 string is made from low carbon steel with ferrite crystals and Ni coating as was also confirmed by SEM-EDS micro analysis. Results of microstructure (Figure 1C) and chemical composition (Table 1) of core indicate that core of A5 is made of martenzite steel with Sn layer.

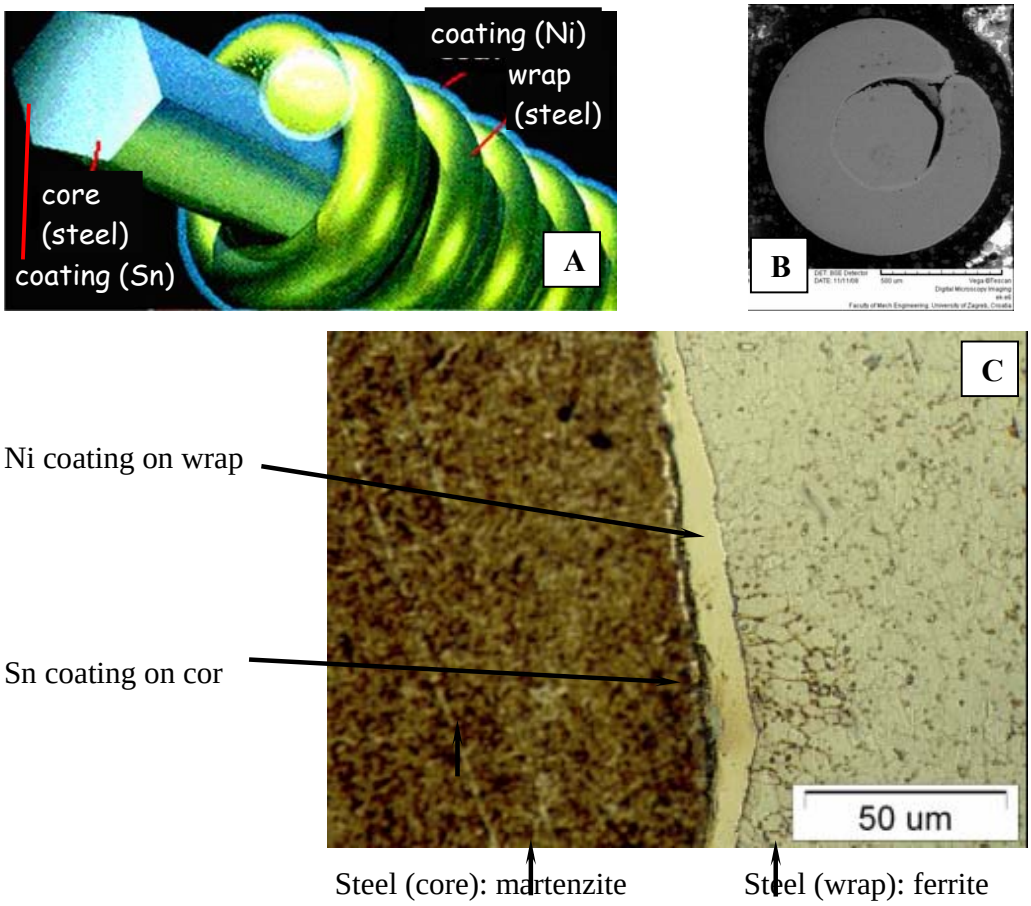

Fig. 1. (**A**) Schematic view of the investigated sample of electric guitar string A5. Sample consist of two different parts: Sn-plated steel core wire which is hexagonal in cross section and Ni-plated steel wrap which is round in cross section. (**B**) SEM micrograph of the cross-section of the core and wrap of electric guitar string A5. (**C**) Optical micrograph of cross-section of A5 electric guitar string microstructure, etched with 2% Nital (2mL of HNO_3 to 98 mL ethanol).

Table 1. Chemical composition of core and wrap of electric guitar string A5.

String A5	w, %						
	Si	Mn	Cu	Cr	Ni	Sn	Fe
core	0.3545	0.5727	0.0107	0.0185	0.0177	0.3126	rest
wrap	0.2124	0.3557	0.0090	0.0467	8.491	0.0115	rest

Results of Vickers microhardness data is presented in Table 2. Results show that Vickers microhardness of core with martenzite microstructure is higher (mean HV0.1 value is 625). Vickers microhardness number for wrap with ferrite microstructure is 200 for A5 string.

Table 2. Microhardness value of electric guitar string A5.

Hardness number	core	wrap
HV0.1	625	200

4. Conclusions

Investigated A5 string is consisting of two parts: martenzite steel core wire with Sn coating which is hexagonal in the cross section and the ferrite steel wrap with Ni coating which is round in the cross section. These observation is in correlation with the determination of microhardness of core (HV0.1 = 625) and wrap (HV0.1 = 200) wires. Ni was confirmed to be a part of the wrap coating (thickness 5μm) as well as in the bulk material. Sn was detected on the core, as very thin layer (under 1 μm).

Acknowledgments

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ESTIMATION OF CAPABILITY ANALYSIS FOR NON-NORMAL DISTRIBUTED DANA

PROCJENA SPOSOBNOSTI PROCESA NE-NORMALNO DISTRIBUIRANIH PODATAKA

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Izvorni znanstveni rad / Original scientific paper

Abstract:
This paper describes the procedure of capability analysis for non-normal distributed datas. For correct interpretation of results, conditions of process normality and stability are defined. In cases when data's cannot be described with normal distribution, procedures of capability analysis are based on one of the well-known distribution models or on the transformation of the data's.
An analysis of process capability on simulated lognormal distribution has been performed. Analyzed process was one-sided, i.e. with only one specification limit or target value. Results are compared and discussed in order to set guidelines for future selection of methods.

Keywords: Capability analysis, Non-normal distributed data's, Specification limits, Target value

Sažetak:
U radu je opisan i razrađen postupak procjene sposobnosti procesa ne-normalno distribuiranih podataka. U cilju pravilne interpretacije rezultata definirani su uvjeti, normalnosti i stabilnosti procesa. Postupci procjene sposobnosti procesa za raspodjele podataka koje se ne ponašaju po normalnoj razdiobi svode se na odabir nekog od već poznatih distribucijskih modela ili na transformaciju samih podataka.
U radu je provedena analiza sposobnosti procesa na simuliranoj lognormalnoj distribuciji. Analiziran je proces koji je jednostran, točnije ima samo jednu granicu ili ciljanu vrijednost. Rezultati su komentirani i uspoređeni, kako bi se mogle dati smjernice za daljnju primjenu određenih metoda.

Ključne riječi: sposobnost procesa, ne-normalno distribuirani podatci, granice specifikacija, ciljana vrijednost

1. Uvod

Analiza sposobnosti procesa, uz statističku kontrolu i planiranje pokusa, statističke su metode, kojima se već godinama pokušava smanjiti varijabilnost proizvodnih procesa i njihovih konačnih proizvoda. Potreba za što uspješnijom kontrolom procesa postaje neizbježna zbog neprestanog rasta kompleksnosti tehničkih sustava u industriji te tržišta koje ju okružuje. Nove metodologije i koncepti upravljanja, ne samo kvalitetom, već i poduzećem u cjelini, sve više se baziraju na statističkim metodama i alatima poput analize sposobnosti procesa. Informacije koje proizlaze iz analize sposobnosti procesa koriste se osim za praćenje procesa i za stalno poboljšavanje njegove sposobnosti. Izračuni sposobnosti procesa bazirani su na statističkim veličinama koje opisuju srednju vrijednost i rasipanje procesa, te poznatim karakteristikama distribucije. Pomoću analize sposobnosti moguće je odrediti koliko će dobro proces pratiti zadane zahtjeve i specifikacije.

2. Analiza sposobnosti procesa

Sposobnost procesa procjenjuje se računanjem tzv. indeksa sposobnosti procesa. Uvažavajući vrijeme odvijanja procesa procjenjuje se sposobnost procesa u dužem vremenskom razdoblju (Long-Term Process Capability), preliminarna sposobnost procesa (Preliminary Process Capability) i sposobnost u kratkom vremenskom razdoblju (Short-Term Capability).

Računanje i pravilna interpretacija spomenutih indeksa temelji se na pretpostavkama da je raspodjelu podataka nastalih iz promatranog procesa moguće aproksimirati normalnom razdiobom, te da je promatrani proces stabilan, odnosno „pod kontrolom“.

2.1. Proračun indeksa sposobnosti za normalno distribuirane podatke

Sposobnost proces koji se odvijaja u dužem vremenskom razdoblju, u kojem su se mogli pojaviti svi mogući utjecaji varijacija, procjenjuje se indeksima C_P i C_{PK} prema izrazima 1 i 2.

Potencijalna sposobnost C_P (Potential Capability)

$$C_P = \frac{USL - LSL}{6\sigma} \tag{1}$$

Demonstrirana izvrsnost C_{PK} (Demonstrated excellence)

$$C_{PK} = min(C_{PL}, C_{PU}) \quad C_{PL} = \frac{\overline{X} - LSL}{3\sigma} \; ; C_{PU} = \frac{USL - \overline{X}}{3\sigma} \tag{2}$$

gdje su :

$\overline{X}$ - aritmetička sredina procesa (središnja linija primijenjene kontrolne karte)

USL – gornja granica zahtjeva

LSL – donja granica zahtjeva

6σ – raspon promatranog procesa

standardno odstupanje - $\sigma = \frac{\overline{R}}{d_2}$ (u slučaju primjene – *R* kontrolne karte)

C_{PL} – donja potencijalna sposobnost

C_{PU} – gornja potencijalna sposobnost

Preliminarna sposobnost procesa (Preliminary Process Capability) procjenjuje se indeksima koji se označavaju kao P_P, P_{PL}, P_{PU}, P_{PK}. U nazivlju indeksa se umjesto termina sposobnost (Capability) koristi termin značajka (Performance). Računaju se na isti način kao C_P, C_{PL}, C_{PU}, C_{PK} osim što se standardno odstupanje, procjenjuje iz svih podataka temeljem izraza (3):

$$\sigma = s = \sqrt{\frac{\sum_{i=1}^{n}(x_i - \overline{x})^2}{n-1}} \tag{3}$$

Preliminarno procjenjivanje sposobnosti procesa provodi se na početku odvijanja procesa ili nakon relativno kratkog vremena praćenja procesa. Preporuka je da se razmatra uzorak od najmanje 100 jedinica.

Za analizu sposobnosti procesa u kratkom vremenskom razdoblju često se koristi termin «analiza sposobnosti stroja» (Machine Capability Analysis). Primjenjuje se, u pravilu, prilikom pred-preuzimanja ili preuzimanja stroja. Preporučuje se provođenje analize na uzorku od najmanje 50 jedinica. Temeljni interes je informacija o rasipanju podataka oko ciljane vrijednosti D.

Potencijalna sposobnost stroja C_{pm} (Potential Machine Capability) dana je izrazom 4.

$$C_{Pm} = \frac{USL - LSL}{6\sigma} \tag{4}$$

C_{pm} se računa korištenjem alternativne procjene standardnog odstupanja koja sadrži efekt slučajne necentriranosti (rasipanja oko ciljane vrijednosti), odnosno:

$$\sigma = s = \sqrt{\frac{\sum_{i=1}^{n}(x_i - D)^2}{n-1}} \tag{5}$$

Procjena sposobnosti procesa tradicionalno se bazira na pretpostavci kako se podatci ponašaju po normalnoj raspodjeli. Takove pretpostavke često puta mogu voditi ka pogrešnim procjenama, a one pak donošenju krivih odluka. Ako podatke nije moguće prikazati normalnom razdiobom, metode procjene sposobnosti će nesposoban proces prikazati kao sposoban i obrnuto.

2.2. Proračun indeksa sposobnosti za ne-normalne distribucije

Ne postoji opće prihvaćen proračun indeksa sposobnosti procesa za ne-normalne distribucijske modele. Za situacije ne-normalne razdiobe, preporuča se transformacija podatka u normalnu distribuciju te izračun koeficijenata baziran na normalnoj razdiobi. Druga metoda procjene sposobnosti procesa temelji se na pravilnom odabiru poznatog distribucijskog modela i primjeni percentilne metode.

2.2.1. Transformacijski modeli

Poznati transformacijski sustavi podataka su Box-Cox transformacije i Johnsonove transformacije. Podatci se transformiraju pomoću odgovarajuće funkcije na način da transformirane vrijednosti odgovaraju poznatom distribucijskom modelu normalne razdiobe. Pomoću tih sustava moguće je sve važne tipove kontinuiranih distribucija pretvoriti u normalnu distribuciju. Uz podatke, potrebno je transformirati i granice specifikacija. Transformacije su danas izrazito dostupne jer su ugrađene u skoro sve statističke programe.

2.2.2. Percentilna metoda

Mnogi tipovi podataka po svojoj prirodi ne slijede normalnu razdiobu. Kao primjer može se navesti Weibullova distribucija koja se primjenjuje kod praćenja vremena trajanja proizvoda, distribucija najekstremnije vrijednosti – primjer su podaci o najduljem zastoju tokom dana, eksponencijalna distribucija koja je povezana sa funkcijom rasta, kao što je na primjer rast i množenje bakterija i dr.

Vrlo čest slučaj u industriji su procesi koji su jednostrani, točnije imaju samo jednu granicu ili ciljanu vrijednost te ne postoji tolerancijski interval. Primjer je proces čija je

najmanja vrijednost promatrane karakteristike 0 i postoji samo gornja granica zahtjeva. Nerijetko, nula je i najbolja vrijednost za procese, kao što je to u slučaju udjela nečistoća u nekom materijalu, zatim u postupku mjerenja odstupanja od ravnosti, paralelnosti, pravocrtnosti i slično.

Percentilna metoda koja se najčešće koristi za rješavanje navedenih slučajeva, bazirana je na želji da se održi, najviše što se može, analogija sa normalnom distribucijom. U njoj se 99,73 % interval, koji odgovara 6σ normalne razdiobe, uspoređuje sa tolerancijskim intervalom promatrane karakteristike. Granice ovog intervala su 0,135 percentil, te 99,865 percentil distribucije. Tako definiran interval baziran na navedenim percentilima sadrži 99,73 % ukupne populacije. To vodi do formula za izračun indeksa, koje su direktno usporedive sa odgovarajućim formulama za normalnu razdiobu.

$$C_P = \frac{USL - LSL}{99{,}865\,percentil - 0{,}135\,percentil} \tag{6}$$

$$C_{PL} = \frac{M - LSL}{M - 0{,}135\,percentil} \tag{7}$$

$$C_{PU} = \frac{USL - M}{99{,}865\,percentil - M} \tag{8}$$

gdje je :

M - 50-ti precentil promatrane karakteristike, odnosno medijan

Kao i u indeksima za normalnu distribuciju, manja vrijednost od C_{PL} i C_{PU} izražava se kao demonstrirana izvrsnost C_{PK} .

3. Eksperimantalni dio

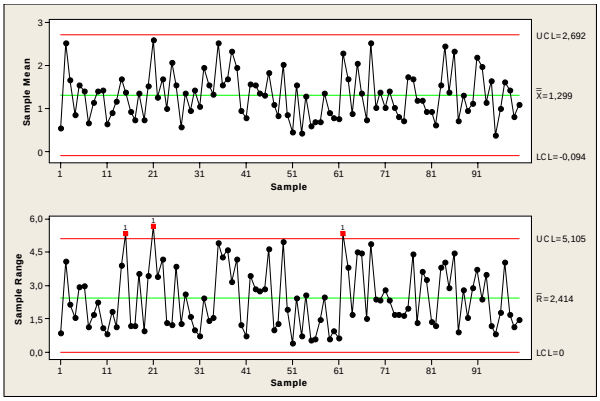
U okviru eksperimentalnog dijela simulirana je lognormalna razdioba (n=500 podataka). Kontrolne karte, izračuni indeksa i grafički prikazi sposobnosti procesa za simulirane podatke, poznate lognormalne distribucije prikazani su na slikama od 1a. do 1f. Simuliran je proces samo sa jednom, donjom, granicom specifikacije L=0 upravo iz razloga što se takovi procesi zbog svoje prirode ne ponašaju po normalnoj razdiobi. Analiza rezultata provedena je korištenjem probne verzije statističkog paketa Minitab.

Ukoliko se proces koji se ponaša po lognormalnoj razdiobi procijeni normalnom razdiobom kontrolne karte ukazuju da proces nije pod kontrolom, a iznosi indeksa C_{PK} =0,27 i P_{PK} =0,28 da proces nije sposoban (slike 1a. i 1b).

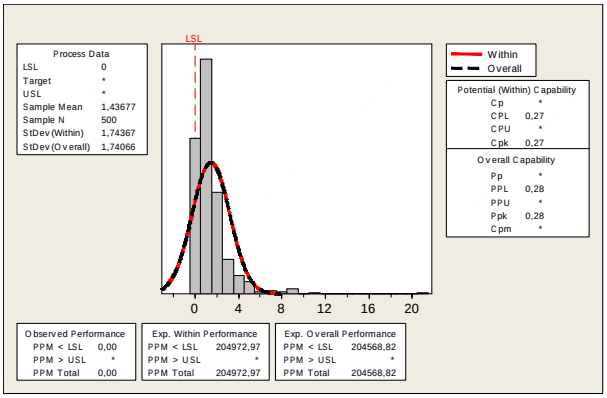
Primjenom BoxCox transformacije, kontrolne karte pokazuju da je proces pod kontrolom, a iznosi indeksa C_{PK} =2,25 i P_{PK} =2,24 da je proces sposoban (sl.1c. i 1d.).

Kod primjene Johnsonove transformacije (slika 1e.) dobiven je podatak o preliminarnoj sposobnosti procesa P_{PK} =1,29. Iznos indeksa govori u prilog sposobnosti procesa (slika 1e.).

Izračun i grafički prikaz sposobnosti procesa koji se temelji na lognormalnom distribucijskom modelu prikazan je na slici 1f. Kao kod primjene Johnsonove transformacije tako je i kod lognormalnog distribucijskog modela izračunat samo koeficijent preliminarne sposobnosti i iznosi P_{PK} =1,05. Posljednja dva modela ne predviđaju pračenje procesa kontrolnom kartom zbog poteškoća kod izračuna kontrolnih granica. Na osnovu dobivenih vrijednosti koeficijenata sposobnosti procesa, te na osnovu grafičkih prikaza može se govoriti o značajnim razlikama u rezultatima koji prvenstveno ovise o primijenjenoj metodi izračuna. Takovi rezultati mogu dovesti do krivih zaključaka o sposobnosti procesa, to jest o očekivanom broju nesukladnosti u procesu.



a)



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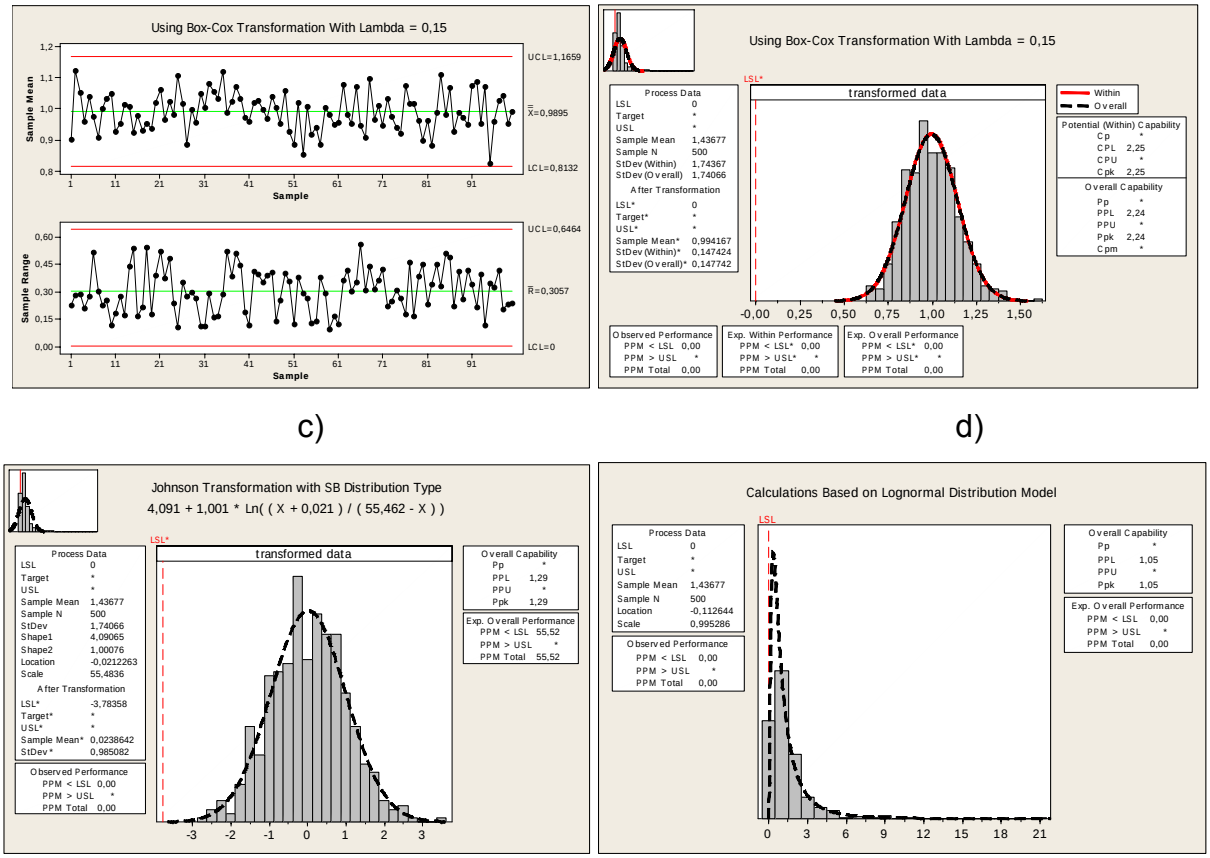

c) d)

e) f)

Slika 1. Sposobnost procesa lognormalno distribuiranih podataka

U situacijama u kojima je potreban distribucijski model, a Gaussov je očigledno pogrešan, postoji nekoliko mogučnosti. Prvi, najlošiji izbor je koristiti alat baziran na normalnoj razdiobi na podatcima koji ju ne slijede. Tu nastaje problem, jer teško je znati kolike su pogreške nastale i kako će se one reflektirati na krajnji rezultat. Druga mogućnost je transformacija podataka i posljednja mogućnost je korištenje poznatog distribucijskog modela za koji je poznata i metoda određivanja sposobnosti.

4. Zaključak

Često ne razumijevanje ne-normalnosti dovodi ka donošenju krivih odluka i rezultira gubljenjem vjere u analizu sposobnosti procesa. Na pitanje što učiniti sa podatcima koji ne slijede normalnu razdiobu dva su odgovora. Prvi je identificirati i riješiti uzroke ne-normalnosti ili pak koristiti alate kojima ne-normalni podaci ne predstavljaju problem. Točno definiranje razloga i izvora ne-normalnosti potrebno je kako bi se na vrijeme mogle poduzeti određene korekcije, ako je to moguće. Ovim radom ukazuje se na probleme olakog prihvaćanja i korištenja normalne razdiobe. Navedeni su

uzroci zbog kojih nastaju stvarni, vrlo često ne-normalni procesi. Literatura govori upravo o tome kako se praktičari vrlo često ne žele zamarati s drugim distribucijskim modelima pa zbog pojednostavljenja biraju upravo normalni, što vrlo često dovodi do netočnih zaključaka.

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ISPITIVANJE UTJECAJA KONCENTRACIJE I VELIČINE ČESTICA NA IONSKU IZMJENU BAKRA NA SINTETSKOM ZEOLITU 13X

THE EFFECT OF CONCENTRATION AND PARTICLE SIZE ON COPPER ION EXCHANGE ON SYNTETIC ZEOLITE 13X

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Izvorni znanstveni rad / Original scientific paper

Sažetak: U ovom je radu proučavano uklanjanje bakra na sintetskom zeolitu 13X u kotlastom reaktoru pri brzini miješanja od 180 okr/min i temperaturi od 293 K. Ispitan je utjecaj veličine čestica i početne koncentracije na kapacitet izmjene i vrijeme uspostave ravnoteže. Dobiveni eksperimentalni podaci su korišteni za izračun konstante brzine korištenjem Richievog modela.
Dobiveni rezultati ukazuju da promjena veličine čestice nema znatnog utjecaja na kapacitet izmjene bakra kao ni na vrijeme uspostave ravnoteže na česticama veličine 0.04-0.063, 0.071-0.09 i 0.1-0.125 mm. Količina uklonjenog bakra se mijenja s promjenom početne koncentracije bakrovih iona i iznosi 0.776, 1.132, 1.134 te 1.410 mmol/g za početne koncentracije od 3.881, 5.661, 7.695, 9.559 mmol/L.

Ključne riječi: bakar, zeolit 13X, kinetika

Abstract: Removal of copper ions from aqueous solutions using zeolite 13X has been studied by a batch technique. The influences of particle size and solute concentration on the capacity of ion exchange and time to establish equilibrium were examined. Ritchie second-order kinetic model was used to test experimental rate data.
The obtained results indicated that impact of zeolite particle size on copper ion exchange for the particles sizes in the range 0.04-0.063, 0.071-0.09 and 0.1-0.125 mm is negligible. The ion exchange capacity is favored by initial concentration. It was observed that the amounts of copper ions exchanged are: 0.776, 1.132, 1.134 and 1.410 mmol/g for initial concentrations of 3.881, 5.661, 7.695, 9.559 mmol/L.

Keywords: copper, zeolite 13X, kinetics

1. UVOD

Interes za istraživanje ionske izmjene teških metala, pa tako i bakra, na zeolitima, može se sagledati sa dva aspekta: prvi je zaštita okoliša odnosno uklanjanje teških metala iz otpadnih voda, a drugi poboljšavanje katalitičkih svojstava zeolita.

S gledišta zaštite okoliša prisustvo teških metala u vodenim ekosustavima velik je problem zbog njihovog negativnog utjecaja na žive organizme. Kako u okoliš dospijevaju iz različitih grana industrije potrebno je posvetiti dodatnu pažnju njihovom uklanjanju iz otpadnih voda. Pri tome se mogu koristiti različite metode, a posljednjih godina naglasak je na istraživanju ionske izmjene korištenjem prirodnih i sintetskih zeolita.

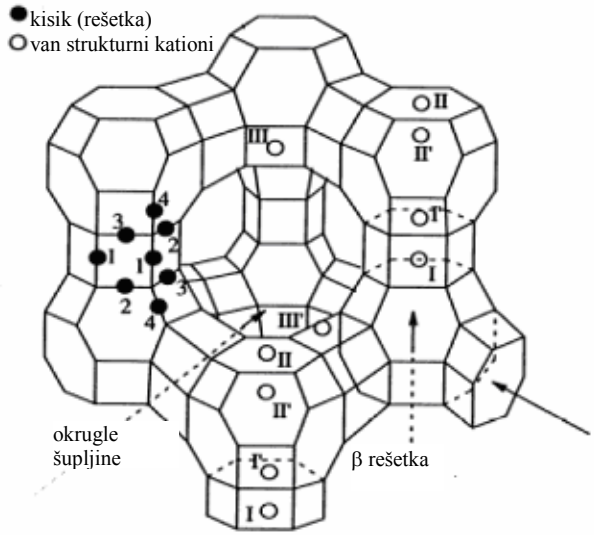
Kod upotrebe zeolita kao katalizatora, naglasak je stavljen na sintetske zeolite, koji se kao katalizatori koriste još od 1962. godine. Bitno je napomenuti da se njihova katalitička svojstva mogu poboljšati modifikacijom odnosno izmjenom originalnih iona iz zeolita (H^+, Na^+, Ca^+) s ionima teških metala pa tako i izmjenom manjeg ili većeg dijela natrijevih iona ionima bakra u zeolitu 13X. Tako pripremljeni katalizatori koriste se za: redukciju NO_x, sagorijevanje metana, različite reakcije s propanom (krekiranje, dehidrogenacija, ciklooligomerizacija) te mokru oksidaciju fenola vodikovim peroksidom. [1-4]

Za razvoj i primjenu zeolita kod uklanjanja teških metala iz otpadnih voda te za pripremu Cu/NaX katalizatora nužno je poznavanje utjecaja različitih parametara kao i kinetičkog modela ionske izmjene. Stoga je u ovom radu ispitan utjecaj koncentracije i veličine čestica na brzinu ionske izmjene u kinetičkom području, te ispitano slaganje Ritchievog modela s eksperimentalnim podacima.

2. EKSPERIMENT

2.1. Zeolit 13X

Zeolit 13X je sintetski oblik prirodnog zeolita faujasita. Jedinična ćelija ovog zeolita sastoji se od osam okruglih šupljina, osam β rešetki i šesnaest heksagonalnih prizmi. Promjer okruglih šupljina iznosi 1.3 nm, a do njih se može doći kroz dvanaestočlane prstenaste kanale promjera 0.74 nm, dok promjer šestočlanih prstena na β rešetki iznosi 0.25 nm. Ioni natrija (ili nekog drugog izmjenjivog kationa) mogu se smjestiti na šest različitih vrsta kristalografskih tj. kationskih mjesta na slici 1. označena su rimskim brojevima I, I', II, II', III, III').[5]



Slika 1. Trodimenzionalna struktura FAU zeolita (preuzeto iz R. Schenkel, Dissertation)

U radu korišteni zeolit karakterizira Si/Al omjer od 1.23 i pripadajuća formula - $Na_{86}(AlO_2)_{86}(SiO_2)_{106}$ x $220H_2O$ (Sigma Aldrich). Poznavanje ove formule te pretpostavka da su izmjenjivi ioni natrija vezani slabim vezama za anionsku zeolitnu rešetku, te da se svi mogu zamijeniti ionima bakra koji se nalaze u otopini omogućava izračunavanje teorijskog kapaciteta izmjene koji za korišteni zeolit, uzimajući u obzir činjenicu da je bakar bivalentan, iznosi 2.47 mmol/g.

BET specifična površina određena je na osnovu mjerenja provedenih na uređaju ASAP 2000 i prikazana u tablici 1.

Tablica 1. Veličine čestica zeolita i pripadajuća BET specifična površina

Veličina čestica mm	BET specifična površina m^2/g
0.1-0.125	573.956
0.071-0.09	576.804
0.04-0.063	576.995

2.2. Utjecaj veličine čestica zeolita na ionsku izmjenu bakra na zeolitu 13X

Ispitivanja su provedena u kotlastom reaktoru u kojem se 0.2 L otopine bakrovog (II) nitrata koncentracije 9.559 mmol/L miješao sa 1 g zeolita 13X brzinom od 180 okr/min pri 293K. Pri tome su korištene različite veličine čestica zeolita (0.1-0.125, 0.071-0.09, 0.04-0.063 mm). U određenim vremenskim intervalima uzimali su se uzorci volumena 0.0015 L koji su se centrifugirali i filtrirali, da bi se koncentracija bakrovih (II) iona u filtratu mogla odrediti UV/Vis spektrofotometrom.

Količina bakra u zeolitu određena je iz razlike koncentracije bakra u otopini prije i poslije ionske izmjene:

$$q = \frac{(c_0 - c_t)V}{m} \qquad (1)$$

gdje je c_0 - koncentracija otopine metala u trenutku t=0, c_t - koncentracija otopine metala u trenutku t, V - volumen otopine metala, m - masa zeolita.

2.3. Utjecaj početne koncentracije na ionsku izmjenu bakra na zeolitu 13X

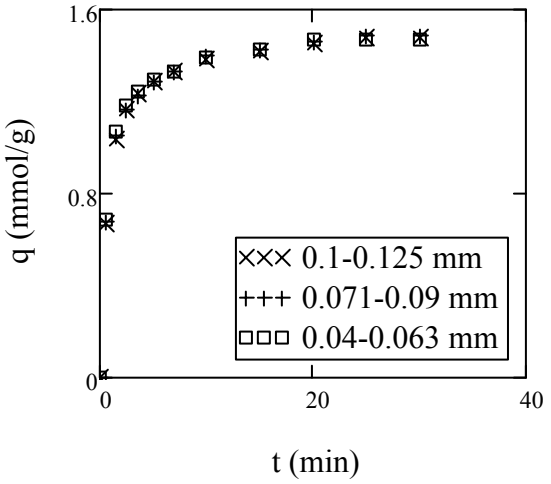
Eksperimenti su izvedeni s otopinama različitih množinskih koncentracija (3.881-9.559 mmol/L). Pri čemu se 0.2 L otopine bakrovog (II) nitrata miješao s 1 g zeolita, veličine čestica 0.1-0.125 mm, pri temperaturi od 293 K.

3. REZULTATI I RASPRAVA

3.1. Utjecaj veličine čestica zeolita na ionsku izmjenu bakra na zeolitu 13X

Slika 2. pokazuje količinu izmijenjenog bakra pri početnoj koncentraciju otopine od 9.559 mmol/L, na česticama zeolita različitih veličina. Iz slike je vidljivo da brzina ionske izmjene bakra kao i kapacitet ionske izmjene ne ovise o veličini čestica zeolita, za ispitivane radne uvjete. Razlog tome je što ukupna površina zeolita uključuje vanjsku površinu čestice te njene pore i kanale. Smanjenjem čestica dolazi do povećanja vanjske površine no unutarnja površina, koja kod zeolita u većoj mjeri pridonosi ukupnoj površini, ostaje nepromijenjena pa je prema tome i sam porast ukupne površine neznatan. Izraženo kroz BET specifičnu površinu smanjenjem čestica zeolita od 0.125 na 0.04 mm BET specifična površina naraste sa 573.956

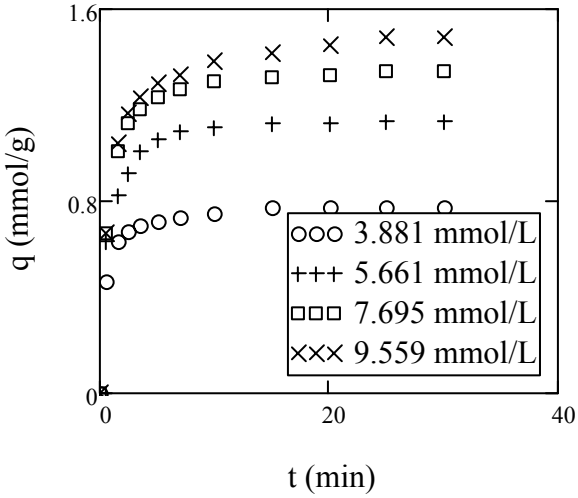
na 576.995 m^2/g. Isto tako, potrebno je napomenuti da su tzv. kationska mjesta koja određuju kapacitet izmjene smještena u porama i kanalima zeolita, a ne na njegovoj površini.



Slika 2. Utjecaj veličine čestica na količinu izmijenjenih iona bakra i brzinu ionske izmjene (c_0 = 9.559 mmol/L; T = 293 K, N = 180 okr/min)

3.2. Utjecaj početne koncentracije na ionsku izmjenu bakra na zeolitu 13X

Utjecaj početne koncentracije bakra na vrijeme uspostave ravnoteže i kapacitet izmjene na zeolitu 13X ispitan je pri temperaturi od 293 K. Kako se može vidjeti sa slike 3. vrijeme pri kojem dolazi do uspostave ravnoteže ovisno je o početnoj koncentraciji. Pri tome je potrebno naglasiti da se porastom koncentracije vremenska razlika smanjuje i kod dvije najviše ispitivane koncentracije gotovo nestaje. Dobivene razlike mogu se objasniti strukturom zeolita 13X odnosno smještajem izmjenjivih kationa. Kao što je već spomenuto u poglavlju 2.1. kod zeolita 13X postoji šest međusobno različitih mjesta (centara) izmjene. Znači na brzinu izmjene može utjecat dostupnost pojedine vrste centara izmjene, veličina hidratiziranog iona bakra (4.19 Å), broj koordinirajućih kisikovih atoma te kation - kation elektrostatsko odbijanje.



Slika 3. Utjecaj početne koncentracije na količinu izmijenjenih iona bakra i brzinu ionske izmjene (d = 0.1-0.125 mm; T = 293 K, N = 180 okr/min)

Uzimajući u obzir položaj pojedinih kationskih mjesta, za različita vremena uspostave ravnoteže može se ponuditi slijedeće objašnjenje. Ionska izmjena bakra na centrima izmjene II, III i III' bi trebala biti brza te kod eksperimentalnih istraživanja kod kojih su korištene niže početne koncentracije bakrovih iona i sama reakcija izmjene je brza. Duže reakcijsko vrijeme bi trebalo biti potrebno za "ulazak" hidratiziranog iona bakra do I' i II' zbog čega povećanjem koncentracije, i porastom broja iona bakra koji se izmjenjuju, raste i vrijeme uspostave ravnoteže.[6]

3.3. Ritchiev model

Osnovne pretpostavke Ritchievog modela (*n=2*) su: da tvar koja se sorbira zauzima dva kationska mjesta, te da brzina sorpcije ovisi samo o udjelu slobodnih centara u trenutku *t*. Ritchiev model na ionsku izmjenu kadmija, praćenu fizikalnom adsorpcijom, na karboniziranim životinjskim kostima prvi put su primijenili Cheung i sur. 2000. međutim dobiveni rezultati nisu bili u potpunosti zadovoljavajući. [7]

Idući koji su primijenili ovaj model na ionsku izmjenu teških metala na zeolitima i sorpciju na glini, i pri tome dobili zadovoljavajuće rezultate slaganja modela i eksperimentalnih podataka, bili su Dávila-Rangel i sur. [8] Primjenom Ritchieva modela na ionski izmjenu bakra na zeolitu 13X također je dobiveno dobro slaganje modela s eksperimentalnim podacima te se zbog toga ovaj model koristio i za opis eksperimentalnih podataka prikazanih u ovom radu.[9]

Ritchiev model općenito se prikazuje kao:

$$\frac{d\theta}{dt} = k\ (1-\theta)^n \qquad (2)$$

gdje je $\theta = \dfrac{q}{q_e}$ (2a)

gdje je q_e - količina uklonjenog metala po masi zeolita u ravnoteži ,q- količina uklonjenog metala po masi zeolita u vremenu t , k - konstanta brzine

Integriranjem izraza (2) uz:

granične vrijednosti: $t = 0 \quad \theta = \theta_0$

$t = t \quad \theta = \theta$

jednadžba (2) ima rješenje:

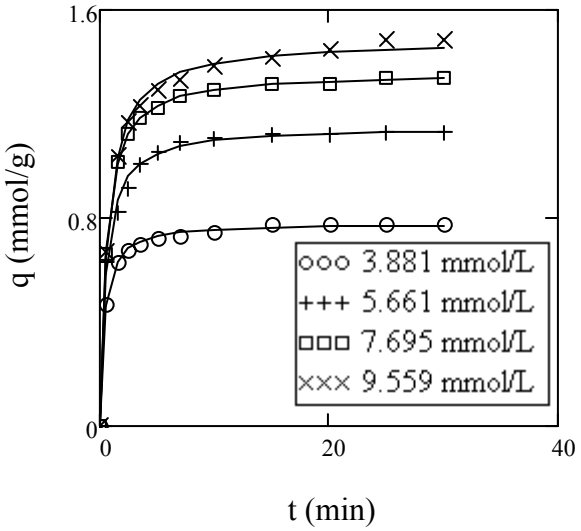
$$q = q_e \left\{ 1 - \left[\frac{1}{\beta_n + k\ (n-1)\ t} \right]^{\frac{1}{n-1}} \right\} \qquad (3)$$

gdje je β_n - $\beta_n = 1 - \theta_0$ (3a)

Za $n = 2$; $\theta_0 = 0$ izraz (3) prelazi u:

$$q = q_e \left\{ 1 - \left[\frac{1}{1 + k\ t} \right] \right\} \qquad (4)$$

Parametri Ritchievog modela (Tablica 2.) izračunati su korištenjem nelinearne regresijske analize. Algoritam za nelinearnu regresijsku analizu razvijen je u Mathcadu 14. Slaganje modela i eksperimentalnih podataka izraženo je kroz koeficijent korelacije, R^2.



Slika 4. Procjena valjanosti Ritchievog modela s eksperimentalnim podacima dobivenim pri različitim početnim koncentracijama bakrovog (II) nitrata
(d = 0.1-0.125 mm; T = 293 K, N = 180 okr/min)

Tablica 2. Parametri Ritchievog modela za ionsku izmjenu bakra na zeolitu 13X kod različitih početnih koncentracija

Parametri	Koncentracija (mmol/L)			
	3.881	5.661	7.695	9.559
q_e eksperimentalni (mmol/g)	0.776	1.132	1.341	1.481
q_e model (mmol/g)	0.778	1.150	1.360	1.485
k (1/min)	2.860	2.062	1.911	1.529
R^2	0.998	0.994	0.997	0.993

Na osnovu podataka prikazanih u tablici 2. može se uočiti da konstanta brzine k opada porastom koncentracije što indicira da se u sustavu s nižom početnom koncentracijom brže uspostavlja ravnoteža. Vrijednosti maksimalnog kapaciteta izmjene, q_e, koje su izračunate korištenjem ovog modela i prikazane u tablici 2. odgovaraju eksperimentalnim vrijednostima kapaciteta izmjene te njihova vrijednost, očekivano, raste porastom koncentracije.

4. ZAKLJUČAK

Cilj ovog rada bio je ispitati utjecaj veličine čestica zeolita i početne koncentracije na vrijeme uspostave ravnoteže i kapacitet ionske izmjene bakra na zeolitu 13X u kinetičkom području. Na osnovu dobivenih eksperimentalnih i računskih rezultata možemo zaključiti slijedeće:
Veličina čestice zeolita nema utjecaja na vrijeme uspostave ravnoteže kao ni na kapacitet ionske izmjene bakra na zeolitu 13X.
Vrijeme uspostave ravnoteže raste porastom početne koncentracije isto kao i kapacitet ionske izmjene.
Ritchiev kinetički model je prikladan za opis kinetičkih eksperimentalnih podataka.

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INFLUENCE OF CHROMIUM CONTENT ON STRUCTURE AND MECHANICAL PROPERTIES OF Ti-10Co-xCr ALLOYS

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Prethodno priopćenje / Preliminary note

Abstract:
Titanium alloys of β-type have become a very important class of biomaterials because of their unique combination of high strength, low Young's modulus, good corrosion resistance and excellent biocompatibility. In this work a new ternary titanium alloys, composed of non-toxic and non-allergic elements like chromium and cobalt, have been designed in order to achieve β-phase structure. Samples of four Ti-10Co-xCr alloys with chromium content 10-25 at.% were prepared by vacuum arc melting technique. They were analyzed by scanning electron microscope, X-ray diffraction and compression tests. The experimental results show that all alloys have two-phases microstructure, with a small portion of third phase. The β-phase with bcc type of crystal structure is dominated and the intermetallic compound Ti_2Co precipitated on the grain boundaries. All alloys exhibited high compressive strength of 1391-1958 MPa, high yield strength 1290-1540 MPa and Young's modulus in the range of 30-59 GPa, together with the large plastic strains. The present results indicate that the combination of high strength and low elastic modulus of Ti-Co-Cr alloys offer potential advantages in a biomedical applications.
Key words: titanium alloys, Ti-Co-Cr alloys, β-phase, Young's modulus

Sažetak:
Legure titana β-tipa postale su vrlo važan biomaterijal zbog jedinstvene kombinacije visoke čvrstoće, niskog Young-ovog modula, dobre korozijske otpornosti i izvrsne biokompatibilnosti. U ovom radu dizajnirane su nove ternarne legure titana, koje ne sadrže toksične elemente ni alergene, kao što su krom i kobalt, da bi se postigla struktura β-faze. Četiri Ti-10Co-xCr legure sa 10-25 at.% kroma, preparirane su elektrolučnim taljenjem u vakuumu. One su analizirane scanning elektronskom mikroskopijom, difrakcijom rentgenskih zraka i kompresijskim testom. Eksperimentalni rezultati pokazuju da sve legure imaju dvofaznu mikrostrukturu, s malim udjelom treće faze. Dominantna je β-faza sa bcc tipom kristalne strukture, a intermetalni spoj Ti_2Co je izlučen na granicama zrna. Sve legure su pokazale visoku tlačnu čvrstoću od 1391-1958 MPa, visoku granicu tlačenja od 1290-1540 MPa i nizak Youngov modul od 30-59 GPa, te veliku plastičnost. Navedeni rezultati pokazuju da kombinacija visoke čvrstoće i niskog modula elastičnosti Ti-Co-Cr legura pruža potencijalne prednosti za primjenu u biomedicini.
Ključne riječi: legure titana, Ti-Co-Cr legure, β-faza, Young-ov modul

Introduction

Among the main metallic biomaterials, i.e. stainless steels and cobalt-based alloys, titanium and its alloys have become the most popular because of their suitable characteristics for biomedical applications. They have an excellent balance of mechanical properties, low density, high biocompatibility and corrosion resistance.

The low Young's modulus of biomaterials is required because it should be as close as possible to that of bone. Although titanium and its ($\alpha+\beta$) alloys have an elastic modulus (100-120 GPa) a much smaller than stainless steel (210 GPa), it is still significantly higher than that of bone tissue (10-40 GPa). Besides, one of the most widely used biomedical titanium alloy, Ti-6Al-4V, with ($\alpha+\beta$) -phase structure and elastic modulus of about 110 GPa, contains cytotoxic elements (V, Al) [1-4]. So, the aim of the current research is to develop a new β-type titanium alloys with low elastic modulus, composed of non-toxic elements.

In this work a new ternary titanium-based alloys, composed of chromium as a β-phase improving element and cobalt as strengthener have been designed in order to obtain alternative titanium alloys applicable as a new biomaterials [5].

Materials and methods

The Ti-10Co-xCr alloys (x = 10, 15, 20, 25 at.%) used for the present study were prepared from titanium, cobalt and chromium with purity better than >99,9%. The melting of pure elements was performed by using a vacuum arc melting technique. The ingots of approximately 7 g weight were re-melted three times to improve their chemical homogeneity. The casting of alloys was realized in the same equipment by means of specially constructed copper anode, which served also as a casting mould. In this way, as-cast cylindrical specimens with dimensions 8 mm x 25 mm were produced directly.

The cast alloys were sectioned using a Buehler Isomet low-speed diamond saw to obtain specimens for different examinations. Then, specimens were mounted in an epoxy resin and they were mechanically grinded and polished via a standard metallographic procedure.

Microstructure of non-etched alloys was examined using a scanning electron microscope (Tescan Vega) with technique SE and BSE, respectively. X-ray diffraction (XRD) phase analysis was conducted using a diffractometer Philips PW 3710 with CuK_{α}- radiation. Phases were identified by matching each characteristic peak with the JCPDS files [6]. Mechanical examinations were performed on cylindrical samples with dimensions 8 mm x 10 mm. The compression test was carried out with an Amsler testing machine at a strain rate of $1 \cdot 10^{-4}$/s at a room temperature.

Results and discussion

The microstructure and crystal structure, as well as the mechanical properties of four as-cast Ti-10Co-xCr alloys have been studied. Their chemical compositions are presented in Fig.1.

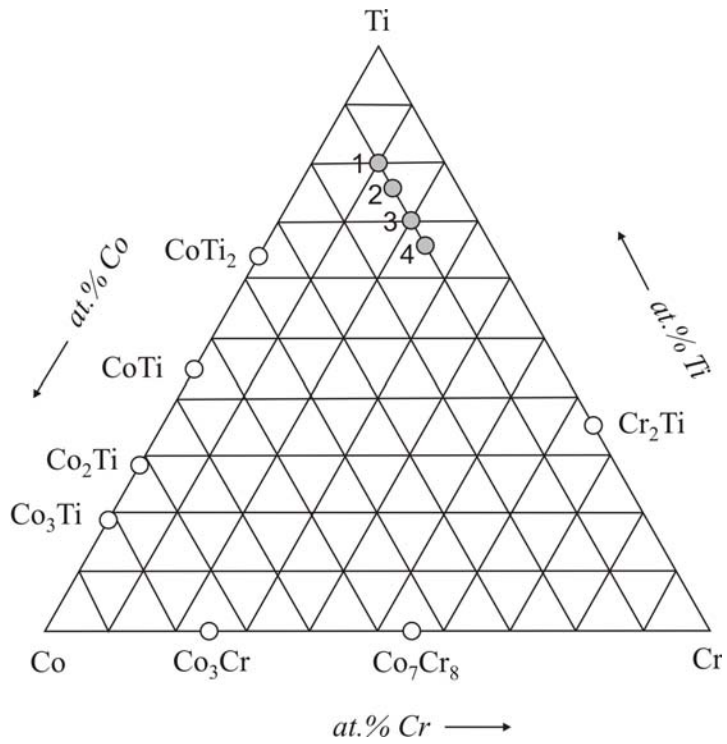
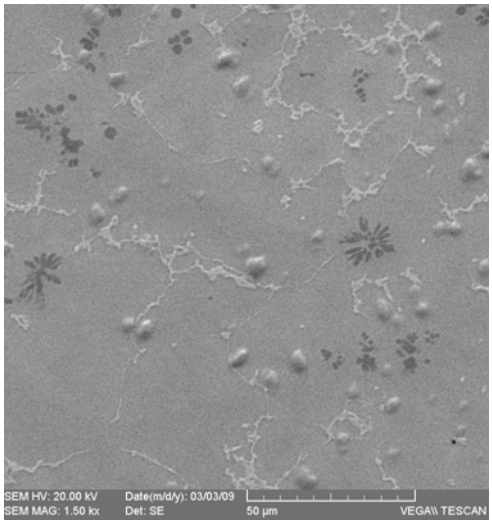
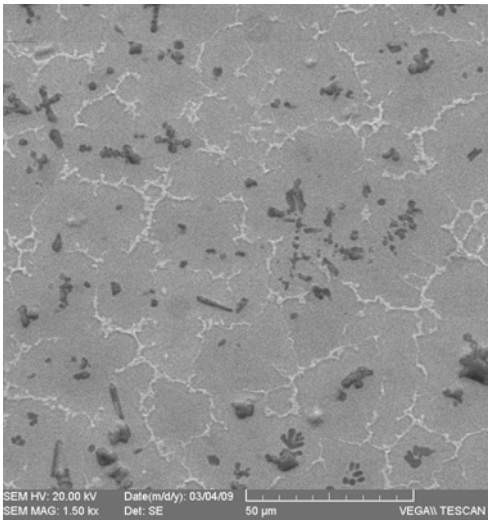


Figure 1. Compositions of experimental alloys presented on the isothermal section of ternary Ti-Co-Cr system at room temperature

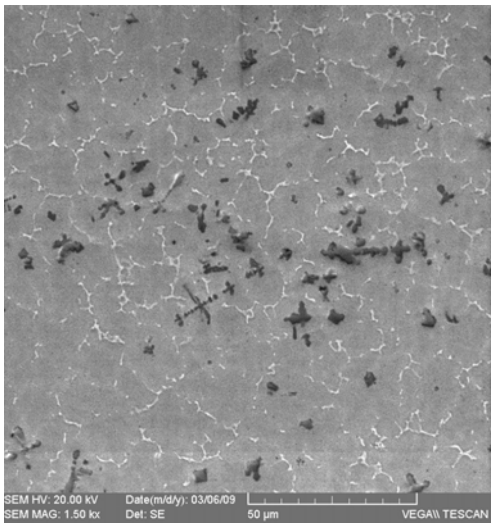
Observation by scanning electron microscope (SEM) shows that all alloys have three-phases microstructure (Figs. 2a-d) which consists of matrix (gray phase), grain boundaries (light phase) and dark phase.



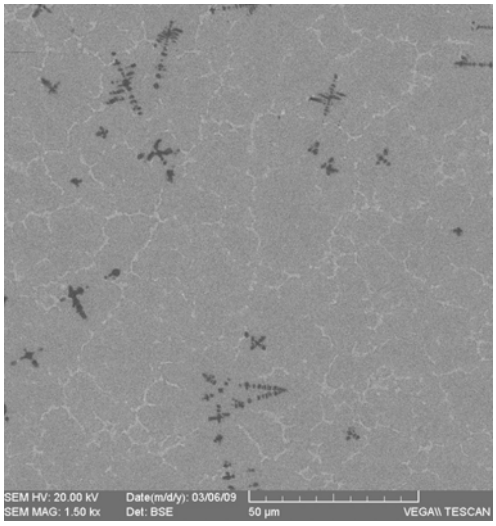
(a) Alloy 1. $Ti_{80}Co_{10}Cr_{10}$



(b) Alloy 2. $Ti_{75}Co_{10}Cr_{15}$



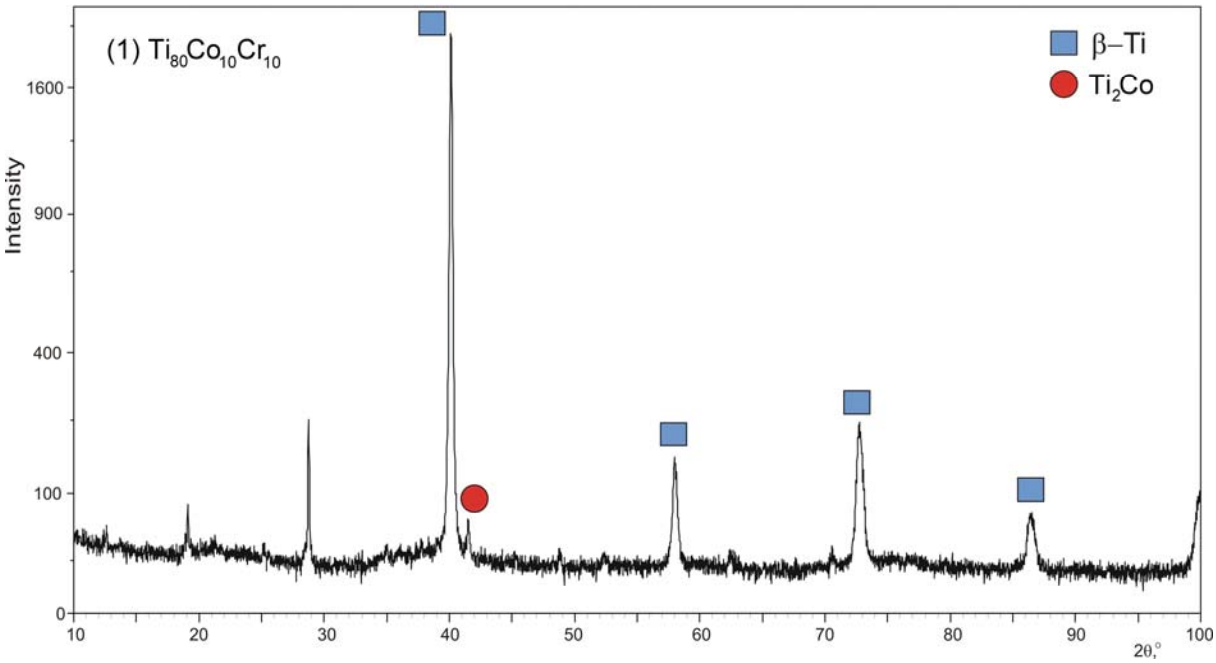
(c) Alloy 3. $Ti_{70}Co_{10}Cr_{20}$



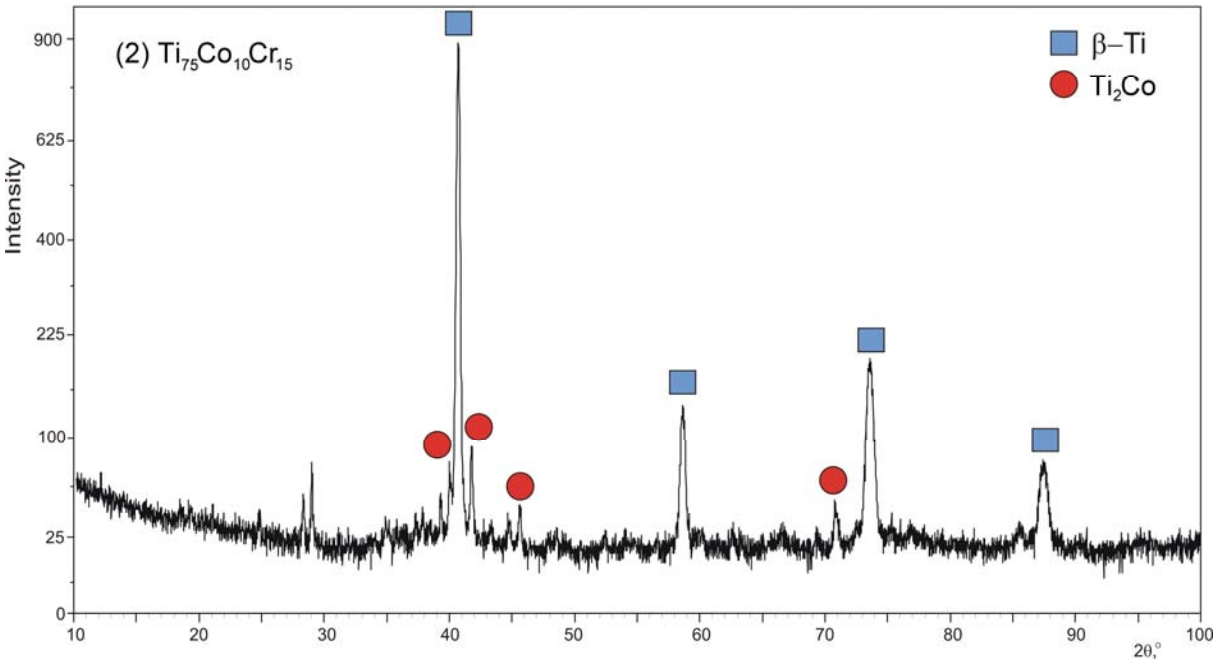
(d) Alloy 4. $Ti_{65}Co_{10}Cr_{25}$

Figure 2. SEM micrographs of as cast Ti-10Co-xCr alloys, 1500x

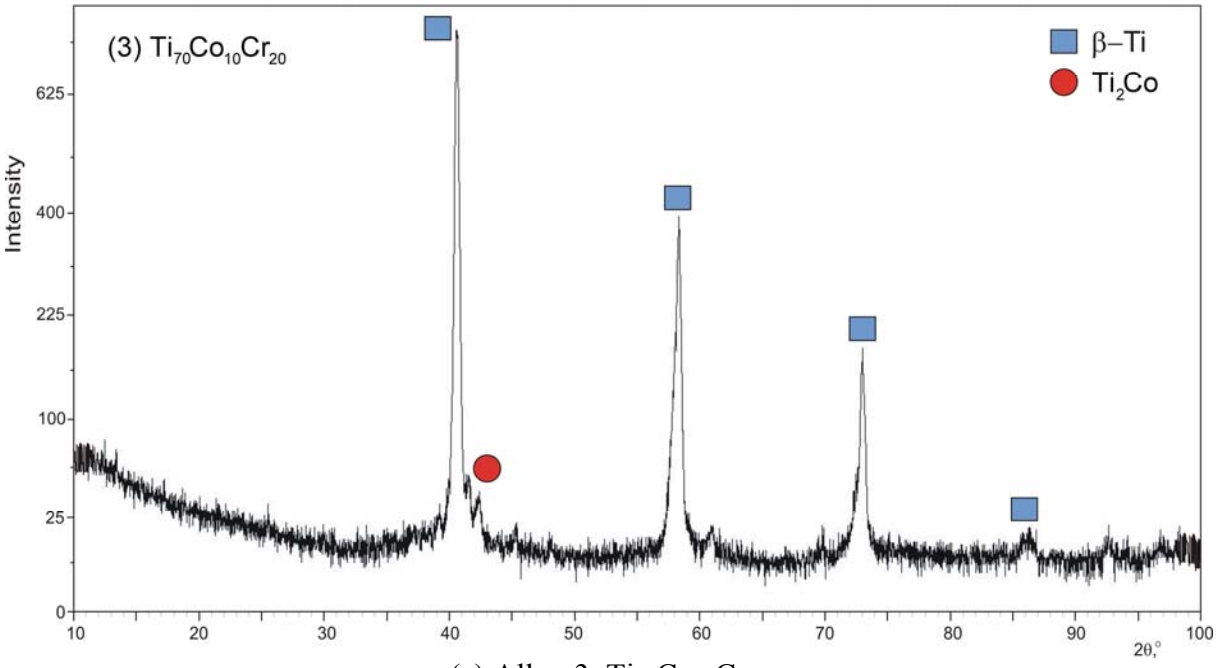
However, XRD patterns exhibits only two phases indicated as β-phase, which is a dominant, and intermetallic compound Ti_2Co (Figs. 3a-d). This mismatch could be explained by a small amount of third phase (a dark) which couldn't be detected by a diffractometer.



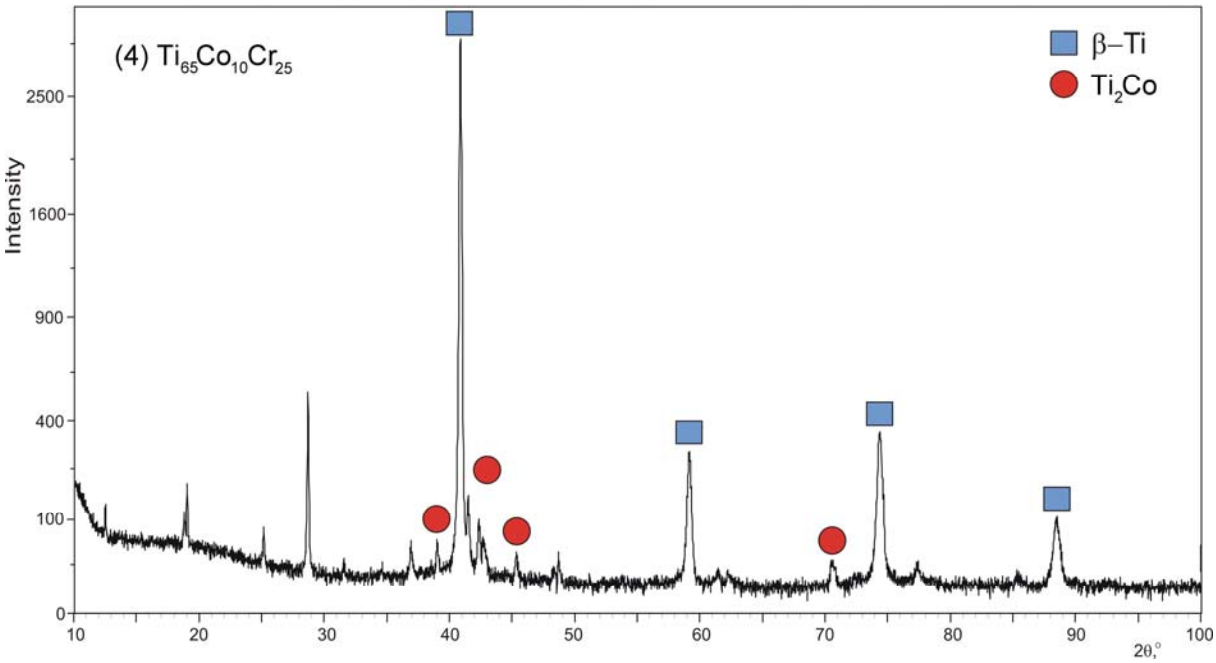
(a) Alloy 1. $Ti_{80}Co_{10}Cr_{10}$



(b) Alloy 2. $Ti_{75}Co_{10}Cr_{15}$



(c) Alloy 3. $Ti_{70}Co_{10}Cr_{20}$



(d) Alloy 4. $Ti_{65}Co_{10}Cr_{25}$

Figure 3. X-ray diffraction patterns for experimental alloys

The mechanical properties (Table 1) were evaluated directly from the obtained stress-strain curves. This results show that all alloys have low values of elastic modulus in the range of 30-59 GPa. The lowest E-value, 30 GPa, has alloy 4 with the highest chromium content of 25 at.% and it is close to the elastic modulus of the bone tissue (10-40 GPa). The highest E-value, 59 GPa, has alloy 1 with the lowest chromium content of 10 at.%. Besides, all alloys exhibited high compressive strength of 1391-1958 MPa, which decreases with increasing chromium content. Their yield strengths are in the range of 1290-1540 MPa and are also high. The values of plastic strains are in the range of 5,5 - 40,5 %. Alloy 4, with the highest chromium content, has the largest plasticity which was found to be 40%.

Table 1. Mechanical properties of experimental alloys

Alloy No.	Alloy composition, at.%	Elastic modulus, GPa	Compressive strength, MPa	Yield strength, MPa	Plastic strain, %
1.	$Ti_{80}Co_{10}Cr_{10}$	59	1958	1300	18,5
2.	$Ti_{75}Co_{10}Cr_{15}$	46	1891	1290	17,0
3.	$Ti_{70}Co_{10}Cr_{20}$	57	1810	1540	5,5
4.	$Ti_{65}Co_{10}Cr_{25}$	30	1391	1355	40,5

Conclusions

The present study results with following conclusions:

- Scanning electron microscopy shows that the microstructure of alloys consists of three phases.
- XRD analysis indicate the presence of two phases, the β-phase which is a dominant in all alloys and the intermetallic compound Ti_2Co.
- Alloy 4, $Ti_{65}Co_{10}Cr_{25}$, with the highest chromium content, exhibits the lowest elastic modulus of 30 GPa, while the other alloys also have low values of E-modulus.
- All alloys show high compressive strengths of 1391-1958 MPa. Among them, alloy 1, $Ti_{80}Co_{10}Cr_{10}$, with the lowest chromium content has the highest value.
- All alloys exhibit high yield strengths of 1290-1540 MPa.
- Alloy 4, $Ti_{65}Co_{10}Cr_{25}$, with the highest chromium content, has the largest plasticity.

Finally, it can be concluded that the combination of high strength and low elastic modulus of investigated Ti-10Co-xCr alloys offer potential advantages for their use in a biomedicine.

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RAČUNALNA SIMULACIJA KALJENJA I POPUŠTANJA ČELIČNE OSOVINE

COMPUTER SIMULATION OF QUENCHING AND TEMPERING OF STEEL SHAFT

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Izvorni znanstveni rad / Original scientific paper

Sažetak: U radu je predviđeno dopušteno radno naprezanje kaljenog i popuštenog čeličnog uzorka. Dopušteno radno naprezanje predstavljeno je granicom razvlačenja i lomnom žilavošću. Računalna simulacija dopuštenog radnog naprezanja primijenjena je na uzorak kompleksnog oblika. Algoritam procjene vrijednosti granice razvlačenja i lomne žilavosti temelji se na tvrdoći, *HV*. Raspodjela tvrdoće predviđena je uključivanjem rezultata jednostavnog pokusa, *Jominy* pokusa u numeričko modeliranje kaljenja čelika. Pri predviđanju vrijednosti granice razvlačenja i lomne žilavosti korišten je Hahn-Rosenfield-ov pristup. Može se zaključiti da se dopušteno radno naprezanje kaljenog i popuštenog čeličnog uzorka može predviđati predloženom metodom. Za konačnu verifikaciju postavljenog modela potrebna su daljnja eksperimentalna istraživanja.
Ključne riječi: toplinska obrada, računalna simulacija, mikrostruktura, granica razvlačenja, lomna žilavost

Abstract: In this paper, the prediction of working stress of quenched and tempered steel workpiece has been done. The working stress was characterized by yield strength and fracture toughness. The method of computer simulation of working stress was applied in workpiece of complex form. The algorithm of estimation of yield strength and fracture toughness was based on steel hardness, *HV*. Hardness distribution is predicted by involving the results of simple experimental test, i.e., Jominy-test in numerical modelling of steel quenching. Yield strength and fracture toughness distributions have been predicted using the Hahn-Rosenfield approach. It can be concluded that working stress of quenched and tempered steel workpiece can be successfully predicted by proposed method. The further experimental investigations are needed for final verification of established model.
Keywords: heat treatment, computer simulation, microstructure, yield strength, fracture toughness

1. UVOD

Glavni problem u simulaciji kaljenja čelika je utvrđivanje fizikalnih i mehaničkih svojstava koje je potrebno uključiti u model kaljenja. Numerička simulacija raspodjele tvrdoće jedan je od glavnih prioriteta u simulaciji kaljenja i predviđanju mehaničkih svojstava čelika. Poznato je da se čvrstoća, žilavost i otpornost na umor čelika može uspješno procijeniti na temelju tvrdoće [1]. U ovom radu, računalnom je simulacijom predviđena raspodjela tvrdoće, čvrstoće, žilavosti i otpornosti na umor kaljenog i popuštenog čeličnog uzorka.

Čvrstoća, žilavost i otpornost na umor materijala kaljenog i popuštenog čeličnog uzorka direktno ovise o mikrostrukturi. Stoga, u simulaciji kaljenja i popuštanja čelika treba predvidjeti promjene temperaturnog polja te sastava mikrostrukture i mehaničkih svojstava.

2. RASPODJELA TVRDOĆE

Matematički model kaljenja čelika može se temeljiti na izračunatim karakterističnim vremenima ohlađivanja od 800 do 500 °C ($t_{8/5}$) [2, 3]. Iz rezultata vremena ohlađivanja u točkama uzorka može se korištenjem relacija između vremena $t_{8/5}$ i udaljenosti od kaljenog čela *Jominy* uzorka te *Jominy* krivulje prokaljivosti procijeniti tvrdoća. Vremena ohlađivanja u točkama uzorka mogu se predvidjeti numeričkom simulacijom ohlađivanja korištenjem metode konačnih volumena [4, 5].

Referentna tvrdoća u točkama uzorka u zakaljenom i popuštenom stanju može biti procijenjena iz referentne tvrdoće u zakaljenom stanju, HRC_{kaljeno} [6-8]:

$$HRC_{pop} = \frac{HRC_{kalj}}{K} \tag{1}$$

gdje je K faktor odnosa između kaljene i popuštene tvrdoće. Faktor K može se izraziti kao:

$$K = C_1 \cdot t^{n_1} \exp\left[A\left(\frac{a}{T_{pop}}\right)^{n_2} - B \right] \tag{2}$$

gdje je T_{pop} [K] temperatura popuštanja, t [h] vrijeme popuštanja dok su A, B, C_1, a, n_1 i n_2 konstante materijala.

3. RASPODJELA MIKROSTRUKTURE

Sastav mikrostrukture moguće je procijeniti na temelju tvrdoće koja je općenito jednaka:

$$HV = \{(\%ferrite + \%pearlite)HV_{(F+P)} + (\%bainite)HV_{(B)} + (\%martensite)HV_{(M)}\}/100 \tag{3}$$

Zbroj količinskih udjela faza jednak je jedinici:

$$\{(\%ferrite + \%pearlite) + \%bainite + \%martensite\}/100 = 1 \tag{4}$$

Ako su poznate ukupna tvrdoća i tvrdoće mikrostrukturnih sastojka te ako je poznat količinski udio faze jednog mikrostrukturnog sastojka, nije teško pomoću izraza 3 i 4 predvidjeti količinske udjele ostalih faza.

Rezultati raspada austenita ovise o kemijskom sastavu i povijesti čelika, intenzitetu gašenja, temperaturi austenitizacije. Rezultati raspada austenita mogu se procijeniti na temelju vremena relevantnog za strukturnu transformaciju. Karakteristično vrijeme ohlađivanja, relevantno za strukturnu transformaciju većine konstrukcijskih čelika jest vrijeme ohlađivanja od 800 do 500 °C ($t_{8/5}$).

Ako su ostali parametri toplinske obrade konstantni, rezultati raspada austenita u pojedinoj lokaciji ohlađivanog uzorka ovisit će samo o vremenu $t_{8/5}$. Može se reći da tvrdoća faze u *Jominy* uzorku ovisi o kemijskom sastavu i brzini ohlađivanja koja odgovara aktualnoj udaljenosti *d* od kraja *Jominy* uzorka. Usvojeno je da je brzina ohlađivanja jednaka log($t_{8/5}$) [9].

$$HV_d^M = HV_{\max}^M - K_M \log \frac{t_{8/5d}^M}{t_{8/5\max}^M} \tag{5}$$

$$HV_d^B = HV_{\max}^B - K_B \log \frac{t_{8/5d}^B}{t_{8/5\max}^B} \tag{6}$$

$$HV_d^{P+F} = HV_N^{P+F} + K_{P+F} \log \frac{t_{8/5N}^{P+F}}{t_{8/5d}^{P+F}} \tag{7}$$

gdje je *N* normalizacija a $HV_{\max}^B$ tvrdoća donjeg bainita. Karakteristične vrijednosti *HV*, *K* i $t_{8/5}$ u izrazima 5, 6 i 7 moraju se, u kombinaciji s rezultatima *Jominy* pokusa izvesti za odgovarajući čelik. Tvrdoća kaljene strukture s karakterističnim udjelom martenzita može se predvidjeti upotrebom dijagrama ovisnosti tvrdoće za različite udjele martenzita o sadržaju ugljika prema Hodge and Orehoski [10] i *Jominy* krivulje prokaljivosti. Na sličan način, regresijskom analizom dobije se ovisnost vremena ohlađivanja $t_{8/5}$ i karakterističnog udjela perlita [9].

4. RASPODJELA MEHANIČKIH SVOJSTAVA

Mehanička svojstva kaljenog ili kaljenog i popuštenog čelika direktno ovisi o stupnju otvrdnjavanja kaljenog čelika [1, 8]. Odnos između tvrdoće, *HV* i vlačne čvrstoće, R_m [Nmm^{-2}] jednak je:

$$R_m = 3.3HV \tag{8}$$

Granica razvlačenja, $R_{p0.2}$ [Nmm^{-2}] i kontrakcija poprečnog presjeka, *Z* [%] može se procijeniti iz vlačne čvrstoće ili tvrdoće[11]:

$$R_e = R_{p0,2} = (0.8 + 0.1C)R_m + 170C\text{-}200 \tag{9}$$

$$Z = 96 - (0.062 - 0.029C)R_m \tag{10}$$

gdje je C odnos između stvarne tvrdoće i tvrdoće martenzita u *HRC* jedinicama.

Lomna žilavost, K_{Ic} [MPam$^{1/2}$] može se procijeniti iz Hahn-Rosenfield relacija [10]:

$$K_{Ic} = \sqrt{\frac{\varepsilon_f n^2 E R_e}{60}} \tag{11}$$

ε_f je stvarna deformacija, n je eksponent očvršćivanja, E [Nmm^{-2}] je modul elastičnosti. Stvarna deformacija se može izraziti kontrakcijom poprečnog presjeka Z:

$$\varepsilon_f = \ln\left(1 - \frac{Z}{100}\right)^{-1} \tag{12}$$

Eksponent očvršćivanja može se definirati kao:

$$\frac{R_m}{R_e} - \left(\frac{n}{0.002e}\right)^n \approx 0 \tag{13}$$

Otpornost na umor materijala može se procijeniti na temelju granice razvlačenja i sastava mikrostrukture:

$$K_{th} = R_e (12\pi d)^{1/2} \tag{14}$$

U nisko do srednje čvrstim čelicima kontrolna mikrostrukturna veličina koju je korisno usporediti s veličinom kristalnog zrna je polumjer plastične zone, $R_{p\pm}$ [12]:

$$R_{p\pm} = \frac{2\Delta K^2}{6\pi (2R_e)^2} \tag{15}$$

Prag rasta pukotine umaranja, ΔK_{th} ispod kojeg nema iniciranja pukotine može se u pojedinoj lokaciji kaljenog i popuštenog uzorka, uključujući učinke mikrostrukture i pretpostavku da je $d = R_{p\pm}$, procijeniti izrazom:

$$\Delta K_{th} = nAR_e d^{1/2} \tag{16}$$

gdje je n parametar koji ovisi o volumnom udjelu ferita, a A konstanta materijala.

5. PRIMJENA

Postavljena metoda primijenjena je u računalnoj simulaciji kaljenja i popuštanja čelične osovine. Materijal osovine je čelik 42CrMo4 (DIN). Kemijski sastav čelika navedene

osovine prikazan je u tablici 1. Rezultati *Jominy* pokusa čelika 42CrMo4 (DIN) prikazani su tablici 2.

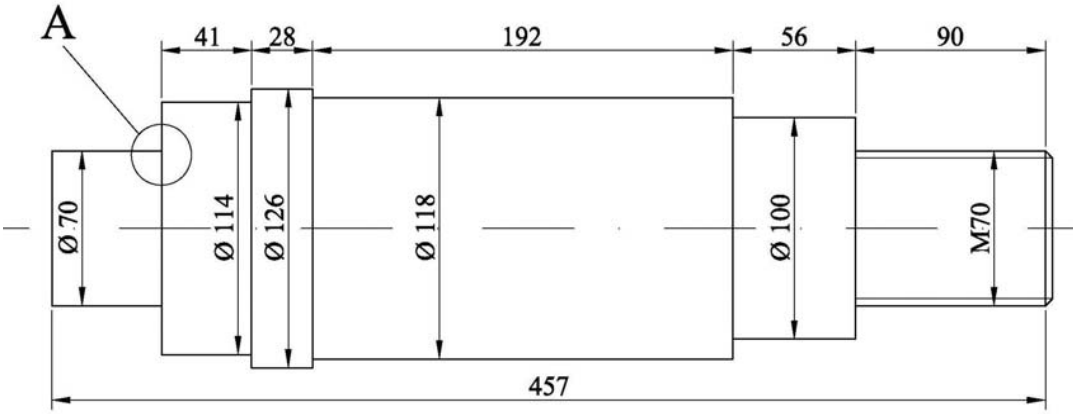
Tablica 1. Kemijski sastav čelika 42CrMo4 (DIN)

C, %	Si, %	Mn, %	P, %	S, %	Cr, %	Mo, %
0.38	0.23	0.64	0.019	0.013	0.99	0.16

Tablica 2. Rezultati *Jominy* pokusa čelika 42CrMo4 (DIN)

Jominy udaljenost [mm]	1.5	3	5	7	9	11	13	15	20	25	30
Tvrdoća [HV]	610	605	590	576	555	524	487	446	379	344	324
Jominy udaljenost [mm]	35	40	45	50	55	60	65	70	75	80	-
Tvrdoća [HV]	311	303	297	293	292	291	289	288	288	288	-

Geometrija čelične osovine prikazana je na slici 1.



Slika. 1. Geometrija osovine

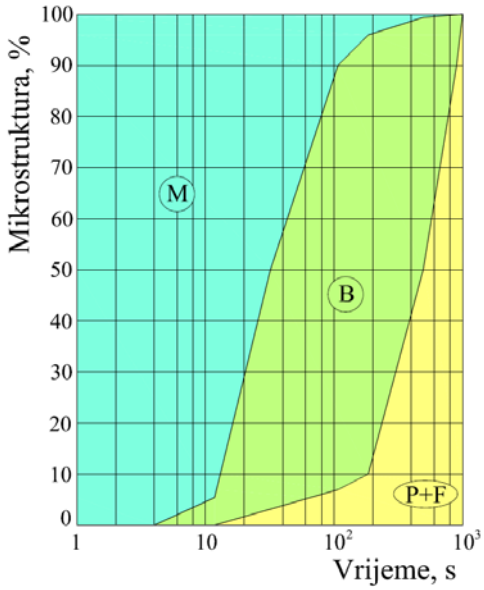
Parametri toplinske obrade osovine prikazani su u tablici 3.

Tablica 3. Parametri toplinske obrade čelične osovine

Kaljenje			Popuštanje		
Temperatura	Vrijeme	Sredstvo	Temperatura	Vrijeme	Sredstvo
850 °C	1 sat	ulje, H = 0.7	600 °C	1 sat	zrak

Na temelju predloženog matematičkog modela, računalnom simulacijom predviđene su raspodjele mikrostrukture i mehaničkih svojstava navedene čelične osovine.

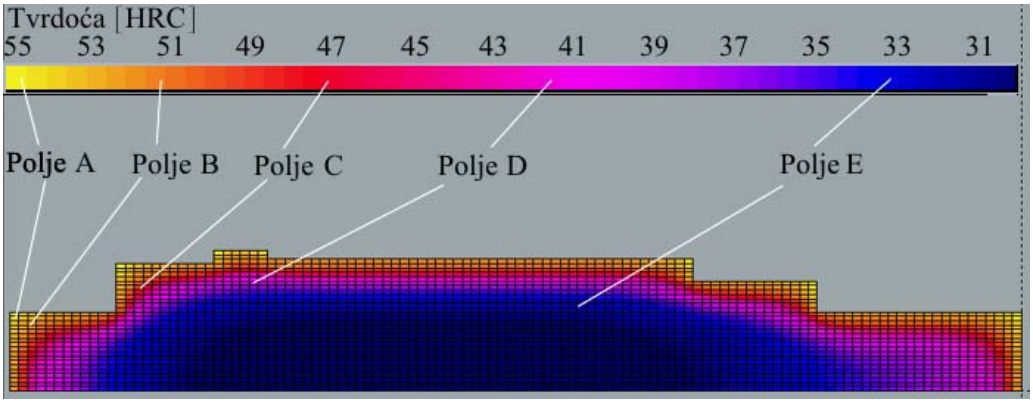
Ovisnost sastava mikrostrukture o vremenu ohlađivanja $t_{8/5}$ istraživanog čelika prikazana je na slici 2.



Slika 2. Ovisnost sastava mikrostrukture o vremenu ohlađivanja $t_{8/5}$;
(P+F) - Perlit + Ferit; B - Bainit; M – Martenzit

Da bi se postigla homogena mikrostruktura u površinskom sloju čelične osovine u zakaljenom stanju i u svrhu postizanja veće otpornosti na umor materijala potrebno je kaljenje izvesti u ulju intenziteta gašenja $H = 0.7$.

Raspodjela mikrostrukture i mehaničkih svojstava čelične osovine u zakaljenom stanju ($H = 0.7$) prikazana je na slici 3.



Slika 3. Raspodjela mikrostrukture i mehaničkih svojstava osovine u zakaljenom stanju

Vidljivo je da se kaljenjem u ulju intenziteta gašenja $H = 0.7$ u površinskom sloju osovine u zakaljenom stanju postiže homogena martenzitna mikrostruktura.

Predviđene vrijednosti sastava mikrostrukture i mehaničkih svojstava čelične osovine u zakaljenom stanju ($H = 0.7$) prikazane su u tablici 4.

Predviđene vrijednosti mehaničkih svojstava čelične osovine kaljene u ulju intenziteta gašenja $H = 0.7$ i popuštene na 600 °C prikazane su u tablici 5.

Tablica 4. Mikrostruktura i mehanička svojstava osovine u zakaljenom stanju

Svojstva		Polje na slici 3				
		A	B	C	D	E
Tvrdoća [HV]		610-575	575-510	510-453	453-370	370-298
Granica razvlačenja R_e [Nmm^{-2}]		2013-1898	1898-1683	1683-1495	1495-1221	1221-983
Lomna žilavost K_{Ic} [MPam$^{1/2}$]		64-68	68-77	77-86	88-100	100-116
Udio faza [%]	F+P	0	0	0	0	0-10
	B	1-2	2-19	19-37	37-64	64-81
	M	99-98	98-81	81-63	63-36	36-9

Tablica 5. Mehanička svojstava kaljene i popuštene osovine

Svojstva	Polje na slici 5				
	A	B	C	D	E
Tvrdoća [HV]	291-290	290-280	280-272	272-256	256-234
Granica razvlačenja R_e [Nmm^{-2}]	960-957	957-924	924-898	898-845	845-772
Lomna žilavost K_{Ic} [MPam$^{1/2}$]	117-118	118-120	120-122	122-126	126-132
Prag rasta pukotine umaranja ΔK_{th} [MPam$^{1/2}$]	22.6-22.5	22.5-21.8	21.8-21.2	21.2-20.1	20.1-10.5

6. ZAKLJUČAK

Razvijen je matematički model procjene mikrostrukturnih sastojaka, mehaničkih svojstava poboljšana čelika. Matematički model zasnovan je na metodi konačnih volumena. Procjena raspodjele tvrdoće u zakaljenom uzorku temelji se na vremenu ohlađivanja od 800 do 500 °C ($t_{8/5}$) i rezultatima *Jominy* pokusa. Raspodjele mikrostrukturnih sastojaka te vrijednosti granice razvlačenja i lomne žilavosti temelje se na tvrdoći čelika. Otpornost na umor materijala temelji se na granici razvlačenja i sastavu

mikrostrukture. Postavljeni matematički model primijenjen je u računalnoj simulaciji poboljšavanja čelične osovine.

Predložena se metoda procjene rezultata poboljšavanja čelika može uspješno koristiti u predviđanju mehaničkih svojstava poboljšana čelika i može se uspješno primijeniti u analizi oštećenja poboljšanog čeličnog strojnog dijela. Za učinkovitiju procjenu lomne žilavosti i otpornosti na umor materijala potrebni su dodatni podaci o mikrostrukturi. Računalnom simulacijom mikrostrukture i mehaničkih svojstava poboljšavanja čeličnog strojnog dijela utvrđeno da se kaljenjem u ulju intenziteta gašenja H = 0.7 postižu zadovoljavajući rezultati kaljenja.

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UTJECAJ INDIJA I KOSITRA NA ELEKTROKEMIJSKO PONAŠANJE ALUMINIJA U OTOPINI NaCl

INFLUENCE OF INDIUM AND TIN ON ELECTROCHEMICAL BEHAVIOUR OF ALUMINIUM IN NaCl SOLUTION

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Izvorni znanstveni rad / Original scientific paper

Sažetak: U radu je ispitano elektrokemijsko ponašanje aluminija te Al-In, Al-Sn i Al-Sn-In slitina u otopini 2M NaCl. Promatrana je promjena potencijala otvorenog strujnog kruga, snimane su potenciodinamičke polarizacijske krivulje te provedena impedancijska mjerenja. U svim promatranim slučajevima, dodatak legirajućeg elementa dovodi do značajne aktivacije aluminija. Aktivacija se očituje u pomicanju potencijala otvorenog strujnog kruga, kao i piting potencijala prema negativnijim vrijednostima (za otprilike 0.6 V) te u značajnom smanjenju pasivnog područja potencijala. Ustanovljeno je da stupanj aktivacije ovisi o vrsti legirajućeg elementa te da se povećava redom: Al < Al-In < Al-Sn ≈ Al-Sn-In. Nadalje, uočeno je da anodno otapanje Al-Sn i Al-Sn-In slitina započinje već na potencijalu otvorenog strujnog kruga, što je samo za 0.45 V pozitivnije od termodinamičkog Al^{3+}/Al potencijala. Impedancijska mjerenja provedena kod različitih vremena stabilizacije na potencijalu otvorenog strujnog kruga također su potvrdila veliku aktivnost Al-Sn i Al-Sn-In slitina u odnosu na aluminij.
Ključne riječi: aktivacija, aluminij, aluminijske slitine, impedancijska spektroskopija, pasivacija, lokalna korozija.

Abstract: The electrochemical behaviour of Al, Al-In, Al-Sn and Al-Sn-In alloys in 2M NaCl solution has been studied using an open circuit potential, potentiodynamic polarization and impedance measurements. The addition of alloying components to aluminium produced in all cases a considerable activation of aluminium. The activation is manifested by shifting of the open corrosion potential and the pitting potential in the negative direction (for about 0.6 V) and significant reducing of the passive potential region. The degree of activation depended on alloying element and it was found that increase in the order: Al < Al-In < Al-Sn ≈ Al-Sn-In. The anodic dissolution of the Al-Sn and Al-Sn-In alloys started at open circuit potential which is only 0.45 V more positive than the thermodynamic Al^{3+}/Al potential. The impedance measurements performed at different stabilization time at open circuit potential also confirmed the great activity of Al-Sn and Al-Sn-In alloys compared to aluminium.
Key words: activation, aluminium, aluminium alloys, impedance spectroscopy, passivation, pitting corrosion.

1. UVOD

Aluminij je vrlo atraktivan anodni materijal za skladištenje i konverziju energije. Prva saznanja o korištenju Al kao elektrodnog materijala u kemijskim izvorima struje datiraju još od 1850. g. kada je Hulot predstavio svoju bateriju s anodom od Zn, katodom od Al i elektrolitom od H_2SO_4 [1]. Anode od Al prvi put se koriste u bateriji koju je 1857. g. opisao Buff, dok je prvi kemijski izvor struje Al/zrak konstruirao Zaromb 1960.g. [1].

Teorijski gledano kemijski izvor struje Al/zrak ima energetski kapacitet od 2980 Ah/kg i napon od 2.70 V. Međutim, smetnju pri ostvarivanju ovih teorijskih mogućnosti predstavlja zaštitni oksidni sloj koji je gotovo uvijek prisutan na površini Al, što dovodi do značajnih gubitaka raspoložive energije. Ovo je usporilo razvoj praktičnih sustava baterija Al/zrak i ograničilo njihovu komercijalnu primjenu.

Sprječavanje sporednih reakcija (pasivacije, samokorozije, izlučivanja H_2) uz istovremeno održavanje elektrokemijske aktivnosti anodnog metala jedan je od ključnih problema koji treba riješiti kako bi se postiglo zadovoljavajuće iskorištenje energije u baterijama Al/zrak.

Polazi se od pretpostavke da se elektrokemijska aktivnost Al može poboljšati legiranjem s malim količinama elemenata koji imaju visoki prenapon izlučivanja vodika (npr. Hg, Mg, Zn, Ga, Tl, Sn, In, Cd, Bi). Udio legirajućih komponenti u ukupnoj masi slitine mora biti što manji, kako se ne bi narušila osnovna kvaliteta čistog Al. Na ovaj način mijenjaju se svojstva oksidnog filma i uklanjaju osnovni nedostaci Al: negativira se potencijal otvorenog strujnog kruga te se smanjuju otpornost zaštitnog oksidnog sloja, negativni diferencijalni efekt, polarizacija elektrode i korozija pri realnim radnim gustoćama anodne struje.

U prvim takvim istraživanjima Reding i Newport [2] proučavaju nekoliko tisuća različitih slitina Al koje bi bile zanimljive za primjenu u baterijama Al/zrak s hidroksidnim i kloridnim elektrolitom. Mnogo detaljnija istraživanja započeli su Despić i suradnici 1976. g. [3]. Proučavaju utjecaj sastava (Al + Ga, In, Tl) i termičke obrade na otapanje i Faradaysko iskorištenje Al anoda u NaCl otopini. Elektrokemijsko ponašanje sličnih slitina u alkalnim elektrolitima studirali su dalje MacDonald i suradnici [4] te Tuck i suradnici [5]. Osamdesetih godina prošlog stoljeća Alcan i njegove partnerske kompanije razvijaju cijelu seriju specijalnih slitina Al (od binarnih, ternarnih do multikomponentnih) za primjenu u sustavima Al/zrak [6-8].

Da bi se sustavi Al/zrak učinili što ekonomičnijim u posljednje vrijeme ispituju se mogućnosti zamjene specijalnih slitina izrađenih od superčistog Al s dvojnim ili trojnim slitinama Al tehničke čistoće [9-11].

U ovom radu ispitano je elektrokemijsko ponašanje Al te Al-In, Al-Sn i Al-Sn-In slitina u otopini 2M NaCl. Promatrana je promjena potencijala otvorenog strujnog kruga, snimane su potenciodinamičke polarizacijske krivulje te provedena impedancijska mjerenja.

2. EKSPERIMENTALNI DIO

Mjerenja su provedena na Al (čistoće 99.8 %) te Al-0.2%Sn, Al-0.1%In i Al-0.2%Sn-0.1%In slitinama. Radna površina elektrode je prije svakog mjerenja mehanički brušena brusnim papirima različite finoće, a površinski oksidni sloj je uklonjen u otopini NaOH. Mjerenja su provedena u 2M otopini NaCl pri 25 ^{o}C. Pri izvođenju mjerenja korištena je protuelektroda od Pt, dok je zasićena kalomel elektroda (ZKE) služila kao referentna elektroda.

Polarizacijske krivulje snimljene su u području potencijala od -2.4 V do - 0.6 V uz brzinu promjene potencijala od 5 mVs^{-1}. Impedancijska mjerenja provedena su kod različitih vremena stabilizacije (do 4 sata) na potencijalu otvorenog strujnog kruga. Spektri su snimani u širokom području frekvencija od 100 kHz do 100 mHz, uz *ac* amplitudu od ±10 mV.

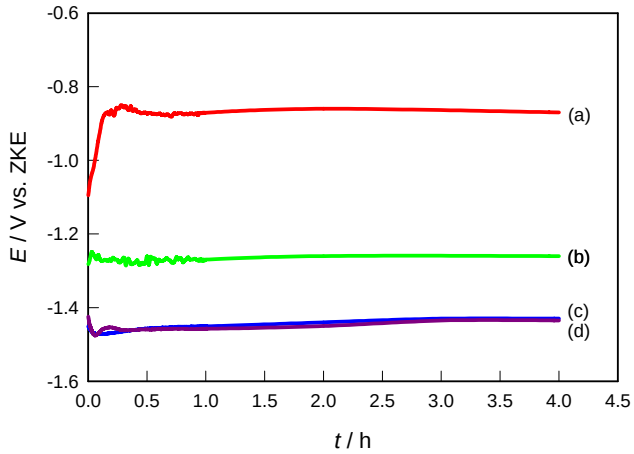
Pri izvođenju mjerenja korištena je oprema sastavljena od potenciostata PAR M237 i fazno osjetljivog pojačala PAR M5210 međusobno povezanih računalom.

3. REZULTATI I RASPRAVA

3.1. Potencijal otvorenog strujnog kruga

Slika 1 prikazuje vremensku promjenu potencijala otvorenog strujnog kruga (OCP) mehanički poliranih Al, Al-In, Al-Sn i Al-Sn-In elektroda u otopini NaCl kroz vrijeme od 4 sata, a dobivene vrijednosti navedene su u tablici 1. Kao što se može vidjeti, aluminijska elektroda vrlo brzo, već nakon 15 minuta, postiže stabilnu OCP vrijednost od -0.87 V.

Dodatak legirnog elementa aluminiju, u svim promatranim slučajevima dovodi do značajnog pomaka potencijala u negativnu stranu. Tako se na Al-In slitini odmah po uranjanju u elektrolit uspostavlja stabilna vrijednost potencijala otvorenog strujnog kruga od -1.26 V. Nadalje, uočavamo da je ponašanje Al-Sn i Al-Sn-In slitina slično te da se izrazito negativna OCP vrijednost od ≈-1.44 V također postiže nakon 15 minuta.



Slika 1. Vremenska promjena potencijala otvorenog strujnog kruga za (a) Al, (b) Al-In, (c) Al-Sn i (d) Al-Sn-In u 2M NaCl.

Tablica 1. Potencijal otvorenog strujnog kruga i pitting potencijal za Al i Al slitine u 2M NaCl

Uzorak	OCP (V)	E_{pit} (V)
Al	-0.87	-0.73
Al-In	-1.26	-1.17
Al-Sn	-1.43	-1.45
Al-Sn-In	-1.44	-1.45

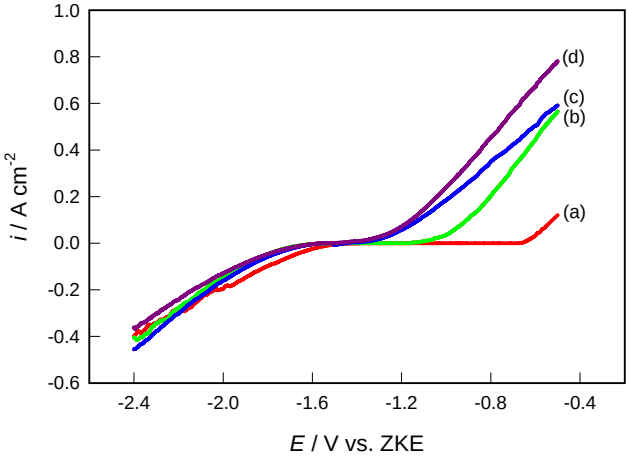
3.2. Polarizacijska mjerenja

Na slici 2 prikazane su polarizacijske krivulje snimljene na Al i Al slitinama u području potencijala od -2.4 V do -0.6 V. Na polarizacijskoj krivulji za Al (krivulja (a)) može se uočiti široki strujni plato, koje se proteže u granicama od -1.5 V do -0.7 V. Strujni plato, neovisnost struje o potencijalu u potenciodinamičkim uvjetima eksperimenta, odgovara rastu oksidnog filma kod konstantne jakosti električnog polja. Nakon prolaza kroz pasivno područje potencijala, postiže se piting potencijal (ili potencijal aktivnog anodnog otapanja) od -0.73 V kod kojeg dolazi do naglog porasta struje (tablica 1). Naime, oksidni sloj na površini metala se razara te dolazi do lokalnog otapanja metala. Daljnjim pomicanjem potencijala u anodnom smjeru struja linearno raste. Nasuprot ovome, kod potencijala od ≈ –1.55 V dolazi do značajnog poraste katodne struje zbog katodne reakcije izlučivanja vodika koja se odvija kroz oksidni sloj na površini metala.

Polarizacijska mjerenja ukazuju na izrazito aktivno ponašanje Al slitina u odnosu na aluminij. Aktivacija se očituje u pomicanju piting potencijala prema negativnijim vrijednostima te u značajnom sužavanju pasivnog područja potencijala. Kao što se može vidjeti sa slike 2 (krivulja (b)), nakon prolaza kroz usko pasivno područje potencijala (od samo 0.4 V) Al-In slitina se počinje otapati na potencijalu od ≈ -1.17 V (tablica 1).

Nadalje, polarizacijska mjerenja provedena na Al-Sn i Al-Sn-In slitinama (krivulje (c) i (d)) ukazuju na izrazito aktivno ponašanje ovih uzoraka u odnosu na tehnički aluminij. Naime, na polarizacijskoj krivulji nije uočeno pasivno područje potencijala, a anodno otapanje ova dva uzorka započinje već na potencijalu od ≈-1.45 V. Interesantno je da ovaj potencijal (koji je za

oba uzorka jednak potencijalu otvorenog strujnog kruga) iznosi -1.22 V vs. NHE, što je samo 0.45 V pozitivnije od termodinamičkog Al^{3+}/Al potencijala od -1.66 V vs. NHE [7].

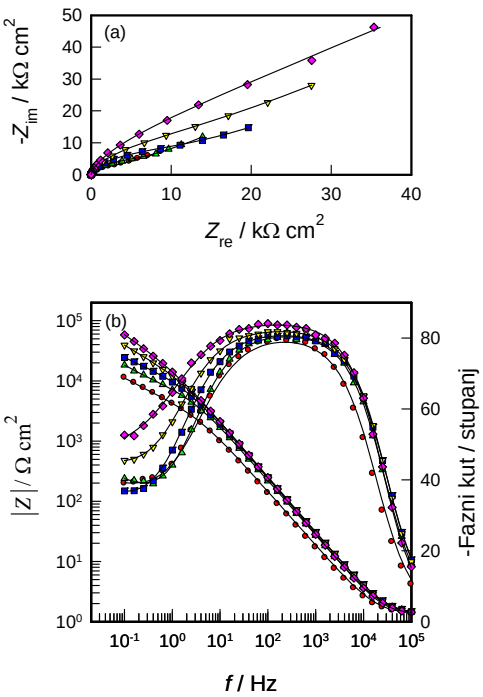


Slika 2. Potenciodinamičke polarizacijske krivulje za (a) Al (b) Al-In, (c) Al-Sn i (d) Al-Sn-In elektrode snimljene u 2M NaCl otopini.

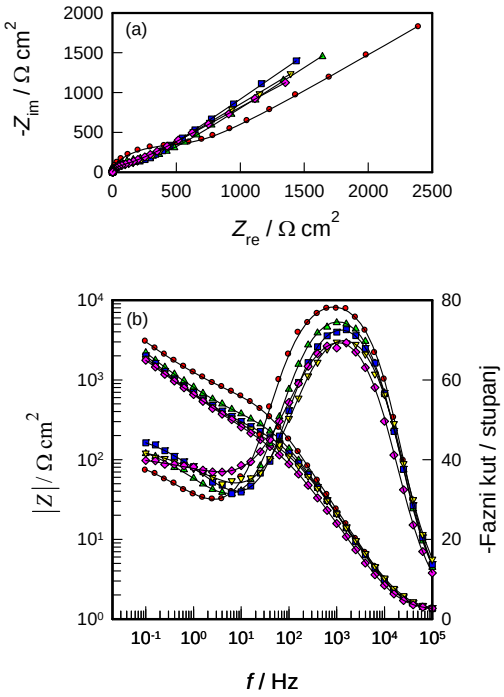
Nadalje, katodni dio polarizacijske krivulje svakog pojedinog uzorka pomaknut je u katodnu stranu, ukazujući na činjenicu da prisutni legirajući elementi povećavaju prenapon izlučivanja vodika na aluminiju.

3.3. Impedancijska mjerenja

Da bi se u potpunosti izvršila elektrokemijska karakterizacija Al i Al slitina izvedena su mjerenja impedancije. Mjerenja su provedena kod različitih vremena stabilizacije na OCP-u, a dobiveni rezultati prikazani su na slikama 3 - 6.



Slika 3. (a) Nyquist i (b) Bode dijagrami za Al u 2M NaCl otopini kod različitih vremena stabilizacije na OCP-u: (●) 0 h, (▲) 1 h, (■) 2h, (▼) 3 h i (♦) 4 h.



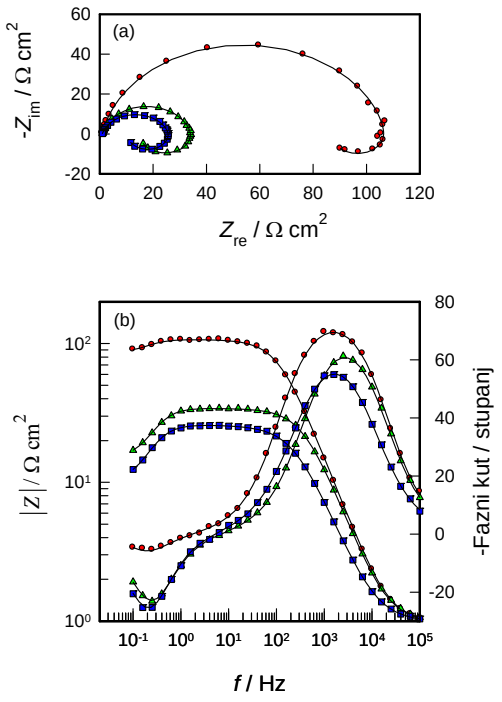
Slika 4. (a) Nyquist i (b) Bode dijagrami za Al-In slitinu u 2M NaCl otopini kod različitih vremena stabilizacije na OCP-u: (●) 0 h, (▲) 1 h, (■) 2h, (▼) 3 h i (♦) 4 h.

U Nyquist kompleksnoj ravnini za Al (slika 3a) nazire se postojanje dviju vremenskih konstanti koje se više-manje preklapaju. Dobiveni spektri pokazuju da se impedancija brzo mijenja s porastom vremena stabilizacije na potencijalu otvorenog strujnog kruga. Promjene se očituju u naglom rastu svake vremenske konstante, a time i ukupne impedancije sustava, dok oblik impedancijskog spektra ostaje nepromijenjen.

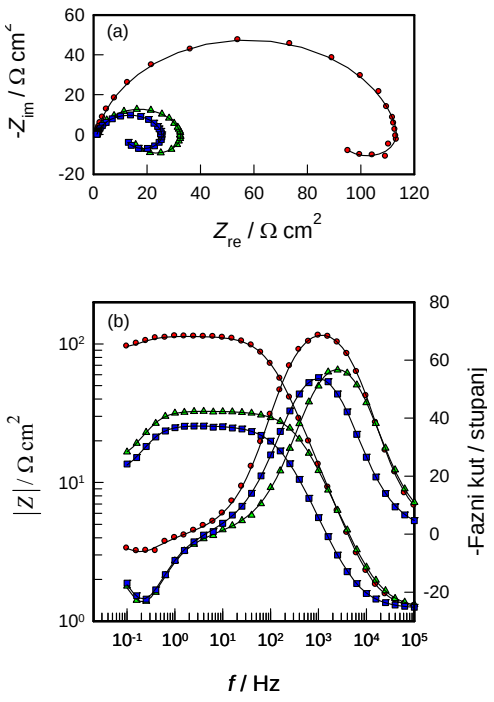
Na slici 3b prikazane su ovisnosti apsolutne vrijednosti impedancije, Z, i faznog pomaka o logaritmu frekvencije, f, u tzv. Bodeovom prikazu (log $|Z|$ vs. log f i fazni kut vs. log f). Ovaj grafički prikaz omogućava jasniji razlučivanje pojedinih vremenskih konstanti u funkciji frekvencije. U području visokih frekvencija (f > 10 kHz) u ukupnoj impedanciji dominantan je utjecaj otpora elektrolita R_{el}. Kod srednjih frekvencija (f < 10 kHz) linearna ovisnost između log $|Z|$ i log f uz karakteristični nagib Bodeovog pravca ≈-1 određuje kapacitivna svojstva promatranog sustava. Fazni pomak poprima vrijednost od ≈80°. Smanjenjem frekvencije dolazi do promjene nagiba linearne ovisnosti, tako da u području niskih frekvencija (f < 1 Hz), nagib Bodeovog pravca od ≈-0.5 i fazni pomak od ≈40° opisuju pojavu difuzijski kontroliranog procesa. Može se uočiti da ukupna impedancija sustava raste porastom vremena stabilizacije na OCP-u.

Impedancijski spektri ukazuju na raznolikost pojava u promatranom sustavu. Vremenska konstanta zabilježena u području visokih frekvencija rezultat je dielekričnih osobina oksidnog sloja na površini metala, dok niskofrekventni dio dijagrama jasno ukazuje na činjenicu da se prijenos mase kroz fazni sloj mora uzeti u obzir pri opisivanju granice faza metal/oksidni sloj/elektrolit.

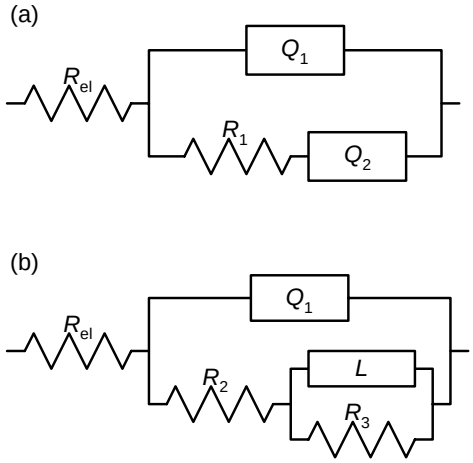
Dobiveni rezultati najbolje se mogu opisati ekevivalentnim krugom prikazanim na slici 7a, koji se sastoji od sljedećih elemenata: R_{el}, Q_1, R_1 i Q_2. U predloženom krugu parametrom R predstavljene su komponente omskog otpora, dok parametar Q predstavlja konstantno fazne elemente (KFE) u krugu.



Slika 5. (a) Nyquist i (b) Bode dijagrami za Al-Sn slitinu u 2M NaCl otopini kod različitih vremena stabilizacije na OCP-u: (●) 0 h, (▲) 1 h, (■) 2 h.



Slika 6. (a) Nyquist i (b) Bode dijagrami za Al-Sn-In slitinu u 2M NaCl otopini kod različitih vremena stabilizacije na OCP-u: (●) 0 h, (▲) 1 h, (■) 2 h.



Slika 7. Ekvivalentni krugovi primijenjeni pri analizi impedancijskih mjerenja: (a) za pasivno stanje metala i (b) za aktivno otapanje metala.

Konstantno fazni element opisuje odstupanje od idealnog ponašanja sustava, a dovodi se u vezu s nehomogenostima unutar mase oksida, kao i činjenicom da elektrodna površina na mikroskopskom nivou nije idealno glatka i ravna, već posjeduje veliki broj površinskih defekata, kao što su razne izbočine, udubljenja, lokalne nehomogenosti naboja itd. Impedancija konstantno faznog elementa, Z_{KFE}, dana je izrazom [13]:

$$Z_{KFE} = \left[Q(j\omega)^n\right]^{-1} \qquad (1)$$

gdje je j imaginarni broj ($j = \sqrt{-1}$), ω je kružna frekvencija *ac* signala ($\omega = 2\pi f$), a Q je konstanta koja ne ovisi o frekvenciji i predstavlja kombinaciju svojstava povezanih sa stanjem površine. Eksponent konstantno faznog elementa, veličina n, također je konstanta koja može poprimiti različite iznose u granicama od -1 do +1. U slučaju kada je n = 0 jednadžba (1) opisuje otpor, za n = -1 induktivitet, te za n = 1 kapacitet. Za difuzijski proces kroz granicu faza elektroda/elektrolit, kroz čvrstu fazu, kao i preko cijele elektrodne površine veličina n poprima iznos od 0.5.

Analizom rezultata ustanovljeno je da n vrijednosti parametra Q_1 iznose oko 0.9, dok su n vrijednosti parametra Q_2 oko 0.5. Stoga, u ekvivalentnom krugu na slici 7a parametar Q_1 predstavlja KFE koji je jednak serijskom spoju kapaciteta oksidnog filma i elektrokemijskog dvosloja, dok Q_2 predstavlja difuzijske procese u oksidnom filmu. R_1 je otpor prijenosu naboja, a R_{el} otpor elektrolita (koji je reda veličine 1 Ω cm^2). Numeričke vrijednosti za Al navedene su u tablici 2. Podaci u tablici pokazuju da porastom vremena stabilizacije raste otpor prijenosu naboja, R_1, dok se kapacitet površinskog sloja, Q_1, te koeficijent difuzije, Q_2, smanjuju. Ovakav smjer promjena pripisuje se poboljšanju zaštitnih svojstava oksidnog sloja na površini aluminija.

Polarizacijskim mjerenjima ukazalo se na izrazito aktivno ponašanje Al slitina u odnosu na aluminij. Aktivacija se očituje u pomicanju piting potencijala prema negativnijim vrijednostima te u značajnom smanjenju pasivnog područja potencijala, što u konačnici može dovesti do aktivnog otapanje pojedinih uzoraka već na potencijalu otvorenog strujnog kruga.

Slika 4 prikazuje utjecaj vremena stabilizacije na oblik impedancijskog spektra Al-In slitine. Spektri su analizirani korištenjem ekvivalentnog kruga prikazanog na slici 7a, a dobivene vrijednosti navedene su u tablici 2. Uočljivo je smanjenje impedancije s porastom vremena stabilizacije na OCP-u.

Razlika između potencijala otvorenog strujnog kruga i potencijala aktivnog otapanja Al-In slitine iznosi samo 0.1 V. Stoga stabilizacija uzorka na potencijalu otvorenog strujnog kruga može, nakon određenog vremena, dovesti do otapanja slitine. Naime, na potencijalu otvorenog strujnog kruga kompetentno se odvijaju dva procesa: adsorpcija pasivirajućih OH^- iona i adsorpcija agresivnih Cl^- iona. Legirajući element, u ovom slučaju indij olakšava adsorpciju Cl^- iona, a time i otapanje slitine [14,15]. Ovo je popraćeno značajnim smanjenjem veličine R_1 te porastom veličina Q_1 i Q_2, dok opći oblik impedancijskog spektra još uvijek ostaje sačuvan. Smanjenje impedancije pripisuje se prodiranju agresivnih iona u oksidni film. Međutim, oksidni film još uvijek donekle pokazuje zaštitna svojstva.

Tablica 2. Optimalne vrijednosti parametara ekvivalentnih krugova sa slike 7 za Al i Al slitine u otopini NaCl

	t (h)	$Q_1 \times 10^6$ (Ω^{-1} s^n cm^{-2})	n_1	R_1 (Ω cm^2)	$Q_2 \times 10^6$ (Ω^{-1} s^n cm^{-2})	n_2	R_2 (Ω cm^2)	L (H cm^2)	R_3 (Ω cm^2)
Al	0	20.7	0.90	3361.5	126.7	0.48			
	1	12.8	0.91	6986.6	84.4	0.54			
	2	11.6	0.91	11050.1	66.3	0.49			
	3	10.4	0.92	15771.3	34.7	0.53			
	4	9.5	0.94	18582.6	18.9	0.51			
Al-In	0	12.5	0.93	520.8	471.6	0.48			
	1	16.8	0.91	279.6	623.2	0.51			
	2	18.4	0.90	208.4	674.1	0.53			
	3	21.4	0.88	163.3	703.9	0.49			
	4	28.5	0.88	135.7	727.6	0.46			
Al-Sn	0	27.4	0.89				85.9	14.3	20.3
	1	33.6	0.88				14.0	8.3	19.2
	2	86.7	0.84				9.3	7.5	15.6
Al-Sn-In	0	30.9	0.89				90.6	16.1	22.3
	1	40.2	0.86				12.9	9.2	18.7
	2	111.3	0.85				10.3	7.0	14.3

Polarizacijska mjerenja provedena na Al-Sn i Al-Sn-In slitinama (krivulje (c) i (d) na slici 2) ukazuju na izrazito aktivno ponašanje ovih uzoraka u odnosu na tehnički aluminij. Naime, na polarizacijskoj krivulji nije uočeno pasivno područje potencijala, a anodno otapanje ova dva uzorka započinje već na potencijalu od ≈-1.45 V (što je jednako njihovim OCP vrijednostima). Stoga, već pri samom uranjanju navedenih slitina u otopinu NaCl dobivaju se impedancijski spektri koji pokazuju sve karakteristike aktivnog anodnog otapanja te je u području niskih frekvencija (f < 10 Hz) zabilježena induktivna petlja (slike 5 i 6). Što je vrijeme stabilizacije na OCP-u duže otapanje uzorka je izraženije. Za ovakav odziv u kompleksnoj ravnini impedancije predložen je ekvivalentni krug prikazan na slici 7b u kojem R_{el} predstavlja otpor elektrolita, Q_1 kapacitete oksidnog filma i elektrokemijskog dvosloja spojene u seriju, R_2 otpor elektrolita kroz film (na područjima zahvaćenim piting korozijom), R_3 otpor prijenosu naboja na površini metala (na području zahvaćenom piting korozijom) te L apsorpcijske procese (najvjerojatnije Cl^- iona na području zahvaćenom piting korozijom). Numeričke vrijednosti parametara ekvivalentnog kruga navedene su u tablici 2.

Kao što se može vidjeti, porastom vremena stabilizacije smanjuju se veličine R_2, R_3 i L, dok kapacitet granične površine, Q_1 raste, što se može objasniti porastom aktivne površine kao i nastajanjem slanog filma na površini metala [16,17]. Nakon 2 sata snažno otapanje legure potvrđeno je malim iznosom veličina R_2 i R_3, te se u konačnici može smatrati da cijela površina metala korodira i da je prekrivena slojem soli (tj. nema netaknutog ili neoštećenog dijela oksidnog filma).

4. ZAKLJUČCI

- Dodatak In i/ili Sn aluminiju dovodi do njegove značajne aktivacije. Aktivacija se očituje u pomicanju potencijala otvorenog strujnog kruga, kao i pitting potencijala prema negativnijim vrijednostima te u značajnom smanjenju pasivnog područja potencijala.
- Stupanj aktivacije ovisi o vrsti legirajućeg elementa u slitini te se povećava redom: Al < Al-In < Al-Sn ≈ Al-Sn-In.
- Al-Sn i Al-Sn-In slitine pokazuju izrazito aktivno ponašanje u odnosu na tehnički aluminij. Anodno otapanje ovih uzoraka započinje već na potencijalu otvorenog strujnog kruga, tj. na -1.45 V. Ovaj potencijal iznosi -1.22 V vs. NHE, što je samo 0.45 V pozitivnije od termodinamičkog Al^{3+}/Al potencijala od -1.66 V vs. NHE.
- Ukazano na pogodnost primijene impedancijske spektroskopije pri analizi elektrokemijskog ponašanja Al i Al slitina, posebice zbog mogućnosti razlučivanja pojedinih elementarnih procesa koji se odvijaju na anodi.
- Pasivno ponašanje aluminija i Al-In slitine na OCP-u određeno je s dvije vremenske konstante. Vremenska konstanta zabilježena u području visokih frekvencija rezultat je dielekričnih osobina oksidnog sloja na površini metala, dok vremenska konstanta u području niskih frekvencija opisuje difuzijske procese u oksidnom sloju.
- Impedancijska mjerenja provedena na Al-Sn i Al-Sn-In slitinama potvrdila su nesmetano otapanje ovih uzoraka na potencijalu otvorenog strujnog kruga. Kapacitivna vremenska konstanta u području visokih frekvencija i induktivna vremenska konstanta u području niskih frekvencija objašnjavaju porast aktivne površine kao i prisutnosti slanog filma na površini metala.

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ANALYSIS OF THE SUBMARINE OUTER HULL MATERIAL FOR RESTAURATION PURPOSES

ANALIZA MATERIJALA VANJSKOG TRUPA PODMORNICE U SVRHU RESTAURACIJE

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Pregledni članak/ Subject review

Abstract: Restoration of any museum display implies use of authentic materials and technology. Technical Museum in Zagreb is in the process of restoring small Italian submarine form the year 1943. During restoration in order to achieve maximum authenticity it was necessary to determine submarine's outer hull material as well as weld material. Metallographic analysis was conducted on the hull's material and weld material in order to determine materials structure. Next step was determination of materials' chemical composition using scanning electron microscopy.

Key words: restoration, submarine materials, welding method

Sažetak: Restauriranje bilo kojeg muzejskog eksponata pretpostavlja korištenje autentičnih materijala i tehnologija. Tehnički muzej u Zagrebu u fazi je restauracije talijanske podmornice koja datira iz 1943.godine. U svrhu postizanja autentičnosti bilo je nužno utvrditi iz kojeg je materijala načinjen vanjski trup podmornice te koji se dodatni materijal koristio prilikom zavarivanja. Na dobivenom uzorku trupa provedena je metalografska analiza koja obuhvaća analizu mikrostrukture osnovnog materijala i materijala zavara. Nakon toga je utvrđen kemijski sastav materijala korištenjem SEM mikroskopa.

Ključne riječi: restauriranje, materijal trupa podmornice, zavarivanje

1. INTRODUCTION

Restauration of any museum monument or display is a very complex process which implies use of authentic materials and technology. Technical Museum in Zagreb is in the process of restoring small Italian submarine CB-20 from the year 1943, built in Caproni factory (Figure1).

Figure1. Submarine CB-20 displayed at Technical Museum in Zagreb

The firm Caproni, originally founded by Giovanni Caproni and well-known around the world for the construction of advanced airplanes, winners of many world records. During the crisis of 1935, his firm was asked to collaborate with the Regia Marina (Italian Navy) in the construction of new assault weapons.
Construction began in earnest at the Caproni factory located in Taliedo, near Milan. This miniscule submarine had a resistant hull with semispherical caps at each end. Ballast tanks, torpedo launchers, and other components were placed externally to the resistant hull. The project called for a crew of two; the commanding officer would sit on a special seat from which he had access to the periscope and the controls, mostly a joystick, just like an airplane, and also navigational instrumentation resembling more a cockpit rather than a control room. [1]
Arc welding with covered metallic electrodes was an accepted process for shipbuilding since 1930. [2]. Submarine pressure hulls were of riveted construction almost up to World War II. Subsequently the pressure hulls were first partially, and then wholly welded. Compared to riveting welding resulted in increased diving depth, greater resistance against shock and reduced danger of leakage under high pressure. In the German and US navies completely welded pressure hulls were introduced during the 1930s [3].

During restoration in order to achieve maximum authenticity it was necessary to determine submarine's outer hull material as well as weld material.

2. MATERIAL ANALYSIS

In order to get necessary information we first needed a segment of submarine's hull material which contained both base and weld material. The segment was cut out from the rear part of the submarine as shown on Figures 2 and 3.

Figure2. Place on the hull from which the segment was taken

Figure 3. Segment of submarines outer hull, one side riveted, one side welded.

Conducted material analysis consisted of base and weld material metallographic analysis as well as chemical composition analysis. For that purpose segment of the submarine's hull had to be prepared for metallographic analysis. Figure4 shows part of the segment from which the specimen was cut out.

Figure 4. Place of cutting the specimen for metallographic analysis

2.1. Metallographic analysis

Specimen was cut out at the weld which provided insight in both base and weld material microstructures. Preparation of specimen was conducted according to recommended procedure for that material: sealing in polymer mass, hard and fine grinding and polishing. After polishing specimen was etched by Nital (Figure 5).

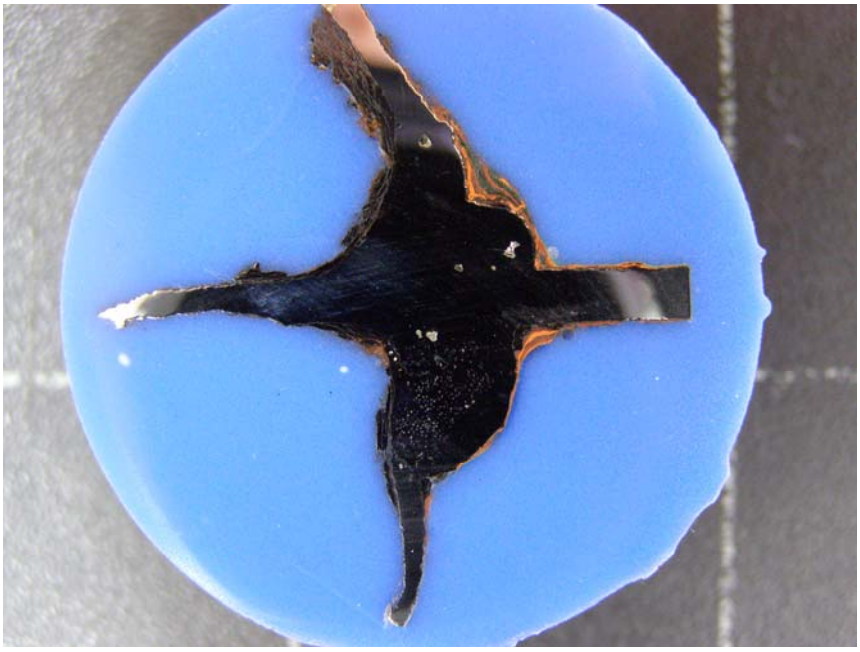
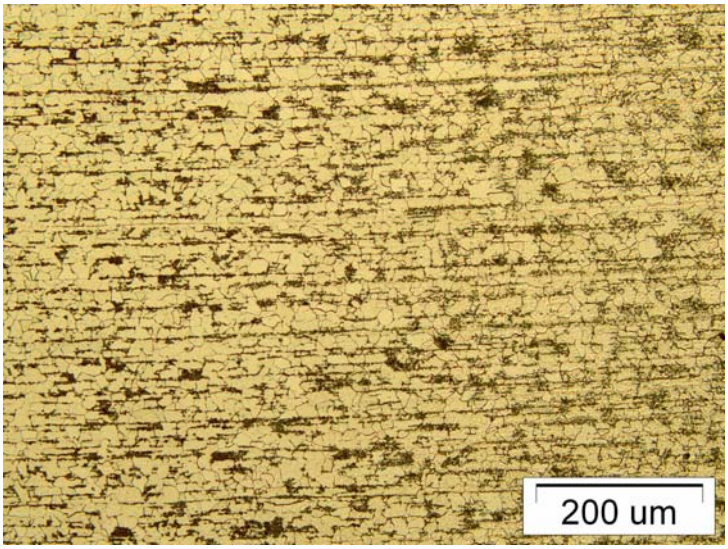
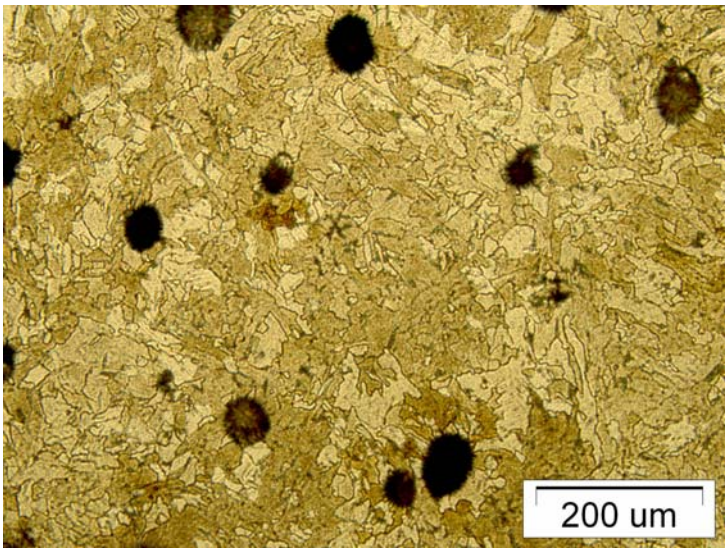


Figure 5. Specimen ready for metallographic analysis

Microstructural analysis was conducted by use of light microscope. Analysis of base and weld material microstructure indicated differences even on small magnifications as shown on Figures 6 and 7.

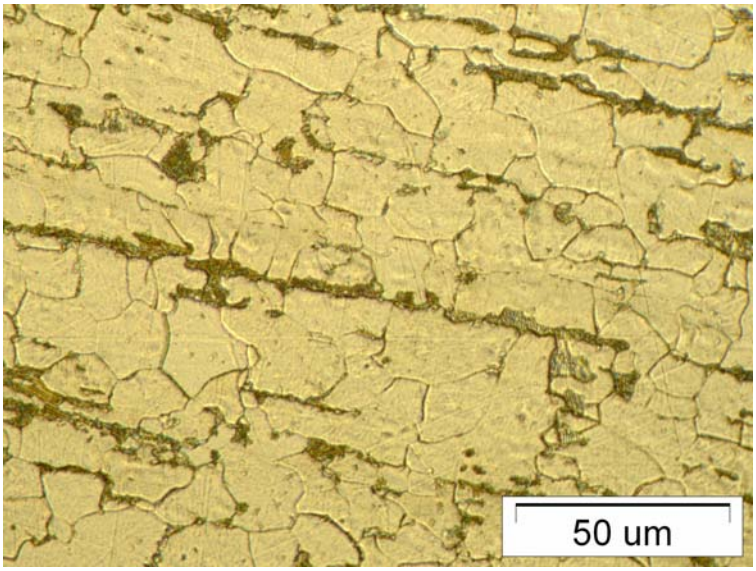


a)



b)

Figure 6. Specimen, magnification 200 x: a) base material
b) weld material



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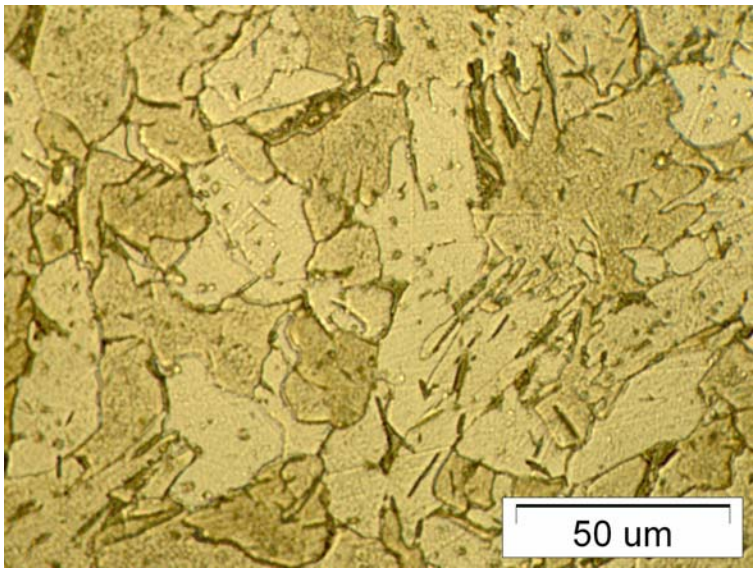


b)

Figure 7. Microstructure, magnification 1000 x: a) base material
b) weld material

Microstructure of base material is mostly ferrite with fine pearlite at grain boundaries. Analysis of the weld material indicates that it has rough moulding (Widmannstätten's) structure. Porosity of the weld material has also been detected. Structure directionality has also been established as a result of cold drawing of the material which was probably used during production of metal plates used for outer hull of the submarine.

2.2. Microhardness testing

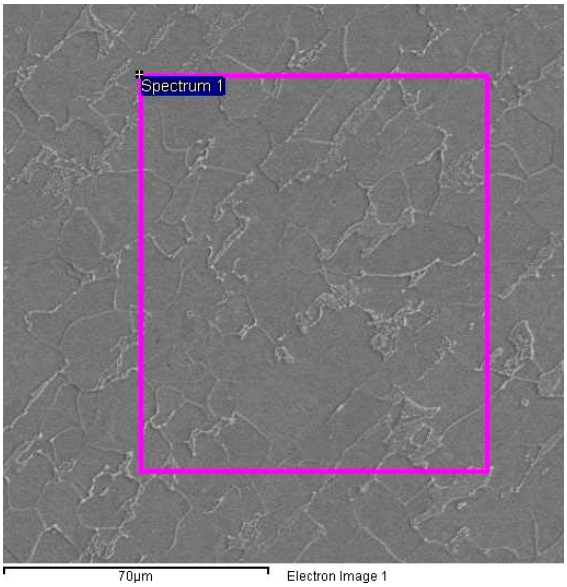
Microhardness testing was also conducted on the specimen prepared for metallographic analysis. Testing was performed on device for microhardness testing according to Vickers method (HV) with load of 2N which corresponds to HV0,2.
Ten measurements were conducted on each material, and their results are shown in Table1.

Table1. Results of microhardness testing

	HV0,2										
	1	2	3	4	5	6	7	8	9	10	$\bar{X}$
base material	161	142	161	148	149	153	155	157	159	149	153
weld material	142	133	136	136	134	131	136	139	142	134	136

2.3. Scanning electron microscope and EDS analysis

Specimen was analyzed using scanning electron microscope TESCAN VEGA TS5136LS in high vacuum at voltage of 20 kV. Microanalysis was conducted using EDS Oxford detector with analysis array of 20 kV.
Figures 8 and 9 show area of chemical composition microanalysis and obtained spectrum.



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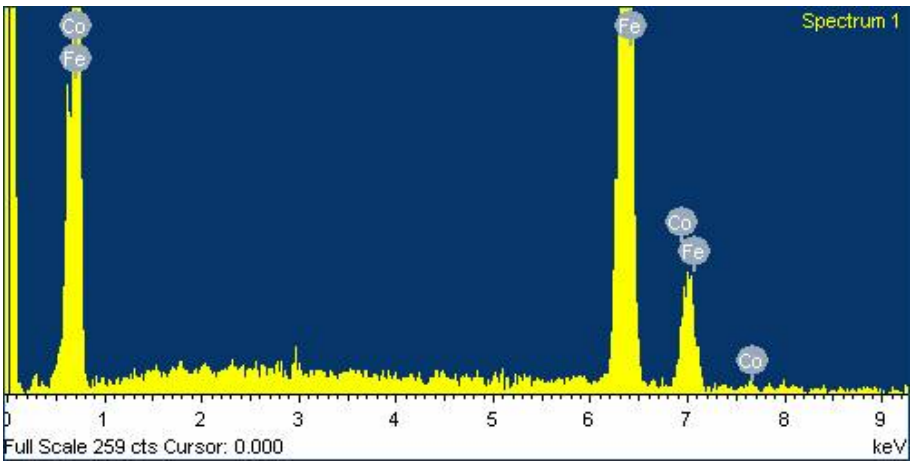
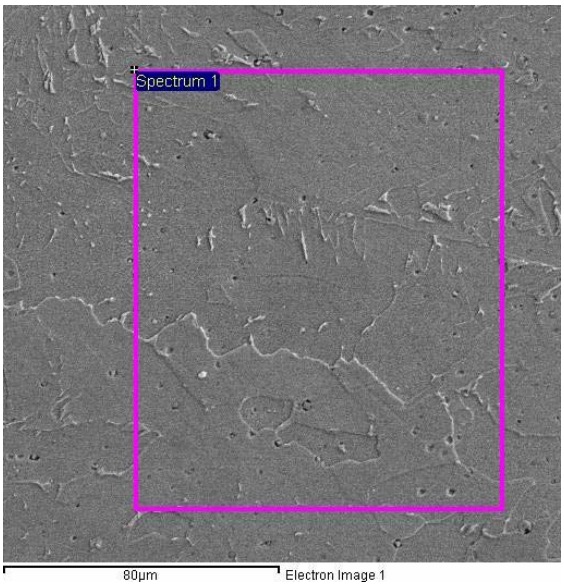


b)

Figure 8.EDS analysis of base hull material: a) area of analysis

b) spectrum(Fe, Co, C)



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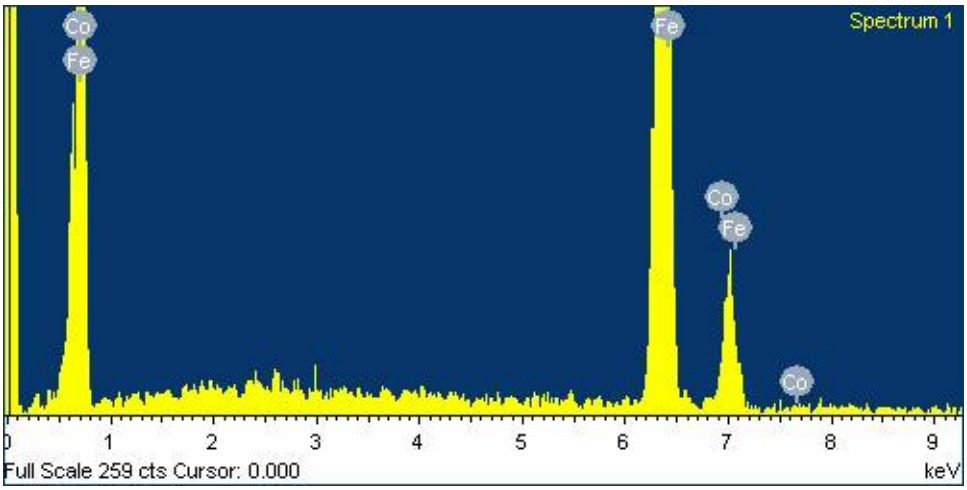

b)

Figure 9. EDS analysis of weld material: a) analysis area
b) spectrum (Fe, Co, C)

Analysis of chemical deposition implies that there are no significant differences between base and weld material. Both materials are mild steel with some content of cobalt.

3. Conclusion

Based on gathered analysis data following conclusions can be made:

- during metallographic specimen macroanalysis considerable porosity in the weld was detected

- Microstructural analysis showed quite difference between base and weld material microstructure. Base material has mostly ferrite microstructure with fine pearlite at grain boundaries. Structure directionality has also been established as a result of cold drawing of the base material used during production of metal plates for outer hull of the submarine. Analysis of weld material shows rough moulding (Widmannstätten's) structure as a consequence of high heat input during welding and improper cooling. Porosity was also detected in weld material.

- Microhardness of base material is at about 153 HV0,2 which is higher then weld material microhardness of 136 HV0,2.

- SEM and EDS analysis of chemical deposition implies that there are no significant differences between two materials. Both have some chemical composition which means that same material was used for both base and deposit material during welding. Base and deposit material is mild steel with some content of cobalt.

- Mechanical properties of base and deposit material and their chemical analysis will be conducted in future investigations to determine exact type of steel.

4. Literature

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[2] …, The Procedure Handbook Of Arc Welding, The Lincoln Electric Company, 1994.
[3] Paul Akermann, Encyclopedia of British Submarines 1901-1955, Google books.

UTJECAJ DUBOKOG HLAĐENJA NA OTPORNOST NA TROŠENJE BRZOREZNIH ČELIKA

EFFECT OF DEEP CRYOGENIC TREATMENT ON WEAR RESISTANCE OF HIGH SPEED STEEL

Pregledni članak / Subject review

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Sažetak: Iako je duboko hlađenje primijenjeno na mnogim materijalima, najviše istraživanja učinjeno je na ispitivanju utjecaja dubokog hlađenja na povećanje otpornosti na trošenja alatnih čelika. Primjena dubokog hlađenja nakon kaljenja brzoreznih čelika dodatno povećava tvrdoću, smanjuje trošenje alata, a time i zastoje u proizvodnji radi promjene alata, čime se smanjuju troškovi do 50%. U ovom radu dan je pregled dosadašnjih spoznaja i ispitivanja utjecaja dubokog hlađenja na svojstva alatnih čelika, s naglaskom na brzorezne čelike.

Ključne riječi: Duboko hlađenje, brzorezni čelici, otpornost na trošenje

Abstract: Although the deep cryogenic treatment has been applied to many materials, most of the research was done to investigate the effect of deep cryogenic treatment on wear resistance of tool steels. Deep cryogenic treatment after quenching of high speed steel additionally upgrades hardness, improves wear resistance and by that reduces equipment set up leading to cost reduction up to 50%. This paper presents results of research about influence of deep cryogenic treatment on tool steels properties with an emphasis on high speed steels.

Key words: Deep cryogenic treatment, high speed steel, wear resistance

1. UVOD

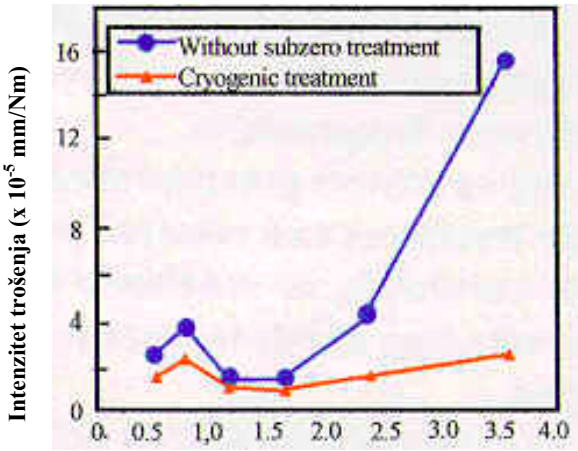
U cilju poboljšanja svojstava postupak dubokog hlađenja primjenjuje se već dugi niz godina. Još prije nekoliko stoljeća urari i kovači u Švicarskoj koristili su ekstremno niske temperature u Alpama, ostavljajući čelik dulje vrijeme u smrznutom području. Time bi mu znatno poboljšali svojstva uslijed završetka pretvorbe pothlađenog austenita u martenzit. Prvi znanstveno utemeljeni pokusi s pothlađivanjem čelika provedeni su početkom 20 st. u cilju eliminacije zaostalog austenita. No zbog slabe opreme i nemogućnosti postizanja temperatura manjih od -80°C rezultati nisu bili zadovoljavajući. Razvojem opreme i nisko temperaturne tehnike 70-tih godina prošlog stoljeća, omogućeno je postizanje vrlo niskih temperatura, do -196°C, što je omogućilo intenziviranje istraživanja na području utjecaja dubokog hlađenja na svojstva čelika.

Pothlađivanje (eng. Cold Treatment), na temperaturama od cca -80°C („suhi led“) dovoljno je za transformaciju zaostalog austenita iz kaljenog čelika u martenzit i u širokoj je komercijalnoj primjeni, posebno za uklanjanje zaostalog austenita u pougljičenim i površinski kaljenim slojevima. Kod visokolegiranih alatnih čelika primjenom dubokog hlađenja dodatno se postiže i toplinska stabilnost. Duboko hlađenje (eng. Deep cryogenic treatment) koje se provodi na temperaturi -196°C (tekući dušik) poboljšava određena svojstva znatno više od pothlađivanja. Pri dubokom hlađenju pojavljuju se dva metalurška fenomena: pretvorba zaostalog (pothlađenog) austenita u martenzit uz istovremeni raspad martenzita te početak nukleacije za naknadnu precipitaciju vrlo finih karbida.

Novija istraživanja pokazala su da je duboko hlađenje postupak koji se provodi tijekom klasične toplinske obrade s ciljem postizanja povećane otpornosti na trošenje kod nekih materijala te poboljšanja toplinske stabilnosti kod drugih. Duboko hlađenje se danas provodi na alatnim čelicima, maraging čelicima, lijevanom željezu, poboljšanim čelicima, TM volfram karbidu, aluminiju te polimerima i kompozitima. Kod svih spomenutih materijala duboko hlađenje povećava otpornost na trošenje, a time i trajnost proizvoda [1-6].

2. MIKROSTRUKTURNE PROMJENE TIJEKOM DUBOKOG HLAĐENJA

Povećanje otpornosti na trošenje nije jednostavno izmjeriti u laboratorijskim uvjetima i ono značajno ovisi o parametrima ispitivanja kao što je prikazano na slici 1 [4]. Ipak u literaturi je moguće naći čitav niz izvještaja o poboljšanju otpornosti na trošenje čelika nakon dubokog hlađenja. U tablici I i II prikazani su rezultati studije o utjecaju plitkog i dubokog hlađenja na povećanje otpornosti na trošenje različitih materijala (tek povećanje iznad 120% smatra se statistički značajno). Stvarno trošenje alata u obradi može se znatno razlikovati od laboratorijskih rezultata. Paralelna istraživanja otpornosti na trošenje alata u proizvodnji prikazana su u tablici III, a ovi rezultati su se potvrdili i kroz laboratorijska istraživanja.



Slika 1: Trošenje u odnosu na brzinu klizanja (pin od disc) za uzorke od Fe-12Cr-Mo-V-1.4C alatnog čelika sa i bez dubokog hlađenja (austenitizacija na 1020°C, popuštanje na 453K/30min). Put trošenja u skliznom kontaktu iznosio je 200 m [4]

Tablica I: Čelici kod kojih je utvrđeno povećanje otpornosti na trošenje dubokim hlađenjem [6]

Alatni čelik (AISI No)	Opis	Hlađeno na -79°C	Duboko hlađeno na -190°C
D-2	Visoko ugljični Cr alatni čelik	316%	817%
S-7	Silicij alatni čelik	241%	503%
52100	Konstrukcijski čelik	195%	420%
0-1	Alatni čelik za hladni rad	221%	418%
A-10	Alatni čelik za hladni rad	231%	264%
M-1	Mo brzorezni čelik	145%	225%
H-13	CrMo čelik za topli rad	164%	209%
M-2	WMo brzorezni čelik	117%	203%
T-1	W brzorezni čelik	141%	176%
CPM-10V	Alatni čelik za hladni rad	94%	131%
P-20	Čelik za kalupe	123%	130%
440	Martenzitni nehrđajući čelik	128%	121%

Tablica II: Materijali kod kojih nije utvrđeno povećanje otpornosti na trošenje hlađenjem i dubokim hlađenjem [6]

Alatni čelik (AISI No)	Opis	Hlađeno na -79°C	Duboko hlađeno na -190°C
430	Feritni nehrđajući čelik	116%	119%
303	Austenitni nehrđajući čelik	105%	110%
8620	NiCrMo čelik	112%	104%
C-1020	Ugljični čelik	97%	98%
AQS	Grafitni ljevovi na bazi željeza	96%	97%
T-2	W brzorezni čelik	72%	92%

Tablica III: Rezultati ispitivanja otpornosti na trošenje alata obrađenih dubokim hlađenjem [6]

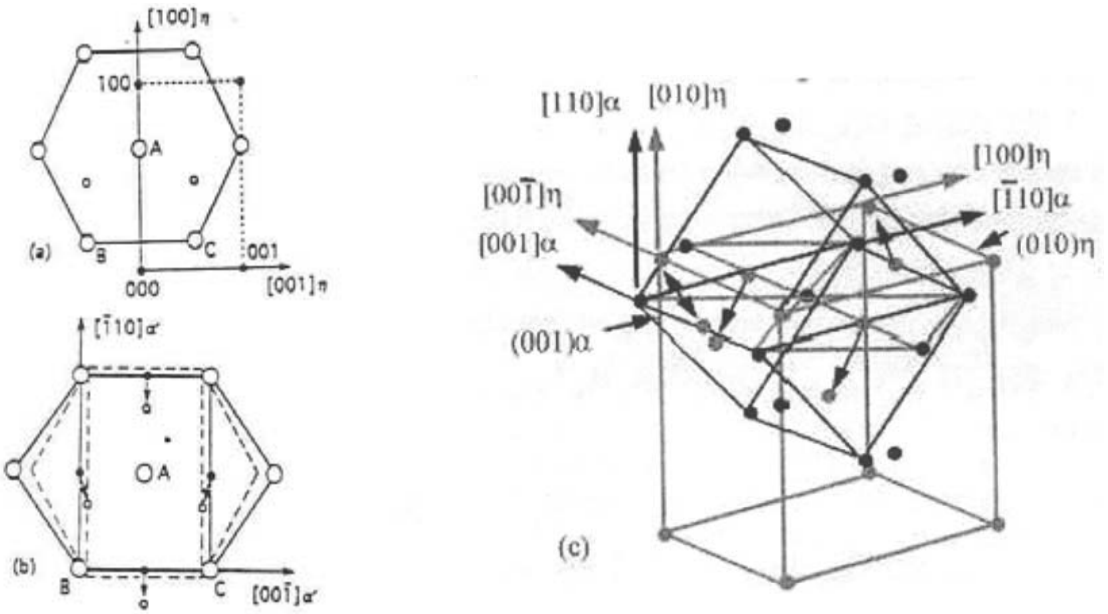
Tip alata	Alatni čelik (AISI No)	Povećanje otpornosti na trošenje (%)
Štanca	D-2	1000
Probijač	M-7	600
Vretenasto glodalo	M-42	450
Svrdla	M-42, M-7, C-2	300
Glodalo	M-7	250
Svrdlo	M-42	200
Probijač	M-2	100

Do danas je provedeno više istraživanja o utjecaju dubokog hlađenja na trošenje alatnih čelika te o mogućim mehanizmima koji utječu na povećanje otpornosti na trošenje. Sva istraživanja su provođena različitim parametrima i različitim kombinacijama toplinskih obrada i dubokog hlađenja, ali su sva dala podjednake zaključke.

Pokazalo se da se efekt dubokog hlađenja odvija u nekoliko stadija. U prvom stadiju, do -130°C, pojavljuje se transformacija zaostalog austenita u martenzit, čime dolazi do povećanja tvrdoće. Ova transformacija kao ni kod klasične toplinske obrade nije vremenski ovisna.

U drugom stadiju, na temperaturi oko -196°C, započinje vremenski ovisno raspadanje primarnog martenzita. To raspadanje uzrokuje omekšavanje čelika, ali dolazi do nukleacije velikog broja fino raspršenih karbida nanometarskih dimenzija. Tijekom naknadnog popuštanja dolazi do formiranja i precipitacije vrlo finih (eta) η-karbida (slika 2)[4,5]. Pokazalo se da se broj ovih karbida

povećava što je dulje trajanje dubokog hlađenja, što je niža temperatura te što je niža temperatura austenitizacije. Meng i sur. [4] su utvrdili da je dominantni mehanizam povećanja otpornosti na trošenje kod alatnih čelika upravo formiranje tih vrlo sitnih (eta) η-karbida.



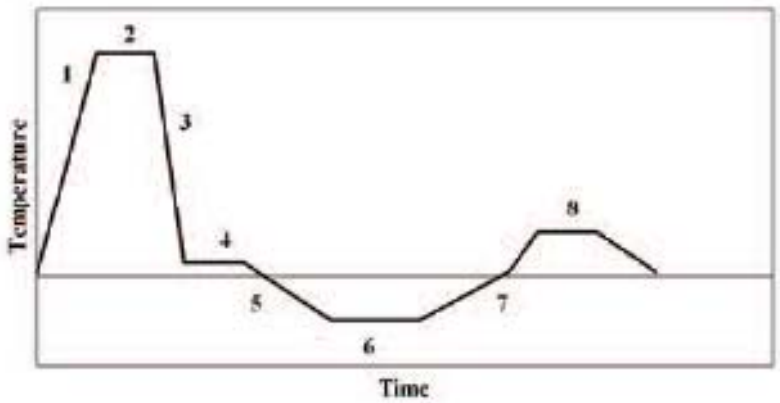
Slika 2: Formiranje η-karbida iz martenzita [4]

Nanometarski η-karbidi izlučuju se između i unutar martenzitnih iglica. Moguće ih je vidjeti samo pri povećanjima većim od 20000x. Pokazalo se, međutim i da dolazi samo do raspadanja primarnog martenzita, a ne i martenzita dobivenog pretvorbom u prvom stadiju dubokog hlađenja, a koji ima veći stupanj tetragonalnosti c/a [5]. Time je moguće donekle objasniti nedosljednost rezultata različitih ispitivanja. Ukoliko je u čeliku visoki udio zaostalog austenita pretvorbe u prvom stadiju znatno povisuju tvrdoću čelika, no ne nužno i njegovu otpornost na trošenje u usporedbi s početnim stanjem. Ukoliko čelik ima malo zaostalog austenita tada uslijed formiranja karbida u drugom stadiju dolazi do znatnog povećanja otpornosti na trošenje bez značajnog povećanja tvrdoće [7].

Pokazalo se i vrlo bitnim da se hlađenje i ponovno zagrijavanje izvodi vrlo sporo radi izbjegavanja pojave pukotina uslijed kontrakcije/ekspanzije materijala te uslijed 4% promjene volumena pri transformaciji zaostalog austenita u martenzit, ali ne utječe značajno na formiranje η-karbida. Preporuke su da bi trajanje dubokog hlađenja trebalo biti minimalno 24h iako su se i višestruka hlađenja pokazala pozitivna.

3. PREPORUČENI PARAMETRI POSTUPKA

Nije moguće dati preporuku parametara postupaka za svaki pojedini čelik jer se pokazalo da jednaki parametri ne daju jednake rezultate čak niti kod različitih alata izrađenih od istog alatnog čelika. Za svaki alat je potrebno prilagoditi postupak ovisno o željenoj kombinaciji tvrdoće, žilavosti i otpornosti na trošenje. Iz različitih ispitivanja moguće je dati neke opće smjernice za postupak toplinske obrade koji uključuje i duboko hlađenje u cilju povećanja otpornosti na trošenje alata. Slika 3 shematski prikazuje preporučeni tehnološki postupak toplinske obrade alatnih čelika koja uključuje i duboko hlađenje.



Slika 3: Shematski prikaz preporučenog postupka toplinske obrade s dubokim hlađenjem [5]

Faze tehnološkog postupka prema slici 3 su slijedeće:

1. Ugrijavanje na temperaturu austenitizacije s koje će se dobiti najmanje austenita [5]
2. Držanje na temperaturi austenitizacije preporučeno vrijeme za pojedini alatni čelik
3. Gašenje nadkritičnom brzinom, a s ciljem postizanja potpuno martenzitne strukture
4. Držanje na 60°C maksimalno 1h za ujednačavanje mikrostrukture [4] i odmah se prelazi na fazu br. 5
5. Ohlađivanje na temperaturu tekućeg dušika (-196°C) dovoljno sporo, preporuka je da bi ohlađivanje i ugrijavanje trebalo provesti konstantnim brzinama od otprilike 0,5°C/min radi izbjegavanja stvaranja toplinskih mikro pukotina. Radi izbjegavanja kondenzacije ohlađivanje bi trebalo provesti u atmosferi dušika [11]
6. Držanje u tekućem dušiku minimalno 24h. Das i sur. [11], Molinari i sur. [9] iznose da držanje u tekućem dušiku oko 35h daje optimalnu kombinaciju željene mikrostrukture i otpornosti na trošenje te dulje držanje na niskim temperaturama ne utječe značajnije na svojstva [9,11].
7. Ugrijavanje na sobnu temperaturu ponovo dovoljno sporo radi izbjegavanja stvaranja pukotina, te u atmosferi dušika s ciljem izbjegavanja kondenzacije.
8. Popuštanje na temperaturama predviđenim za određeni čelik. Iako se dubokim hlađenjem smanjuje krhkost i unutarnja naprezanja u materijalu radi vrlo sporog mehanizma pretvorbe na niskim temperaturama, nisko temperaturnim popuštanjem na 150-200°C se uklanja eventualna krhkost u materijalu zaostala nakon dubokog hlađenja.

4. UTJECAJ DUBOKOG HLAĐENJA NA TRIBOLOŠKA SVOJSTVA BRZOREZNIH ČELIKA

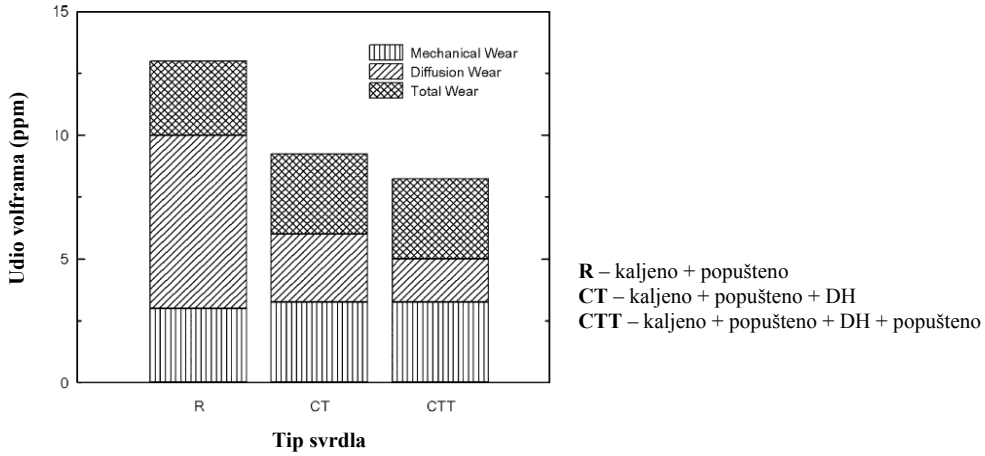
Različiti literaturni izvori navode čitav niz ispitivanja na različitim alatnim čelicima iz kojih je vidljivo da otpornost na trošenje ovisi o vrsti čelika, o temperaturama austenitizacije, o fazi toplinskog postupka u kojoj će se primijeniti duboko hlađenje tj. da li će biti prije ili nakon popuštanja, koliko faza popuštanja će prethoditi ili slijediti, te o samom trajanju dubokog hlađenja. Molinari i sur [9], pokazali su da duboko hlađenje povisuje i tvrdoću i otpornost na trošenje AISI M2 brzoreznog čelika. Utjecaj dubokog hlađenja je najveći kada se provodi nakon kaljenja i popuštanja [9].

Tablica IV: Utjecaj toplinske obrade na trošenje i tvrdoću brzoreznog čelika M2 [9]

Provedene toplinske obrade	Intenzitet trošenja (g/mx10^{-6})	Tvrdoća HV 30
K + P + P	3,7	826
K + P + P + DH	1,8	894
K + DH + P	2,2	888
K + DH + P + P	2,4	874

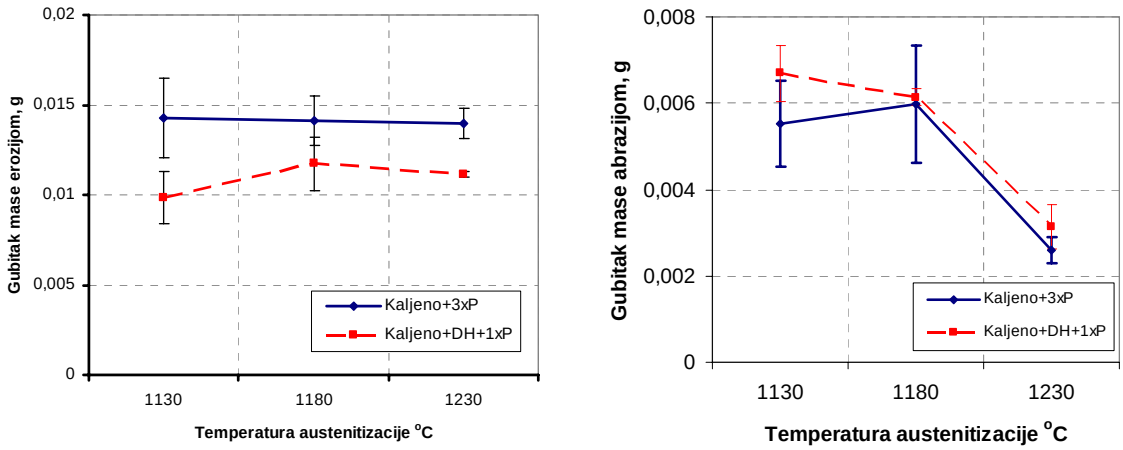
K- kaljeno, P – popušteno, DH – duboko hlađeno

Firouzdor i sur. [10]. kod ispitivanja utjecaja dubokog hlađenja na vijek trajanja svrdla od brzoreznog čelika M2 također su dobili povećanje tvrdoće primjenom dubokog hlađenja kao i povećanje vijeka trajanja svrdla, i to za otprilike 77% kod duboko hlađenih nakon kaljenja i 126% kod kaljenih, duboko hlađenih i popuštenih svrdala. Također su ispitivali i difuzijsko trošenje alata što je prikazano na slici 4., a koje je pokazalo da difuzijsko trošenje odgovara mjerenjima otpornosti na trošenje i trajanju alata, tj. minimalno je kod kaljenih, duboko hlađenih i popuštenih svrdla.



Slika 4: Utjecaj dubokog hlađenja na difuzijsko i mehaničko trošenje svrdla od brzoreznog čelika M2 mjereno preko povećanja udjela volframa u odvojenoj čestici

Istraživanja utjecaja dubokog hlađenja na brzoreznom čeliku PM S390MC provedena na FSB-u (12, 13) dala su slijedeće rezultate, slika 5. U usporedbi s klasičnom toplinskom obradom, primjenom dubokog hlađenja nije došlo do povećanja tvrdoće, ali je povećana otpornost na erozijsko trošenje. Primjena dubokog hlađenja nije utjecala na abrazijsko trošenje niti na lomnu žilavost ali je temperatura austenitizacije imala značajan utjecaj.



Slika 5: Gubitak mase pri abrazijskom i erozijskom trošenju uzoraka od PM S390MC brzoreznog čelika [12, 13]

5. ZAKLJUČAK

Primjenom pothlađivanja (hlađenja do temperatura oko -80 ^{o}C) postiže se završetak pretvorbe pothlađenog austenita u martenzit kod nelegiranih i niskolegiranih čelika. Za visoko legirane čelike temperature završetka martenzitne pretvorbe niže su od 100°C, pa je kod njih preporučljiva primjena dubokog hlađenja (na temperaturama do -196°C) u trajanju od 24 do 35 sati.

Dubokim hlađenjem kaljenog alatnog čelika i naknadnim (jednostrukim) popuštanjem dodatno se povećava otpornost na trošenje u odnosu na samo kaljeno i popušteno stanje. Dubokom hlađenjem osim eliminacije zaostalog austenita dolazi do nastanka klica i izlučivanja nanometarski sitnih eta-karbida u čitavom volumenu alata. Stoga se kod kaljenog i duboko hlađenog alata podjednaka svojstva postižu i nakon ponovnog brušenja istrošenih površina (oštrica) alata.

Primjena dubokog hlađenja pokazala je značajne efekte povišenja otpornosti na trošenje i postizanja dimenzijske stabilnosti kod alata od brzoreznih čelika. Stoga će se daljnja istraživanja efekata i utjecaja dubokog hlađenja na svojstava čelika i otpornost na trošenje reznih alata spomenuta u radu [13] usmjeriti na suvremene brzorezne čelike proizvedene metalurgijom praha, poput čelika PM S390 MC.

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PLASTOMERNE FOLIJE OD OMEKŠANOG POLI(VINIL-KLORIDA) – TEHNIČKE KARAKTERISTIKE I ISKUSTVA U IZVEDBI HIDROIZOLACIJA U TUNELOGRADNJI

THERMOPLASTIC PVC-P-NB FILMS – TECHNICAL CHARACTERISTICS AND EXPERIENCES IN TUNNEL HYDRO INSULATION

Prethodno priopćenje / Preliminary note

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Sažetak: U radu su analizirana fizičko-mehanička svojstva omekšanog PVC-a, te su iznesena iskustva u primjeni folija od istog materijala pri hidroizolaciji cestovnih tunela. Neka svojstva novih materijala uspoređena su sa svojstvima uzoraka izvađenih iz konstrukcije nakon trogodišnje eksploatacije. Pokazalo se da folije i dalje zadovoljavaju sve propisane uvjete, ali da su pod djelovanjem naprezanja pri eksploataciji lokalno plastično deformirane što je dovelo do porasta anizotropnosti materijala.

Ključne riječi: omekšani PVC, hidroizolacija, mehanička svojstva

Abstract: Physical-mechanical properties of plasticised PVC films are analysed and the experiences in application for tunnel hydro insulation are presented. Some of the properties are compared to those of films after 3 years of usage. After the exposure to the environmental conditions all the properties are in agreement with acquired conditions , but an increase in anisotropy as a consequence of plastic deformation is noticed.

Key words: plasticised PVC, hydro insulation, mechanical properties

1. Uvod

1.1. O hidroizolaciji u cestogradnji općenito

Primjena hidroizolacije u cestogradnji uglavnom se veže uz tunele, mostove i vijadukte, podvožnjake i pothodnike. Uloga hidroizolacije kod ovih objekata uglavnom je usmjerena na zaštitu armiranobetonskih konstrukcija od negativnog djelovanja vode/vlage, a posebno od vlage/vode obogaćene kloridima iz različitih sredstava kojima se tijekom zimskih mjeseci tretiraju prometnice (npr. soli protiv poledice). Kod cestovnih tunela njihova je uloga višestruka i to u prvom redu sprečavanje prodiranja odnosno procjeđivanja vode u unutrašnjost tunela iz okolne stijenske mase, potom zaštita armiranobetonskih konstrukcija od negativnog djelovanja vode/vlage, ali i sprečavanje miješanja čiste vode iz okoliša s onečišćenom vodom s prometnih površina.

1.2. Hidroizolacija u izgradnji cestovnih tunela

Plastomerne folije od omekšanog poli(vinil-klorida) nekompatibilnog s bitumenom, PVC-p-NB, masovno se primjenjuju pri hidroizolaciji cestovnih tunela (u građevini se ovaj materijal često naziva termoplastične sintetičke PVC folije). Razlog tome jest prilično jednostavna instalacija, jednostavno izvođenje spojeva susjednih traka i mogućnost kontroliranja kvalitete izvođenja spojeva, mogućnost izvođenja narednih faza radova odmah po instalaciji i spajanju folija (ne zahtijeva vrijeme otvrdnjavanja ili sušenja) i zadovoljavajuća dinamika izvođenja radova. Materijal je otporan i na mehanička oštećenja do kojih može doći prilikom transporta, deponiranja i čestog premještanja rola materijala zbog ograničenog manipulativnog prostora u tunelu.

Ovisno o vrsti stijenske mase u kojoj se vrši tunelski iskop postoji nekoliko različitih tipova podgradnih sklopova koji se primjenjuju pri iskopu tunela. Kao podložni sloj za izvođenje hidroizolacije na izvedenu podgradu nanosi se sloj od mlaznog betona (slika 1). Obzirom na postupak nanošenja i morfologiju drobljenih kamenih frakcija (0-8mm) od kojih se pripravlja, površina mlaznog betona je grube teksture, pa se na tako pripremljenu podlogu postavlja zaštitni sloj od netkanog geotekstila (slika 2). Zahtjevi za zaštitni sloj od netkanog geotekstila u tunelogradnji propisani u [1] prikazani su u tablici 1.

Slika 1. Podloga od mlaznog betona.

Slika 2. Čepovi od PVC-a na geotekstilu su osnova za pričvršćivanje PVC-p-NB folija.

Tablica 1. Svojstva materijala podloge od netkanog geotekstila

Ispitno svojstvo		**Mjerna jedinica**	**Opći tehnički uvjeti za radove na cestama, Knjiga V, IGH - Zagreb, 2001**	**Metoda ispitivanja**
Debljina		mm	/	HRN EN 964-1:2001
Masa po jedinici površine		g/m²	≥500 (-10%)	HRN EN 965:2001
Sila proboja		N	≥2500	HRN EN ISO 12236:2001
Prekidna čvrstoća:	uzdužno	MPa	≥15	HRN EN ISO 10319:2001
	poprečno		≥15	
Istezanje:	uzdužno	MPa	≥70	HRN EN ISO 10319:2001
	poprečno		≥70	

Netkani geotekstil ima zadatak spriječiti mogućnost mehaničkog oštećenja folije od PVC-p-NB-a na sučelju s grubom površinom mlaznog betona. Uzdužne, poprečne i dijagonalne deformacije trebaju osigurati kontinuitet podložnog sloja u uvjetima vlačnih naprezanja u materijalu do kojih može doći od pritiska betona obloge na grubu i neravnu površinu mlaznog betona. Osobito su važna hidraulička (drenažna) svojstva, koja trebaju osigurati gravitacijsko otjecanje vode kroz geotekstil. Kapacitet otjecanja vode u ravnini (transmisivnost) pri normalnom tlaku od 0,2 MPa i hidrauličkom gradijentu i=1, mora biti veći od 1×10^{-6} m^2/s (HRN EN ISO 12958), iako i sama površinska tekstura mlaznog betona može imati dobra drenažna svojstva (šupljikava površina). Geotekstil mora biti kemijski stabilan u području ph-vrijednosti između 2 i 13.

Plastomerna PVC folija ugrađuje se na zaštitni sloj od netkanog geotekstila zavarivanjem na prethodno pričvršćene čepove od PVC-a (slika 2). Susjedne PVC-p-NB folije nepropusno se zavaruju samohodnim strojem za kontinuirano zavarivanje (slika 3), a kvaliteta spojeva

kontrolira se komprimiranim zrakom do 2,5 bara u crijevu između dva vara. Spoj se smatra kvalitetno izvedenim ukoliko tlak u roku od 10 min ne padne ispod 2,0 bara.

Slika 3. Zavarivanje PVC-p-NB folija u tunelu.

Slika 4. Kontrola spoja dviju folija komprimiranim zrakom.

2. Plastomerne PVC-p-NB folije - rezultati

Tijekom izgradnje važnih prometnih pravaca hrvatskih autocesta na dionicama Rijeka – Zagreb i Zagreb – Split u proteklih nekoliko godina, u sklopu nadzora nad izvođenjem radova, odnosno kontrole kvalitete primijenjenih materijala i izvedenih radova na hidroizolacijama cestovnih tunela, proveden je niz laboratorijskih ispitivanja PVC folija. U radu su predstavljeni rezultati 11 uzoraka analizirana u posljednjih 6 godina. Nadalje, opisana je kontrola ugradnje i spojeva i izloženi su iskustvo i problemi koji su se pojavljivali tijekom izvođenja radova.

2.1. Zahtjevi i rezultati ispitivanja prije ugradnje

Primarna funkcija ovih folija je vodonepropusnost, i to u uvjetima bez dodatnih opterećenja kao i u uvjetima naprezanja i deformacija kojima su podvrgnute pri instalaciji, tijekom ugradnje narednih slojeva (betonske obloge) i tijekom vremena eksploatacije (vanjski utjecaji). Folija mora biti otporna na starenje, skupljanje, djelovanje kiselina i lužina iz tla, soli otopljenih u vodi i kemijskim reakcijama u kontaktu s drugim materijalima u području ph-vrijednosti između 2 i 13.

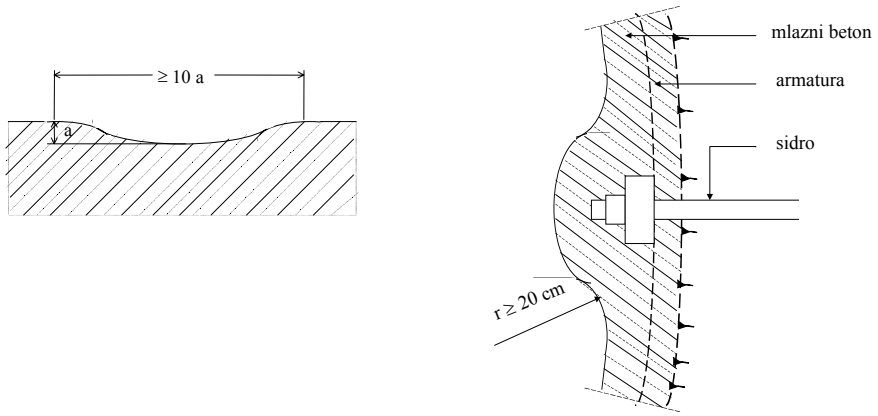
U tablici 2 načinjena je usporedba fizičko-mehaničkih svojstava propisanih u [1] s rezultatima određenim eksperimentalno.

Tablica 2. Fizičko mehanička svojstva plastomerne PVC folije.

Ispitno svojstvo	**Mjerna jedinica**	**Opći tehnički uvjeti za radove na cestama [1]**	**Metoda ispitivanja**	**Srednja vrijednost izmjerenih rezultata**	**Standardna devijacija**
Vizualna ocjena		ne stvaraju se mjehuri		ne stvaraju se mjehuri	
Debljina: - srednja vrijednost	mm	1,9 - 2,2	HRN EN 1849-2	1,94	0,03
- najmanja pojedinačna vrijednost		1,7		1,92	0,03
Prekidna čvrstoća (rastezna): - uzdužno	MPa	≥10	DIN EN ISO 527-3	17,07	0,69
- poprečno		≥10		15,29	0,59
Istezanje: - uzdužno		≥200	DIN EN ISO 527-3	524,61	39,07
- poprečno		≥200		514,64	33,96
Ponašanje pri savijanju na – 20°C		nema pukotina	DIN 16267	nema pukotina	
Ponašanje pod tlakom vode; 5,0 bara 72 sata		nepropusna	DIN 16267	nepropusna	
Promjena dimenzija kod 80°C/6h	%				
- u uzdužnom smjeru		≤ 3%	DIN 16267	-1,74	0,67
- u poprečnom smjeru		≤ 3%		0,41	0,25
Promjena svojstava nakon stajanja pri 80°C/7 dana					
Promjena prekidne čvrstoće: - uzdužno	%	± 20	DIN 16267	-1,93	1,14
- poprečno		± 20	DIN EN ISO 527-3	0,02	1,90
Promjena istezanja: - uzdužno	% (rel)	± 20	DIN 16267	1,58	2,62
- poprečno		± 20	DIN EN ISO 527-4	-0,25	3,56
Ponašanje pri savijanju pri 20°C		nema pukotina	DIN 16267	nema pukotina	
Promjena svojstava nakon stajanja 28 dana u zasićenoj otopini vapnenog mlijeka					
Promjena prekidne čvrstoće: - uzdužno	%	± 20	DIN 16267	-1,27	2,44
- poprečno		± 20	DIN EN ISO 527-3	-1,03	1,68
Promjena istezanja: - uzdužno	% (rel)	± 20	DIN 16267	0,24	4,96
- poprečno		± 20	DIN EN ISO 527-4	1,10	5,32
Ponašanje pri savijanju na - 20°C		nema pukotina	DIN 16267	nema pukotina	

Iz tablice 2 vidljivo je da sva svojstva folija zadovoljavaju propisane uvjete. Bolja mehanička svojstva u uzdužnom smjeru posljedica su proizvodnog postupka folija ekstrudiranjem, tj jednoosnim izvlačenjem, uslijed čega dolazi do lagane anizotropije. Upadljivo je, međutim, koliko je uzdužno i poprečno istezanje određeno eksperimentalno (oko 500 %) veće od propisanog (>200 %). Ovo izvanredno svojstvo omogućuje da folija i u potencijalno lošim uvjetima i dalje zadrži svoju primarnu funkciju.

Naime, čest problem u praksi je neravnost podloge od mlaznog betona (Slika 1). Dopuštena neravnost prikazana je na slici 5.



Slika 5. Uvjet za ravnost, odnosno dopuštena neravnost površine za izvođenje hidroizolacije [1].

Pokazalo se da nije uvijek jednostavno postići traženu ravnost podloge prvenstveno zbog geološkog sastava stijenske mase u kojoj se vrši iskop. Često je jednostavnije i brže rješenje pažljivije postavljati slojeve hidroizolacijskih materijala dobrih mehaničkih svojstava, nego dodatno uređivati podlogu od mlaznog betona. U izvanrednim okolnostima na nekim manjim površinama tehnološki je vrlo zahtjevno strojno nanositi mlazni beton, u svrhu uređenja podloge za hidroizolaciju. Rješenje se traži u pripremi grube stijenske mase otucavanjem oštrih rubova i dodatnom ojačanju (višeslojnom polaganju) zaštitnog sloja od netkanog geotekstila. U ovim slučajevima veliku ulogu u kvalitetnom obnašanju hidroizolacijskih svojstava PVC-p-NB folija ima njezina velika deformabilnost prije negoli dođe do pukotina u materijalu. Naime, nakon izvedbe hidroizolacijskih slojeva namješta se tunelska oplata i u prostor između oplate i hidroizolacije ugrađuje se svježi beton. Svježi beton pri ugradnji tlačno djeluje na slojeve hidroizolacije uslijed čega se istezljiva PVC-p-NB folija prilagođava neravnoj podlozi od mlaznog betona.

Uz zahtjeve propisane [1] određen je i restezni modul elastičnosti pri uzdužnom i poprečnom opterećenju, i iznosi 23,8 MPa uz standardnu devijaciju 2,2 MPa, odnosno 20,6 MPa uz standardnu devijaciju 1,3 MPa.

2.3. Rezultati laboratorijskih ispitivanja nekih svojstava PVC-p-NB folije na uzorcima izvađenim iz mjesta ugradnje

Prilikom zahvata u kojem su cijevi tunela povezane dodatnim prolazima za vozila i pješake, uzorkovane su folije koje su bile izložene realnim uvjetima u tunelu 3 godine.
Vizualnim pregledom (slika 6) instalirane hidroizolacije ustanovljeno je da je folija tijekom izvođenja radova na betoniranju sekundarne betonske obloge izvrgnuta znatnom opterećenju

od pritiska betona, te da se u skladu s tim, a imajući u vidu karakteristike podloge, znatno deformira. No usprkos tome, zahvaljujući iznimno velikoj istezljivosti, zadržala je kontinuitet (nije došlo do pucanja, odnosno probijanja) i time osigurala svoju osnovnu ulogu – vodonepropusnost.

Slika 6. Uzorak folije s mjesta ugradnje

S obzirom na ograničen pristup uzorcima uz vodonepropusnost su analizirana samo osnovna mehanička svojstva (tablica 3)

Tablica 3. Rezultati ispitivanja folija prije ugradnje i nakon uzorkovanja s mjesta ugradnje.

Svojstvo	Mjerna jedinica	Prije ugradnje	Poslije 3 godine eksploatacije
Prekidna čvrstoća: - uzdužno	MPa	17,1	19,6
- poprečno	MPa	15,3	15,9
Rastezni modul elastičnosti: - uzdužno	MPa	23,8	41,9
- poprečno	MPa	20,6	29,8
Istezanje: - uzdužno	%	524,6	228,4
- poprečno	%	514,6	263,8
Debljina	mm	1,94	1,91

Folija je više godina bila u uvjetima višeosnog naprezanja, izložena promjenjivim vremenskim uvjetima, ali i dalje ispunjavaju uvjete iz [1]. Pri tome je u tunelu bila zaštićena od UV zračenja. Mehanička svojstva su se u eksploataciji poboljšala, s iznimkom istezljivosti, kao posljedica toga što su folije u konstrukciji uslijed djelovanja gravitacije opterećenije u uzdužnom, nego u poprečnom smjeru (folija se ugrađuje na način da uzdužni smjer slijedi opseg cijevi tunela). Rezultat je veća uzdužna plastična deformacija. Iz tablice 3 vidi se da je anizotropija u korist uzdužnog smjera znatno izraženija nakon višegodišnjeg izlaganja naprezanjima, nego samo uslijed postupka prerade. Na molekularnoj razini pri djelovanju naprezanja pojavljuje se poželjniji smjer orijentiranja makromolekula i to paralelno sa smjerom većeg naprezanja (uzdužnog) što dovodi do pojačane anizotropije u materijalu. Dok se ovaj efekt obično postiže istezanjem pri povišenoj temperaturi, isto se dogodilo zahvaljujući izraženim viskoelastičnim svojstvima polimernih materijala pri temperaturi okoliša na dugoj vremenskoj skali, odnosno trogodišnjem naprezanju u materijalu.

Budući da se radi o omekšanom PVC-u, koji je u vrijeme eksploatacije bio zaštićen od UV zračenja, efekt koji utječe na smanjenu istezljivost je gubitak plastifikatora starenjem, odnosno difuzijom iz materijala. Materijal postaje krući, a istezljivost postaje značajno manja.

Ovaj je proces dodatno induciran smanjenim udjelom slobodnog volumena u polimernoj bazi kojeg zauzima plastifikator, te je on mehanički prisiljen difundirati iz materijala.

Debljina materijala i dalje je u dopuštenom intervalu, no radi se o prosječnim vrijednostima. Lokalno najmanja izmjerena debljina iznosi je 1,58 mm, što ukazuje na lokalnu veliku plastičnu deformaciju s vremenom. Najveće naprezanje očekuje se u trenutku ugradnje svježeg betona, dok je on još žitka masa i ponaša se kao kapljevina, usprkos zaostalim naprezanjima u materijalu, pretpostavlja se da se folije s vremenom neće stanjivati, odnosno da nema opasnosti od loma.

3. Zaključak

Podloge od mlaznih betona na koje se ugrađuju slojevi hidroizolacijske folije od PVC-p-NB-a kod izvođenja cestovnih tunela, a pogotovo njihove devijacije u smislu ravnosti u odnosu na propisane zahtjeve, u praksi često dovode u pitanje prilagodljivost primijenjene folije površini, odnosno preuzimanje naprezanja i deformacije uzrokovane neravnošću površine bez da dođe do njihova oštećenja, odnosno pucanja, a time i gubitka njihove temeljne funkcije – vodonepropusnosti.

Pokazalo se da se pažljivom ugradnjom ovih materijala može očekivati da će njihova izuzetna mehanička svojstva, premostiti lokalne, pa i veće neravnosti podloge bez štetnih posljedica. Treba imati na umu da su ovdje prezentirani rezultati ograničenog broja uzoraka, te da bi trebalo obraditi puno veći broj pogotovo „in situ“ uzorkovanih materijala, kako bi se mogli dati konačni zaključci.

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ANALIZA OŠTEĆENJA VODEĆIH KLIZNIH LEŽAJA VODNE TURBINE AGREGATA B SNAGE 1100 kW HE OZALJ 1

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Izvorni znanstveni rad / Original scientific paper

Sažetak: Hidroelektrana (HE) Ozalj 1 sastoji se od tri agregata A, B i C s Francisovim vodnim turbinama. Na vodnoj turbini agregata B snage 1100 kW izvršena je zbog povećanog trošenja rukavca rekonstrukcija gumene klizne blazinice turbinskog ležaja podmazivanog vodom. Rekonstrukcija se sastojala u zamjeni gumene klizne blazinice ležaja s blazinicom od materijala novilon oilon. Klizne blazinice od novilon oilona podmazivane vodom pokazale su se u radu povoljnije od gumenih blazinica glede na trošenje rukavca ležaja. U tijeku rada rekonstruiranog turbinskog ležaja došlo je do havarije klizne blazinice od novilon oilona. Klizna blazinica od novilon oilona bila je potpuno razorena. U ovom radu dan je prikaz i analiza oštećenja blazinice od novilon oilona kliznog ležaja vodne turbine agregata B u HE Ozalj 1. Istraživan je i analiziran mogući uzrok oštećenja blazinice kliznog ležaja. Dan je prijedlog sanacije oštećenog turbinskog kliznog ležaja.

Ključne riječi: vodna turbina, klizni ležaj, klizna blazinica od novilon oilon, oštećenje.

1. UVOD

HE Ozalj sastoji se od HE Ozalj 1 smještenoj na desnoj obali rijeke Kupe i HE Ozalj 2 smještenoj na lijevoj obali Kupe s Francisovim i Kaplanovim vodnim turbinama. U HE Ozalj 1 na agregatima A, B i C s Francisovim vodnim turbinama puštenim u pogon 1908. godine, bili su ugrađeni klizni vodeći ležajevi s blazinicama od bijele kovine podmazivani uljem. Na kliznim ležajevima nije bilo mogućnosti nadzora brtvenja i sakupljanja ulja u turbinskim ležajevima, tako da je ulje iz njih odlazilo u rijeku. Zbog propuštanja ulja iz ležajeva i rijeku Kupu iz ekoloških razloga rekonstrukcijom su u ležajeve ugrađene gumene blazinice podmazivane riječnom vodom.

U tijeku pogona s rekonstruiranim ležajevima došlo je do povećanog trošenja čeličnih rukavaca ležajeva, dok je trošenje gumenih blazinica bilo zanemarujuće, a očekivalo se da će biti obrnuto. Do povećanog trošenja rukavaca dolazilo je zbog toga što su se sitne čestice pijeska iz vode za podmazivanje zabijale u kliznu površinu gumene blazinice i abrazivno djelovale na površinu rukavaca [1]. Brzina abrazivnog trženja u obliku riseva na čeličnim rukavcima bila je neprihvatljiva za normalni pogon hidroelektrane. Najveća oštećenja rukavca bila su uočena na turbinskim ležajevima agregata B. Zbog toga su prvo na agregatu B rekonstrukcijom zamijenjene gumene blazinice s blazinicama od novilon oilona također podmazivane vodom. Blazinice od novilon oilona pokazale su se u eksploataciji veoma povoljne i nije više dolazilo do povećane brzine trošenje rukavaca. Međutim, nakon nekog vremena eksploatacije došlo je do oštećenja i loma kliznih blazinica od novilon oilona.

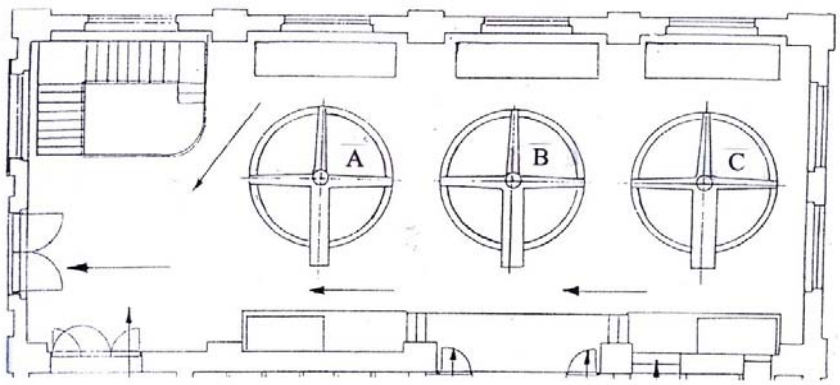
U ovom radu dani su osnovni tehnički podaci vodne turbine agregata B HE Ozalj 1. Dan je prikaz rekonstruiranih turbinskih ležaja s kliznim blazinicama od novilon oilona. Prikazano je i analizirano potpuno oštećenje kliznih blazinica od novilon oilona. Utvrđen je mogući uzrok oštećenja i dan je prijedlog za sprečavanje takovih oštećenja kliznih blazinica od novilon oilona na vodnim turbinama.

2. OSNOVNI TEHNIČKI PODACI VODNE TURBINE AGREGATA B I NJENIH VODEĆIH KLIZNIH LEŽAJA

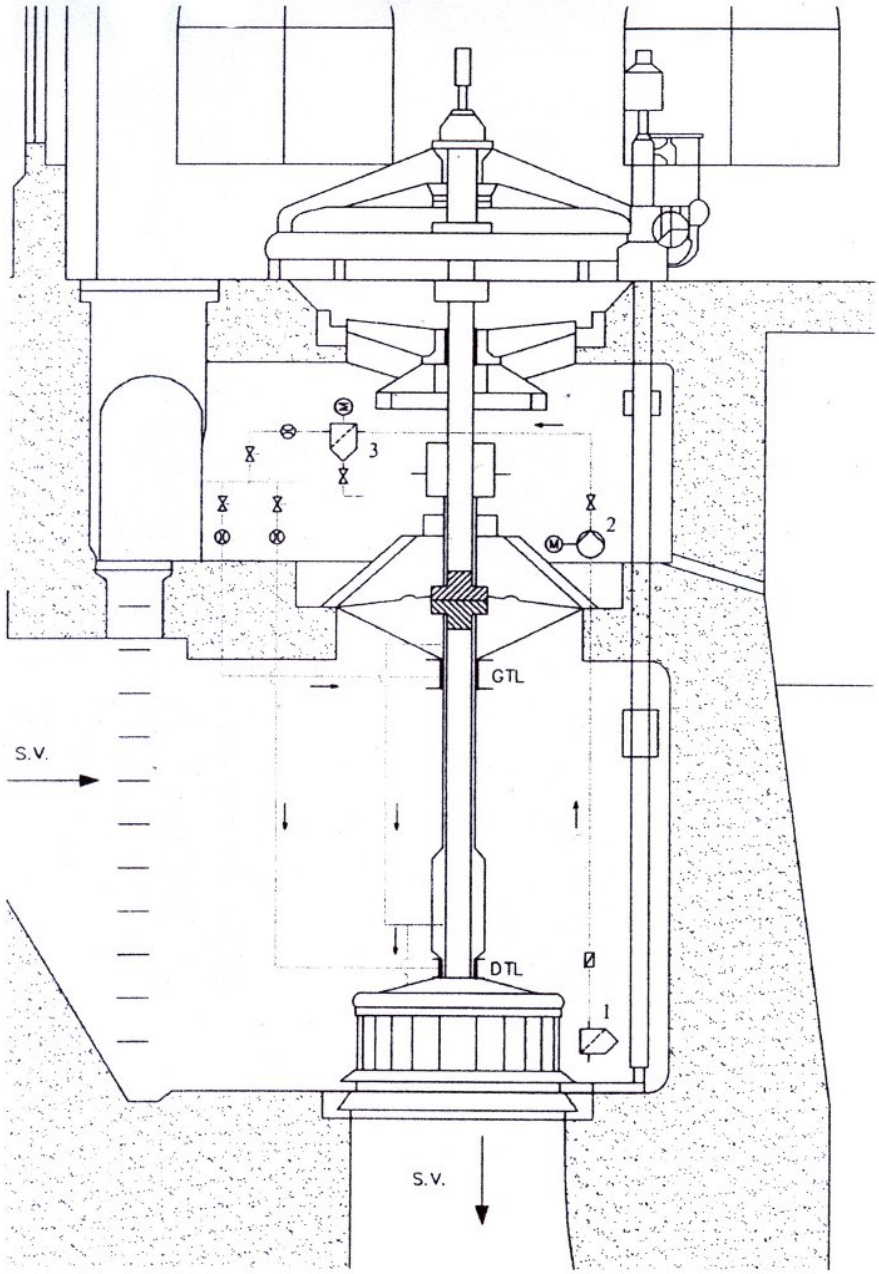
Francisova vodna turbina agregata B proizvodnje tvrtke VOITH iz Austrije puštena je u pogon 1908. godine. Nakon cca 450000 sati rada 1990. godine zamijenjen je agregat s novom Francisovom vodnom turbinom proizvodnje Litostroj Ljubljana i električnim generatorom proizvodnje Končar Zagreb. Osnovni tehnički podaci vodne turbine su [2]:

- nazivna snaga 1100 kW
- instalirani protok 17 m^3 /s
- neto pad 9,2 m
- brzina vrtnje 107 min^{-1}.

Na slici 1. prikazan je tlocrt strojarnice HE Ozalj 1. Iz dane slike je vidljiv razmještaj tri agregata A, B i C s Francisovim vodnim turbinama [3]. Prikaz agregata B sa shemom podmazivanja vodom gornjeg i donjeg turbinskog ležaja s rekonstruiranom blazinicom od novilon oilona dan je na slici 2. Iz dane slike je vidljivo da su vodna turbina i električni generator vertikalne izvedbe. Generator je smješten iznad turbine. Turbina i generator su spojeni krutom spojkom što ih čini jedinstvenim agregata. Generator je uležišten na jedan noseći aksijalni klizni ležaj i dva vodeća klizna ležaja. Noseći aksijalni ležaj nosi, tj. na njega su ovješeni generator i turbina. Ležajevi imaju klizne blazinice od bijele kovine i podmazivani su uljem. Turbina ima dva radijalna vodeća klizna ležaja, gornji i donji. Ti ležajevi su iz ekoloških razloga podmazivani vodom. Na gornjem i donjem vodećem ležaju turbine su rekonstrukcijom zamijenjene klizne blazinice od gume podmazivane vodom s kliznim blazinicama od novilon oilona, također podmazivane vodom.

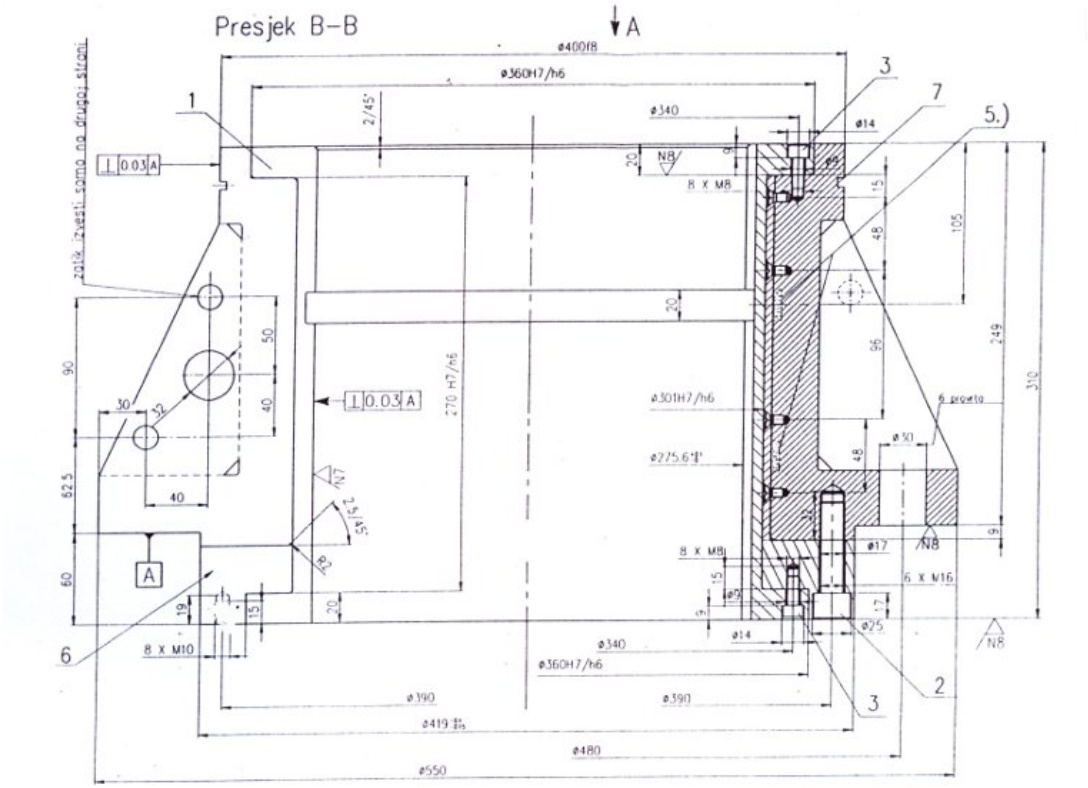


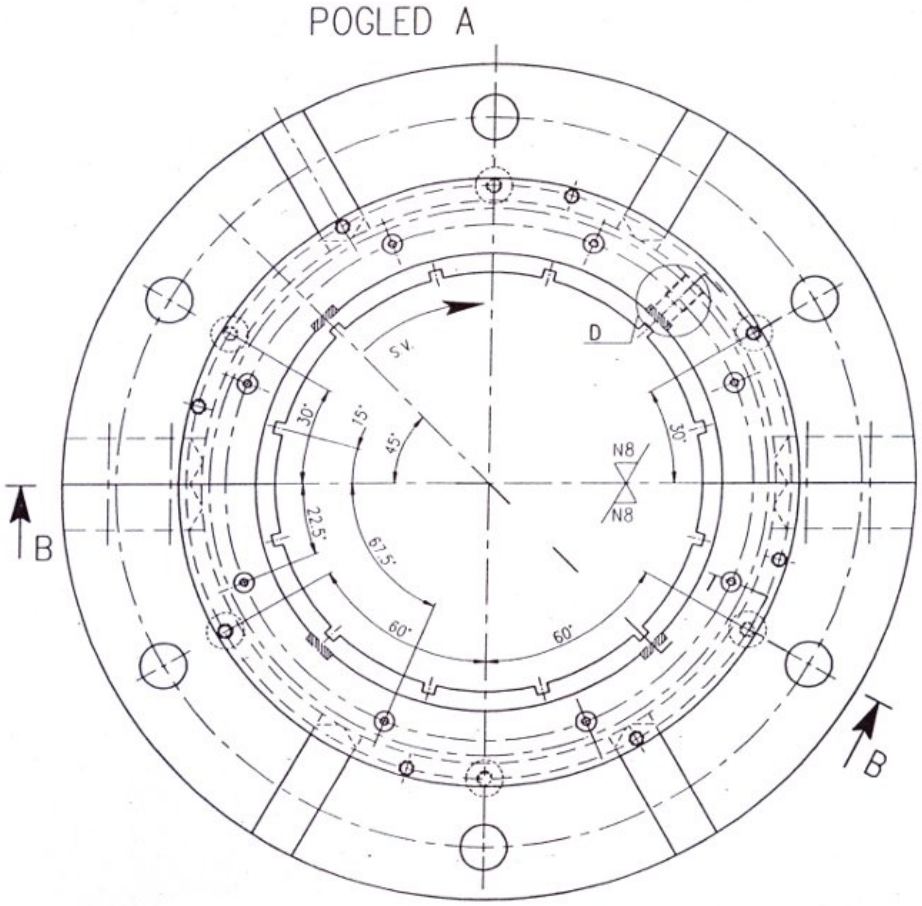
Sl. 1. Tlocrt strojarnice HE Ozalj 1: A, B, C - agregati s Francisovim vodnim turbinama



Sl. 2. Prikaz agregata B sa shemom podmazivanja vodom gornjeg i donjeg vodećeg ležaja turbine: 1-usisna košara, 2-pumpa za vodu, 3-filtar za vodu, GTL, DTL-gornji i donji ležaj

Na slici 3. dan je prikaz rekonstruiranog donjeg vodećeg turbinskog ležaja s blazinicom od novilon oilona. Promjer vodećeg kliznog ležaja je ϕ 275,6 mm, duljina 310mm.





Sl. 3. Nacrt turbinskog vodećeg ležaja s kliznom blazinicom od novilon oilona

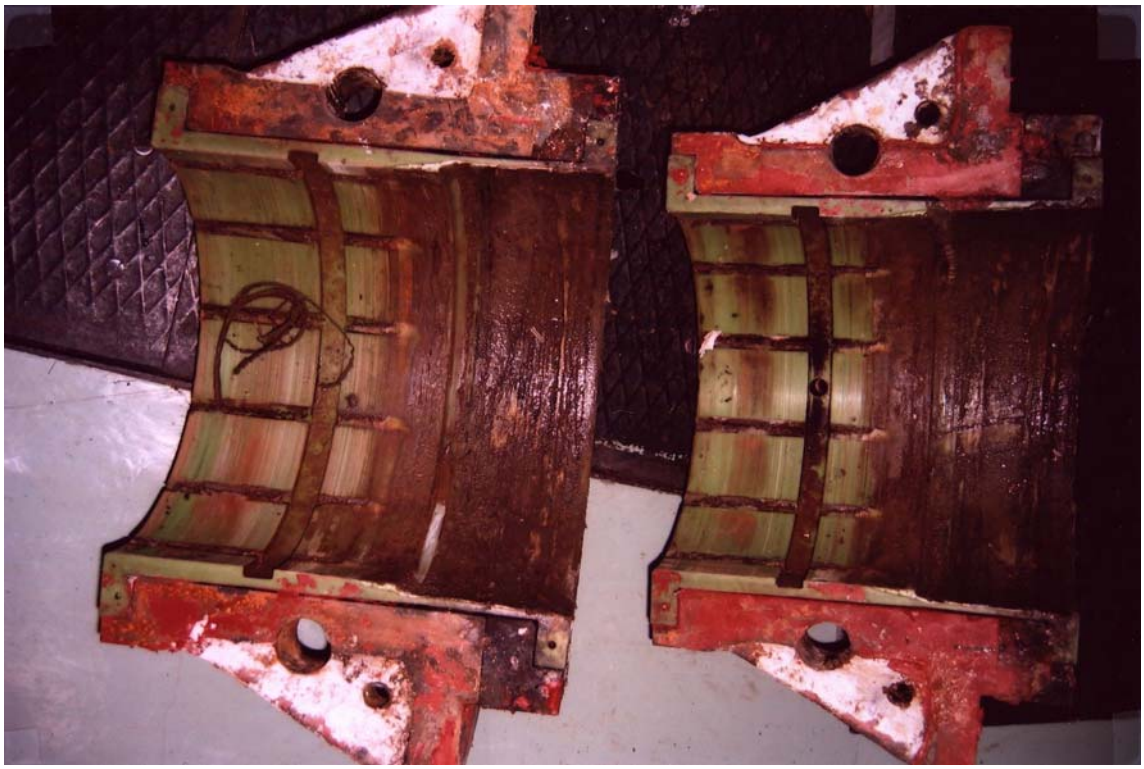
Debljina klizne blazinice od novilon oilona je 15 mm. Blazinica je za kućište ležaja pričvršćena vijcima M8x20. Zračnost između kliznog ležaja i rukavca iznosi 0,6 mm. Približno iste konstrukcije su gornji i donji vodeći klizni ležaj turbine.

Vodeći ležajevi turbine podmazivani su riječnom vodom koja se filtrira u automatskim filterima, finoće 80 do 100 mikrona. Voda za podmazivanje ležajeva uzima se ispred ulaza u turbinu i preko usisne košare u kojoj se vrši grubo filtriranje dovodi pomoću pumpe tlaka 6 bara u filtar i dalje u gornji i donji ležaj s kliznom blazinicom od novilon oilona. Za podmazivanje gornjeg i donjeg turbinskog vodećeg ležaja potrebno je 25 do 35 l/min vode.

Klizne blazinice od novilon oilona pokazale su se u eksploataciji bolje od gumenih blazinica, glede trošenja rukavca ležaja. Nakon jednogodišnje eksploatacije turbine od 6000 sati rada s blazinicama od novilon oilona podmazivanih vodom, pregledom i mjerenjem utvrđeno je zanemarivo trošenje blazinice u rukavca ležaja. Međutim, nakon nekog vremena daljnje eksploatacije turbine došlo je do havarijskog oštećenja blazinice na oba turbinska ležaja.

3. PRIKAZ I ANALIZA OŠTEĆENJA TURBINSKIH VODEĆIH KLIZNIH LEŽAJA

U tijeku revizije vodne turbine agregata B u 2008. godini utvrđeno je jako oštećenje kliznih blazinica od novilon oilona gornjeg i donjeg turbinskog vodećeg ležaja. Došlo je do loma po dubini blazinica. Jedan dio blazinice se otkinuo po dubini i rotirao zajedno sa rukavcem. Na slici 4. dan je prikaz oštećenja donjeg vodećeg ležaja vodne turbine. Iz dane



Sl.4.Prikaz oštećenja donjeg vodećeg kliznog ležaja vodne turbine

slike je vidljivo jako oštećenje klizne površine blazinice ležaja od novilon oilona. Došlo je do oštećenja i otkidanja blazinice po dubini. Dio blazinice se otkinuo po dubini i napravio čahuru koja je zalijepljena na rukavac rotirala zajedno s njim. Prikaz otkinute blazinice u obliku čahure koja se zalijepila za rukavac i rotirala zajedno s njim dan je na slici 5. Iz dane slike je vidljiv

otkinuti dio klizne blazinice od novilon oilona koja je rotirala zajedno s rukavcem ležaja.

Sl.5. Prikaz otkinutog dijela klizne blazinice od novilon oilona, koji je rotirao zalijepljen na rukavac ležaja

Vidljivo je, da je klizna blazinica turbinskog ležaja potpuno uništena. Približno tako je oštećena i klizna blazinica od gornjeg vodećeg turbinskog ležaja.

Za sanaciju oštećenog gornjeg i donjeg vodećeg turbinskog ležaja ugrađeni su pričuvni klizni ležajevi s novim kliznim blazinicama od gume. Pričuvni ležajevi s blazinicama od novilon oilona nisu postojali. Izrada novih kliznih blazinica od novilon oilona i njihova ugradnja bi dugo trajala. Zbog što bržeg puštanja turbine u pogon ugrađeni su postojeći pričuvni ležajevi s gumenim kliznim blazinicama. Promjer pričuvnih ležaja obrađen je na konačnu mjeru prema dimenziji rukavaca. Nakon ugradnje novih pričuvnih ležajeva vodna turbina je uspješno puštena u pogon.

Za utvrđivanje uzroka oštećenja kliznih blazinica od novilon oilona detaljno su pregledane oštećene blazinice. Izvršena je detaljna analiza oblika oštećenja kliznih blazinica. Na temelju pregleda i analize oštećenja kliznih blazinica može se pretpostaviti, da je do oštećenja blazinica došlo zbog njihovog zaribavanja i zaljepljivanja za rukavce. Nakon zaljepljivanja blazinica za rukavce došlo je do trganja kliznih blazinica po dubini. Zalijepljeni dio klizne blazinice se otkinuo od ostalog dijela blazinice i rotirao zajedno s rukavcem ležaja turbine.

Do zaribavanja i zaljepljivanja kliznih blazinica od novilon oilona za rukavac ležaja, može se pretpostaviti da je došlo zbog njihovog nabubrivanja i deformacije tijekom pogona i za takvo stanje premale zračnosti ležaja i rukavca. Zračnosti ležaja s blazinicama od novilon oilona uzete su iste kao i za ležajeve s gumenim blazinicama. Za ležajeve s blazinicama od novilon oliona trebalo bi primijeniti nešto veće zračnosti u odnosu na ležajeve s gumenim blazinicama.

Za sprečavanje ovakvih havarija kliznih blazinica od novilon oilona predlaže se njihovo kondicioniranje namakanjem neko vrijeme u vodi. Kondicioniranjem blazinica

smanjila bi se promjena njihovog oblika tijekom eksploatacije. Zatim se predlaže da se klizna blazinica pored pričvršćivanja vijcima i zalijepi na kućište ležaja. Zaljepljivanjem cijele površine blazinice za kućište ležaja smanjile bi se mogućnosti njene deformacije tijekom pogona. Također se predlaže da se nešto poveća zračnost ležaja i rukavca, koja bi mogla podnijeti eventualne male deformacije klizne blazinice.

4. ZAKLJUČAK

U tijeku revizije vodne turbine agregata B HE Ozalj 1 u 2008. godini uočeno je jako oštećenje kliznih blazinica njenih vodećih ležajeva. Na vodećim ležajevima turbine su rekonstrukcijom zamijenjene gumene klizne blazinice podmazivane vodom s blazinicama od novilon oilona također podmazivane vodom. Gumene klizne blazinice su rekonstrukcijom zamijenjene zbog jakog abrazivnog trošenja čeličnih rukavaca ležajeva s blazinicama od gume. Do abrazivnog trošenja rukavca ležaja je dolazilo zbog toga što su se sitne čestice pijeska iz vode za podmazivanje ležaja zabijale u gumene klizne površine i abrazivno djelovale na kliznu površinu rukavca.

Klizne blazinice od novilon oilona su se u eksploataciji pokazale dobre glede trošenja klizne površine rukavca ležaja. Međutim, nakon nekog vremena eksploatacije turbine došlo je do jakog oštećenja, loma, zaribavanja i zaljepljivanja za rukavce ležaja blazinica od novilon oilona. Zbog tog oštećenja morali su se ležajevi zamijeniti s novim blazinicama.

Pregledom i analizom oblika oštećenja kliznih blazinica može se pretpostaviti da je do oštećenja, loma i zaribavanja blazinica došlo zbog njihovog bubrenja i deformacije tijekom pogona, kao i za te uvjete premale zračnosti ležaja i rukavca, koja je uzeta ista kao i za gumene blazinice.

Za sprečavanje ovakvih havarija kliznih blazinica od novilon oilona predlaže se njihovo kondicioniranje, zaljepljivanje za površinu ležaja i povećanje zračnosti ležaja i rukavca.

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COMPARISON OF MECHANICAL BEHAVIOUR DURING INDENTATION OF SYSTEMS THIN FILM – SUBSTRATE FROM DIFFERENT TECHNOLOGY PROCESS

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Prethodno priopćenje / Preliminary note

Abstract

The paper is devoted to evaluation and comparison of properties and behaviour of systems thin films – basic materials. Thin films were prepared by different technology of deposition of thin films: reactive arc evaporation in vacuum, magnetron sputtering and PA CVD method. The basic material was HSS. Deposited thin films were TiN and TiAlN eventualy TiCN optimised for each technology process. There were analysed mechanical properties and behaviour by static indentation tests nad scratch indentation test. In the paper [1] were analysed basic properties and in this paper was advanced analysis for refinnement of analysis method. Scratch indentation was realised with indentor Rockwell with radius of tip 0.5 mm. Nanoindentation measurement is expanded by cyclic indentation tests for more information. Chemical composition and depth profile of chemical composition were analysed by GDOES

University of West Bohemia in Pilsen

Introduction

Different application of thin films need to select the optimised method for deposition on concrete products and based on real stress conditions in practice. Different technology process of deposition give different possibility for creation systems thin film – basic material for application on products. Optional properties and behaviour is possible prepare by optimalisation thin films, systems thin film – substrate, changing deposition parameters at all. Thin films give the highest effect if the technology is dirrected on concrete products. From this point of view is very difficult to find optional systems only based on standard analysis of basic mechanical and chemical properties. Analysis are dirrected on aproximation real conditions too [2].

Scratch indentation test

Scratch indentation was changed for changing stress from deformation process on namely friction by changing of type of indentor on Rockwell diamond indentor with radius of tip 0.5 mm. Measurement are provided on all systems thin film (TiN, TiAlN and TiCN) – HSS substrate. The measurement was realised in the mod increased acted normal force during measurement from 0 N to 80 N. The resulted morphology after scratch indentation is on fig. 1.

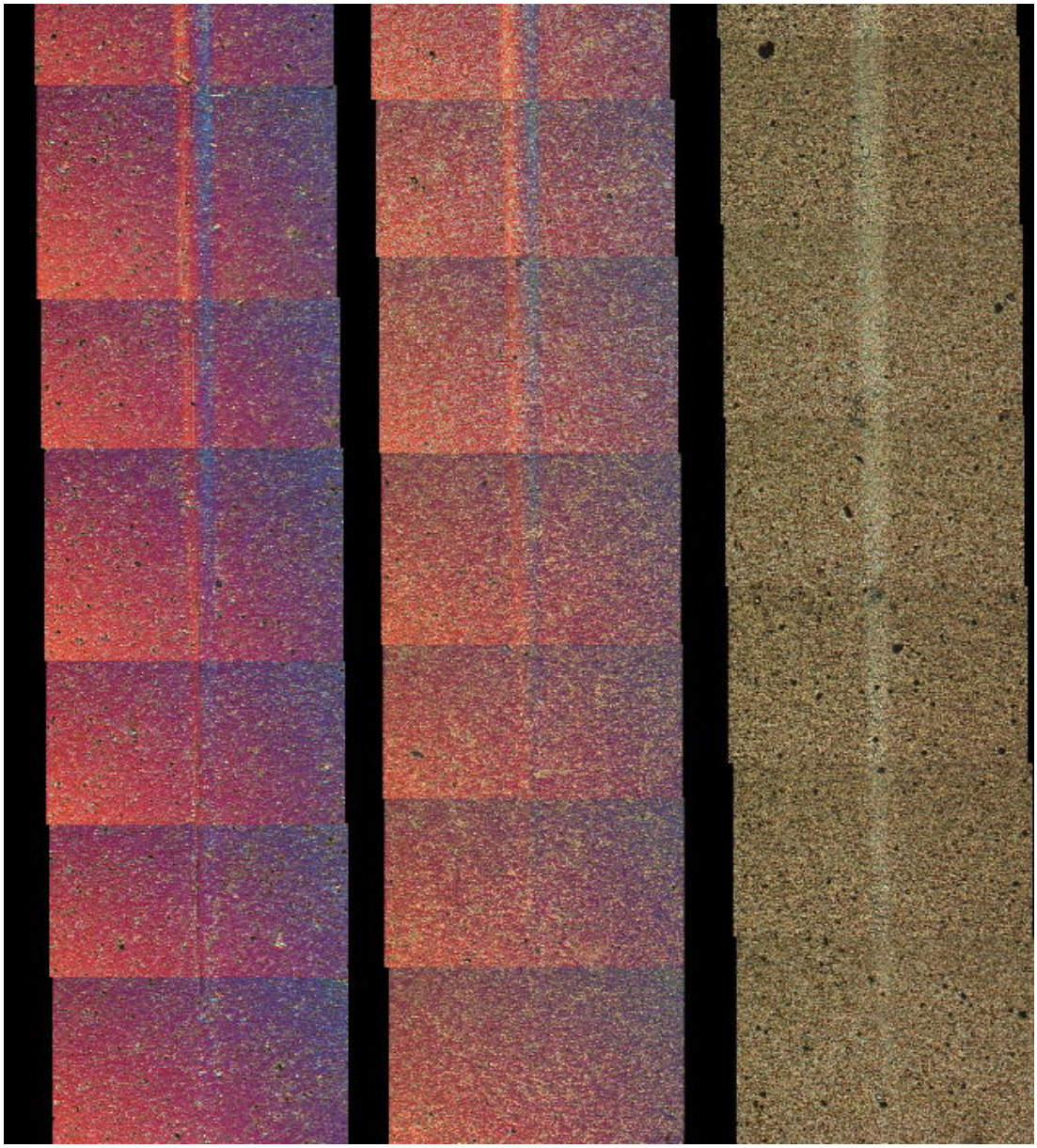

Fig. 1: Morphology of surface after scratch indentation of systém with TiN

Morphology of surface after scratch indentation is on fig. 1. Normal force is in the range 0 N to 40 N. Here are systems TiN-HSS (arc evaporation the first and the second and magnetron sputtering the third). Here are only small failures and small deformation by scratch indentation. The best systém is the second and the highest failures are on systém the third. The character of failures not changed with increasing of normal force in this range. The highest hardening of surface is on the third systém.

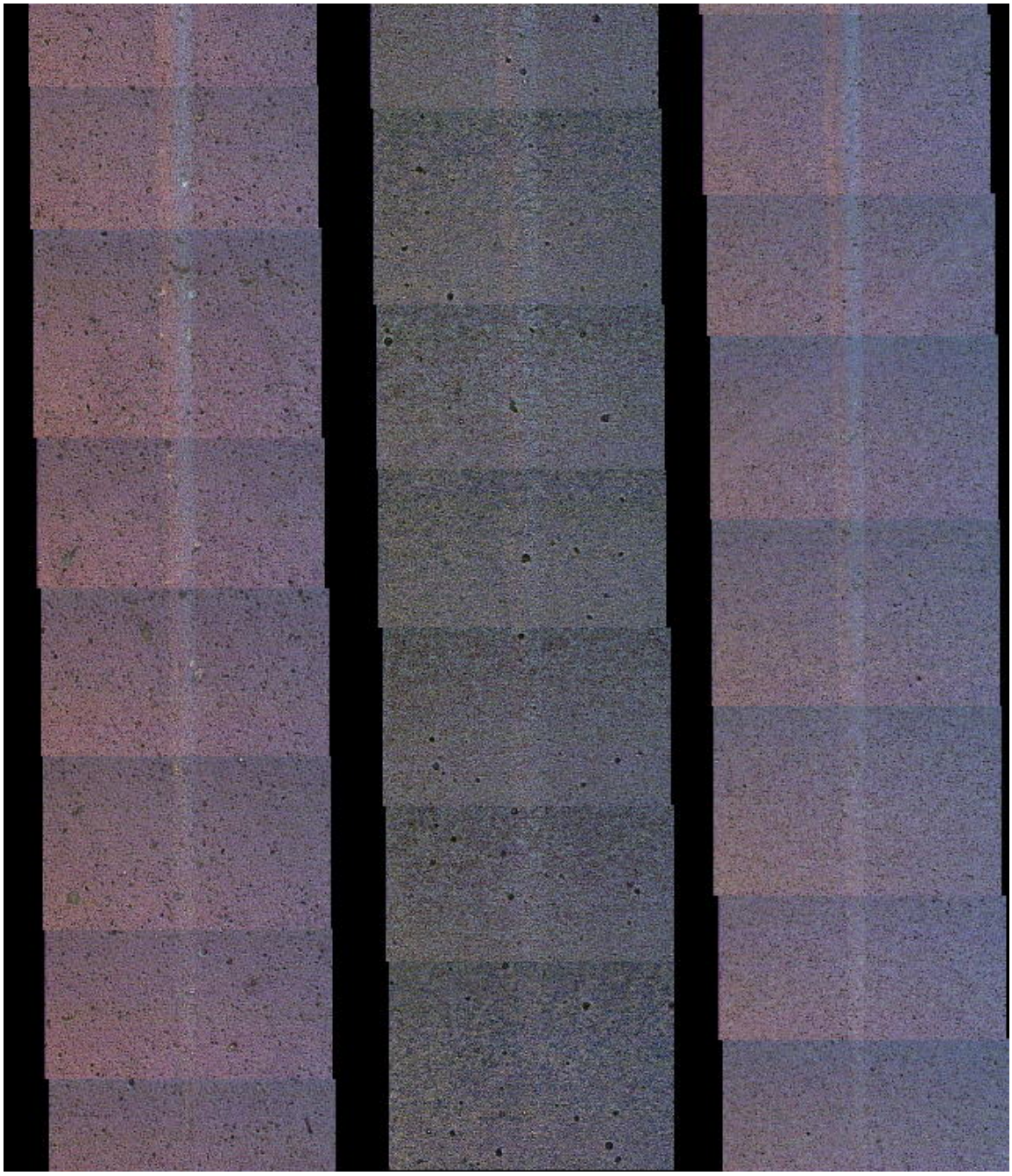

Fig. 2: Morphology of surface after scratch indentation of systém with TiAlN

On fig. 2 are morphology of surface after scratch indentation on systems (arc evaporation and magnetron sputtering as in fig. 1) thin film TiAlN – HSS. Normal force is in the range 0 N to 40 N. Deformation process is smaller then with scratch indentation with indentor 0.2 mm. The stress of surface is namely by friction. Deformation process is the smallest on systém the second, the hardening of surface is the highest. The system the second has small adhesive cohesive failures along scratch. The highest resistance before scratch indentation is on the third systém.

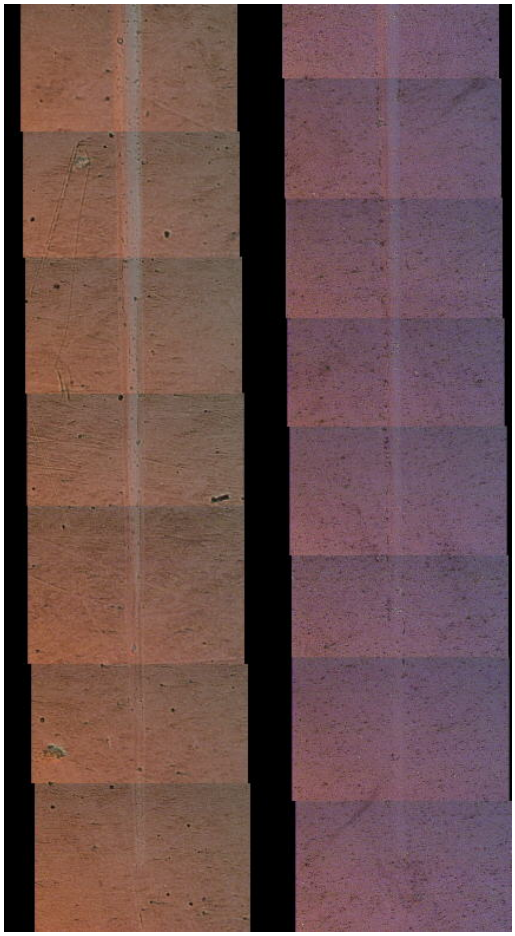

Fig. 3: Morphology of surface after scratch indentation of systém with films PA CVD

The morphology of surface after scratch indentation on systems TiN – HSS and TiCN – HSS with thin films deposited by PA CVD method is on fig. 3. The deformation process is smaller then in [1] and stress is smaller too and failures do not expanded..Normal force is in the range 0 N to 40 N. The depth of indentation increase rapidly from 15 N of normal force on systém with TiN and surface in the scratch is failured to the substrate. The second systém is more resistance to the friction. Failures on systém with TiCN are along the scratch. It is given by higher brittless. Width of scratch is smaller by higher hardening of surface by TiCN thin film.

Nanoindentation

The measurement by nanoindentation in the mode 2 was presented in [1]. Here are completed measurement by other mode of measurement. Selected measurement is cyclic indentation by mode 7. Repeatively measurement indentation curves with increasing maximal force step by step in 20 steps. This mode give possibility to evaluate resistance to repeated stress by indentation and analyse changing properties during this stress and changing properties in different depth of systems thin film – substrate. The measurement was provided with maximal normal force 200 g and 25 g for evaluation properties and behaviour under thin films and evaluation influences of thin films on behaviour all systems.

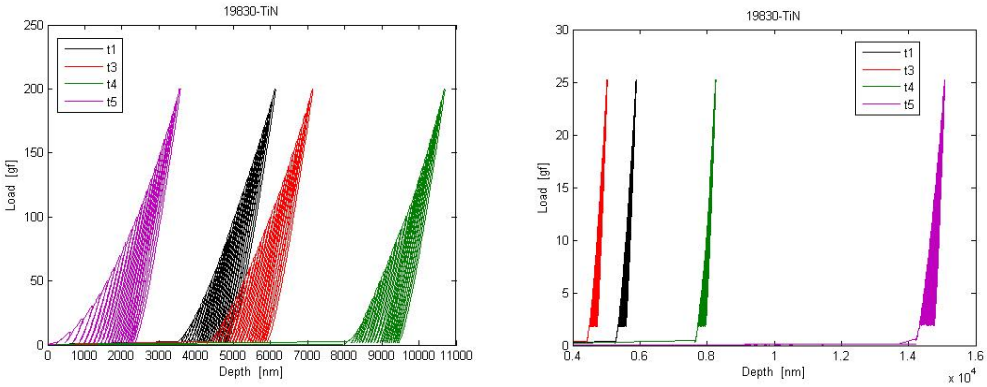

Fig. 4: Cyclic indentation curves on systems with TiN – maximal load 200 g and 25 g.

Fig. 4 show cyclic indentation curves on different systems t1, t2, t3, and t4 (same as in fig. 1). The highest hardening is on systems t1 and t4. The highest depth of indentation is on systém t5. Indentation curves give result by smaller adhesion and bigger failuring during indentation on systém t5 and t4 too. Cyclic indentation curves with maximal normal force 25 g are on fig. 4. The highest depth of indentation is on systém t5. The hardening of surface is not on this systém in the range of measured cycles and applicated normal forces. The highest hardness is on systems t3 and t1. The systems t1, t3 and t4 has similar behaviour.

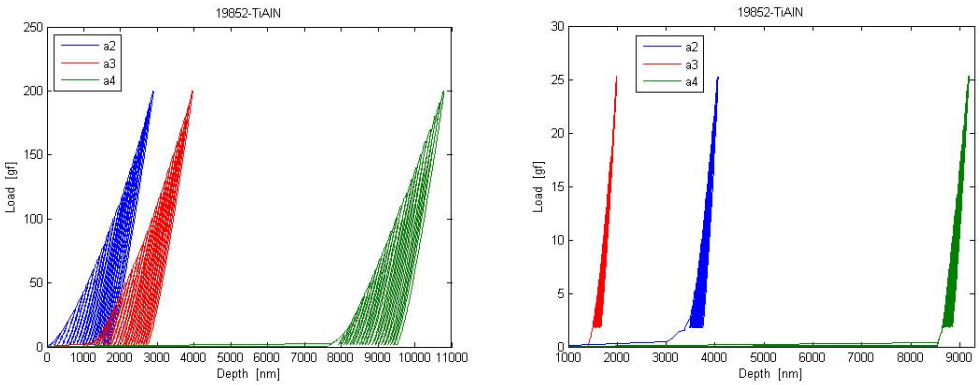

Fig. 5: Cyclic indentation curves on systems with TiAlN – load 200 g and 25 g.

Indentation curves on fig. 5 are in correlation with measurement by scratch indentation. The highest hardening is on systém a3 and here is the highest hardness too. The smallest hardening by thin film is on systém a4 and hardening by cyclic indentation is the smallest too. Cyclic indentation curves show differences in resistance to the cyclic indentation. The highest resistance is on systém a3 and the other the highest resistance is on systém a4. The highest depth of indentation is for systém a2, what can be done by differences thin films from multilayer systém from point of view deformation.

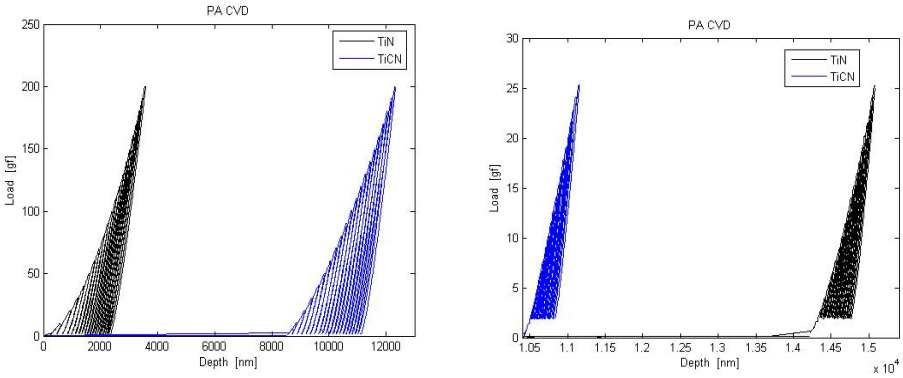

Fig. 6: Cyclic indentation curves on systems with PA CVD films – load 200 g and 25 g.

Indentation curves (fig. 6) give information what higher hardening is on systém t5. Depth of indentation is bigger on start of cyclic indentation on this systém. Thin film on systém c5 give higher hardening of surface but has less resistance to the cyclic indentation with increasing normal force. Systém c5 has higher hardening near the surface then systém t5 (fig. 6).

X-ray fluorescent analysis

This method is used for evaluation thickness and profile of thickness across samples for catching homogeneity of thickness across area of sample. The possibility of this analysis is measurement in very small area and its was used for analysis changing of x-ray spectrum after scratch indentation in created scratches.

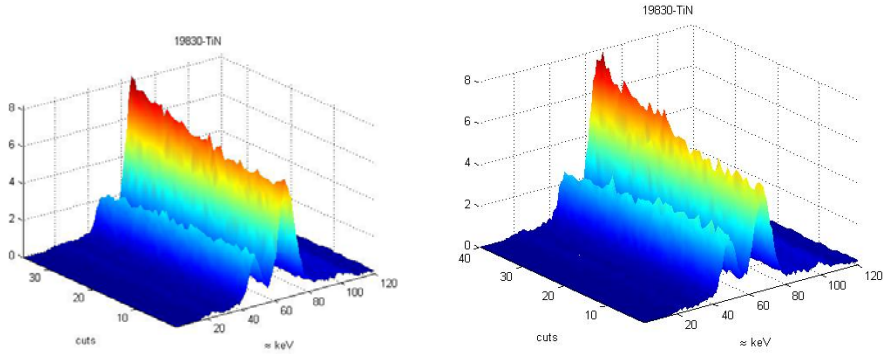

Fig. 7: Development of x-ray spectrums in the scratches on systéms with TiN

The changing of spectrum on systém t3 thin film TiN – HSS is on fig. 7. The highest maximum is for Fe and lower for Ti. The maximum for Fe is changed by failures in scratch and wearing in scratch. The failures in scratch increase from 35 N of normal force. Here is spectrums (fig. 7) measured on surface of TiN – HSS of systém t4 in scratch after indentation. Small failures are from small value of normal force. Here is bigger failures from 40 N of normal force. These failures are bigger then on fig. 7 – the first graph.

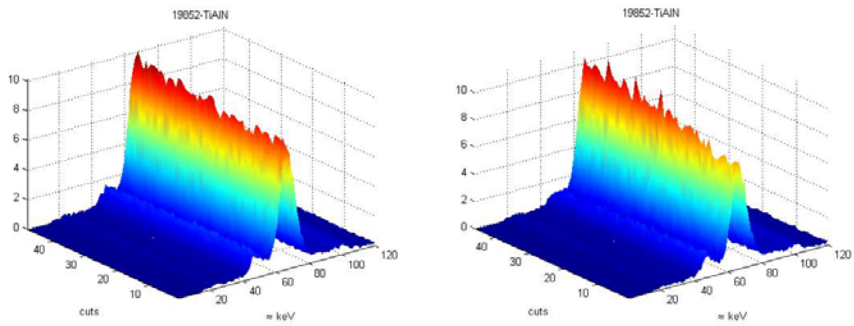

Fig. 8: Development of x-ray spectrums in the scratches on systéms with TiAlN

Here is slowly increasing wearing (fig. 8) of surface during scratch indentation with increasing of normal force. In the center of normal force the bigger failures are created. The changing of spectrums (fig. 8) in the scratch on systém a4 TiAlN – HSS is with bigger slope of increasing of wearing and bigger failures in scratch.

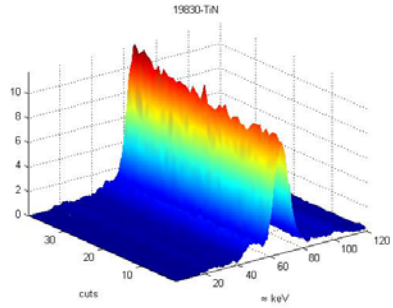

Fig. 9: Development of x-ray spectrums in the scratches on systéms with TiN from PA CVD.

The changing of spectrums (fig. 9) on system t5 TiN – HSS show bigger wear on start of scratch, but then failures decrease and increasing is rapidly again from 25 N of normal force.

GDOES

The analysis of depth profile of chemical composition was provided by GDOES (Glow Discharge Optical Emission Spectroscopy).

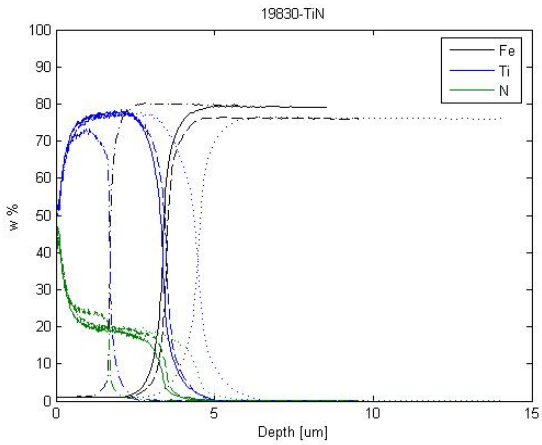

Fig. 10: Depth profile of chemical composition of systems with TiN

Here are depth profile of chemical composition for systems with TiN thin films (fig. 10). Defferences are only in thickness of thin films. Only the systém t5 has higher amount of N and less amount of Ti.

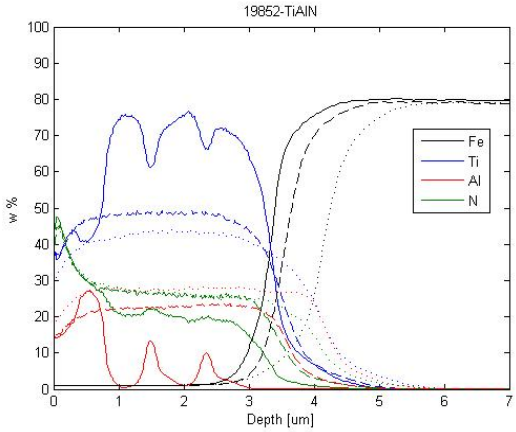

Fig. 11: Depth profile of chemical composition of systems with TiAlN

Differences between systems with TiAlN films are bigger (fig. 11). Thin films has different thickness and different chemical composition. The systém a2 has multilayer thin film with change TiN and TiAlN layer. This composition influence behaviour during scratch indentation and nanoindentation too.

Conclusion

The evaluation of mechanical properties and behaviour is the most complex by scratch indentation analysis with completation by nanoindentation and x-ray fluorescent method. The results from measurement are: The highest resistance to scratch indentation has TiN from arc evaporation 2 and the least resistance is on systém from PA CVD deposition. The highest hardening of surface is on systém from arc evaporation. Systems with TiAlN has lower resistance. The highest resistance for TiAlN is also for arc evaporation – here for arc evaporation 2. TiAlN thin films has the highest nanohardness from sputtering process, but it give brittle properties too. The lowest resistance at all is for systems with PA CVD thin films namely TiCN. Depth profile of chemical composition give information what TiN thin films are similar, but TiAlN has differences namely for systém from arc evaporation 1 in multilayer systém, what influence behaviour during indentation and increase resistance before scratch indentation.

The paper is realised by financial support from state budget of Ministry of Industry and Trade of Czech Republic, project n. FT-TA4/082.

Literature

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INFLUENCE OF SELECTED DEPOSITION PARAMETERS ON PROPERTIES AND BEHAVIOUR OF SYSTEMS THIN FILM - SUBSTRATE

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Prethodno priopćenje / Preliminary note

Abstract

The paper is devoted to evaluation of properties and behaviour of systems thin film – substrate prepared by low voltage arc evaporation in vacuum. Thin films were created on the similar substrate from HSS with different deposition parameters namely pressure of deposition process, bias voltage during deposition process and chemical composition of target for deposition process. These systéms thin film – substrate were evaluated by enhanced method of evaluation by scratch tester with refinement of measurement, nanoindentation with using cyclic indentation. Complete analysis was prepared by x-ray fluorescent method for other evaluation of scratches and by GDOES for evaluation of depth profile chemical composition.

University of West Bohemia in Pilsen

Introduction

Different application of systems thin film – substrate need concrete optimalisation of deposition parameters for deposition on different basic material, for different kind of stress in practice conditions, changing not controled deposition parameters as geometry of target, decontamination of deposition chamber and so on. Different parameters of deposition process are important for different technology process [1] and deposition different kind of thin film. Very important parameters is basic material and its properties mechanical and structural, preparing of surface, cleaning process before deposition and during deposition process too. The analysis by indentation static and scratch is possible expand for evaluation not only basic properties but for evaluation behaviour during different stress too [2]. It is very important for optimalisation properties and behaviour for concrete application.

Scratch indentation test

Scratch indentation on this samples was provided in [1] with standard parameters of scratch indentation by using diamond Rockwell indentor with radius of tip 0.2 mm. Here are other measurements with conditions developed normal force from 0 N to 80 N with constant rate of increasing normal force and constant rate of samples under indentor. Diamond indentor Rockwell type has radius of tip 0.5 mm.

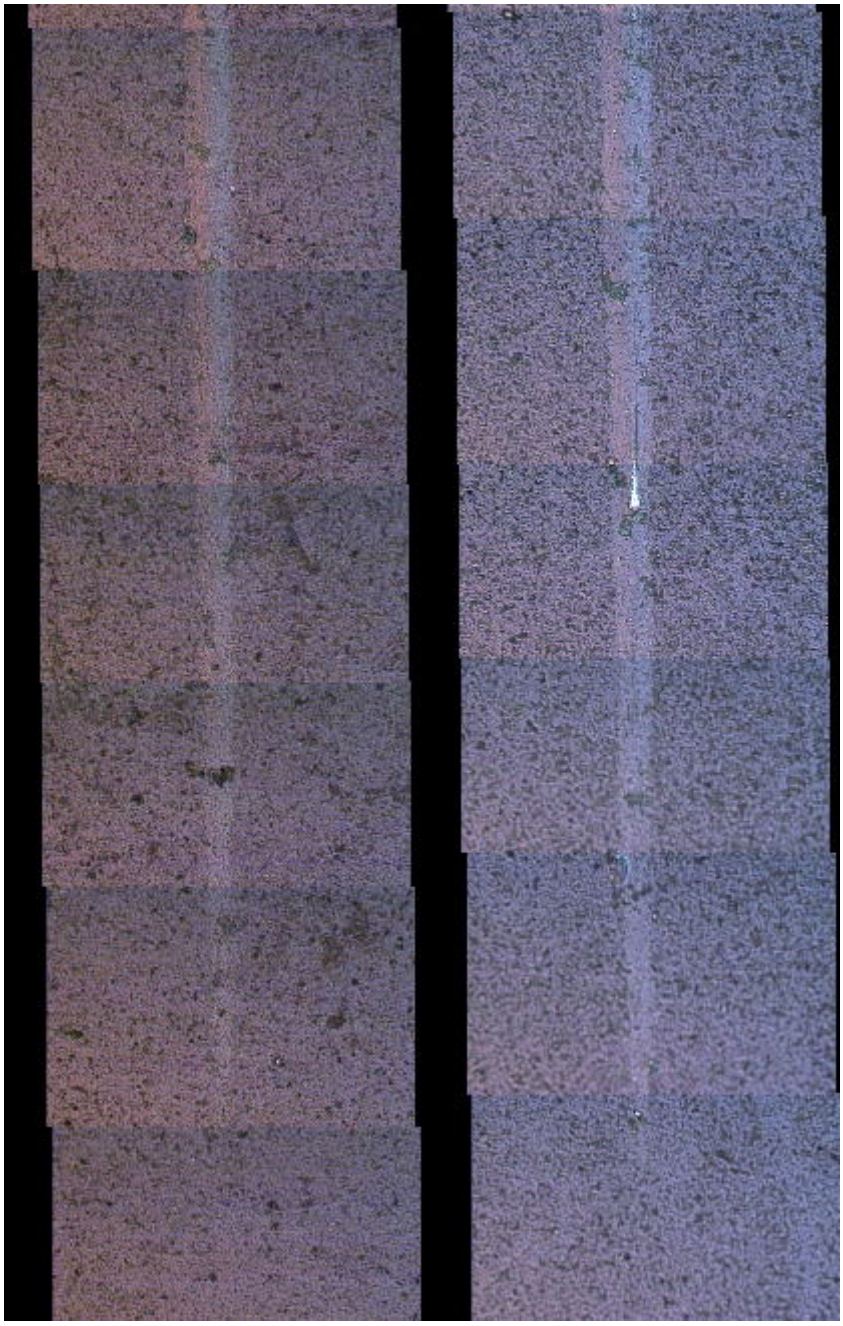

Fig. 1: Morphology of surface after scratch inentation of systém deposited by different pressure

Here are morphology (fig. 1) of surface after scratch test measurement on systems which áre different with pressure of deposition process. The first systém is with higher pressure and the second has standard conditions. Behaviour of both systems is similar. Failures on both systems expand with increasing normal force. The larger expansion is on the first systém with higher presure of depositon. The first systém more hardening surface and give higher resistance before scratch indentation.

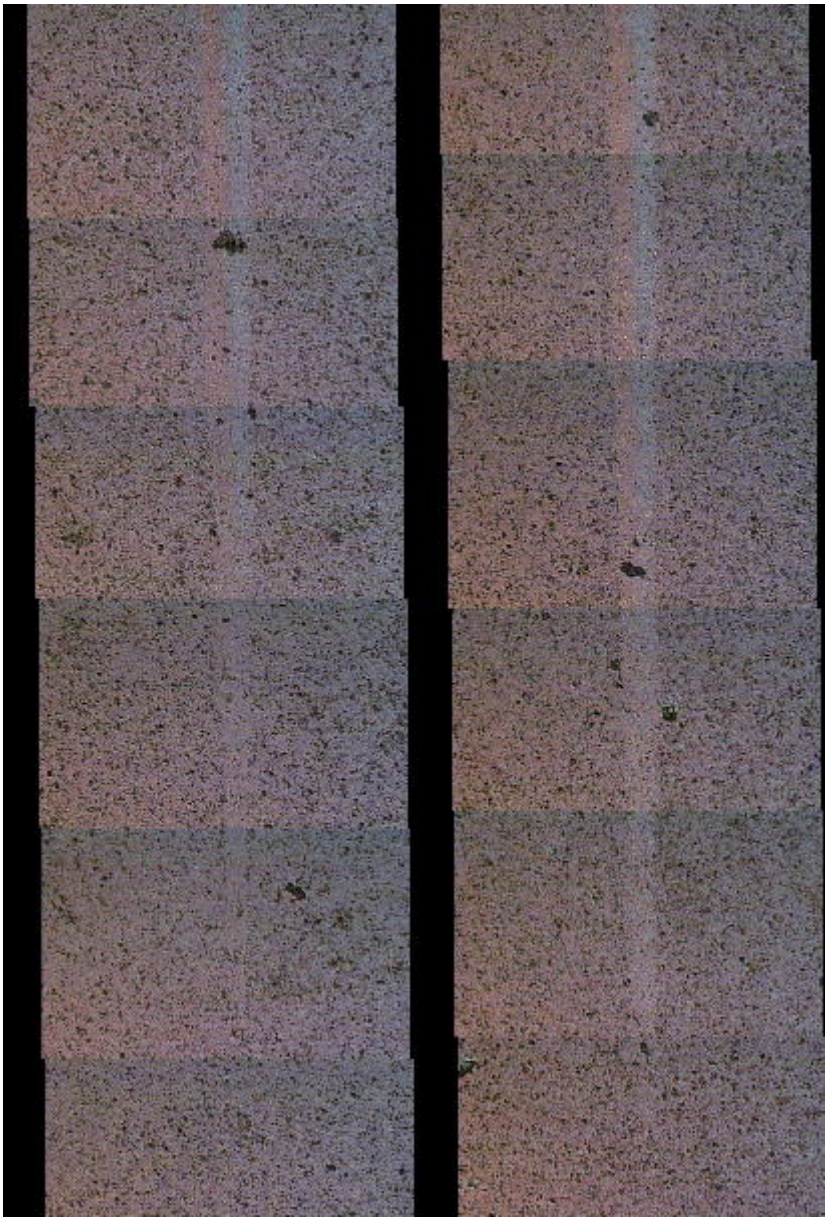

Fig. 2: Morphology of surface after scratch indentation of systém deposited by different bias voltage

Here are morphology (fig. 2) of surface after scratch test measured on systems which áre different with bias during of deposition process. The first systém is with higher bias and the second has standard conditions. Behaviour of both systems is similar. The first systém with increasing of normal force has bigger failures but in smaller count then the second systém. The width of scratches is similar for both systems.

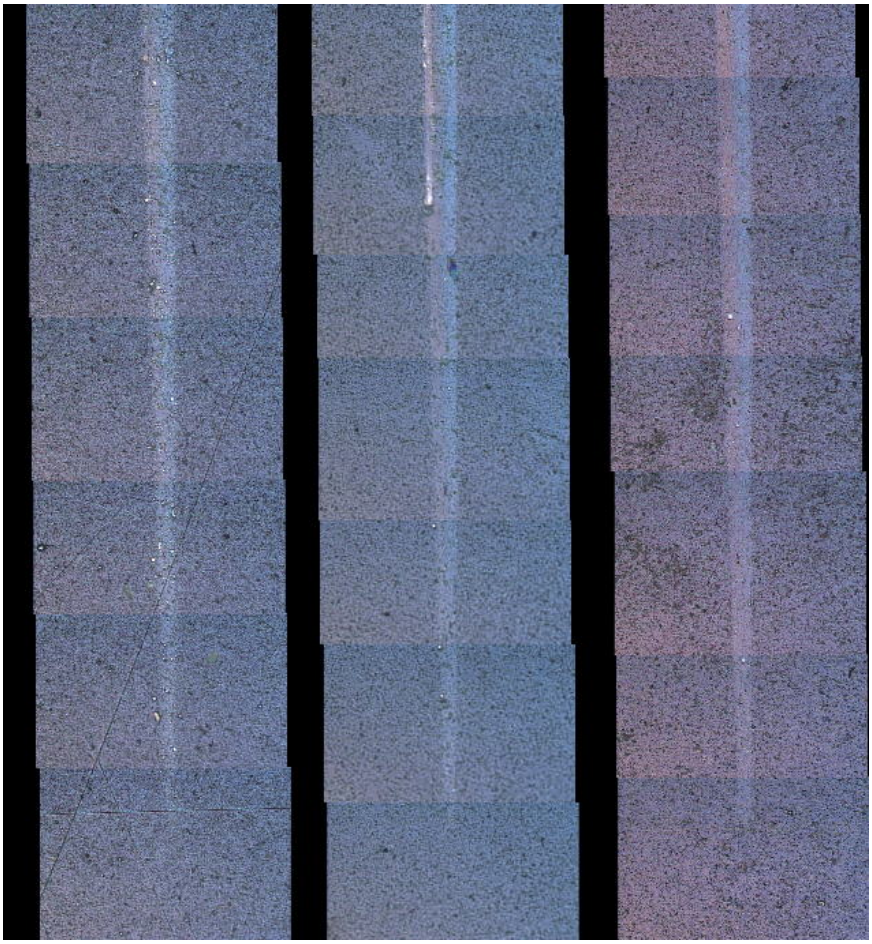

Fig. 3: Morphology of surface after scratch indentation of systém deposited with different target

Here are morphology (fig. 3) of surface after scratch test measurement on systems which áre different with composition of target for deposition process. The first systém is deposited from target composition 60% Al, 40% Ti, the second systém 50% Al, 50% Ti and the third systém 70% Al, 30%. The behaviour of all systems is similar in the range of normal force from 0 N to 80N. The first systém has small failures, the second systém has less failures. The least of failures is on systém the third.

Nanoindentation

Nanoindentation measurement was realised by setting mode 7 (mode 2 was used in [1]). This mode is cyclic indentation with step by step increasing maximal normal force and measuring indentation curves during loading and unloading. The measurement was provided with maximal normal force 200 g and 25 g. Load of 200 g is for evaluation modification of surface of basic material by deposition process. Load of 25 g is for evaluation behaviour of thin films and interface between thin film and substrate. Evaluation by cyclic indentation is interesting for getting information about local properties from point of view fatique properties and from point of view hardening surface by this deformation process. We can get information about properties and behaviour from different depth of materials systém with thin films.

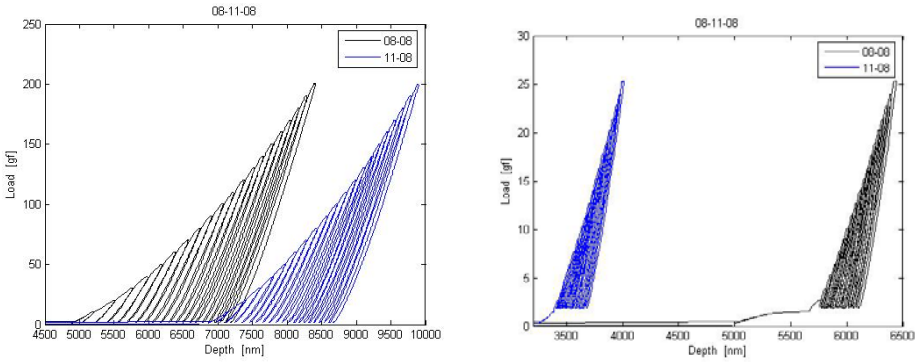

Fig. 4: Cyclic indentation curves on systems - different pressure – load 200 g and 25 g.

Here is presented (fig. 4) cyclic indentation curves for systéms differing in pressure of deposition. Increasing of pressure give higher hardening of surface.

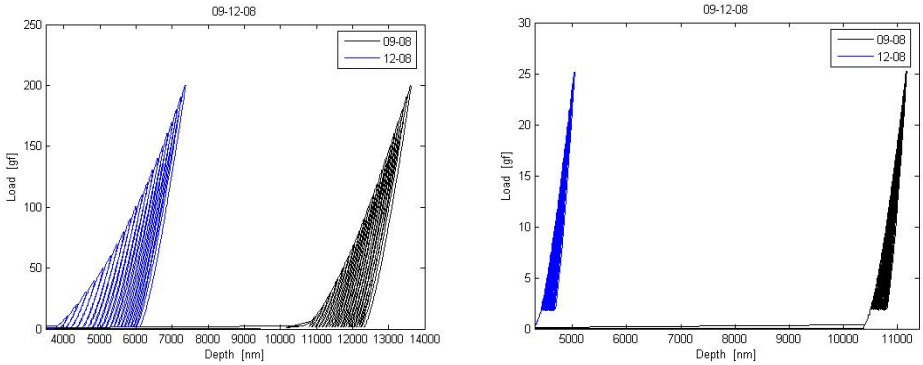

Fig. 5: Cyclic indentation curves on systems - different bias – load 200 g.and 25 g

Here is cyclic indentation curves (fig. 5) for systéms differing in bias voltage on substrate during deposition process. The higher hardening is on systém with standard deposition conditions. The systém with higher bias show bigger hardening by cyclic indentation - the second systém. The hardness is from measurement higher for systém with standard bias voltage.

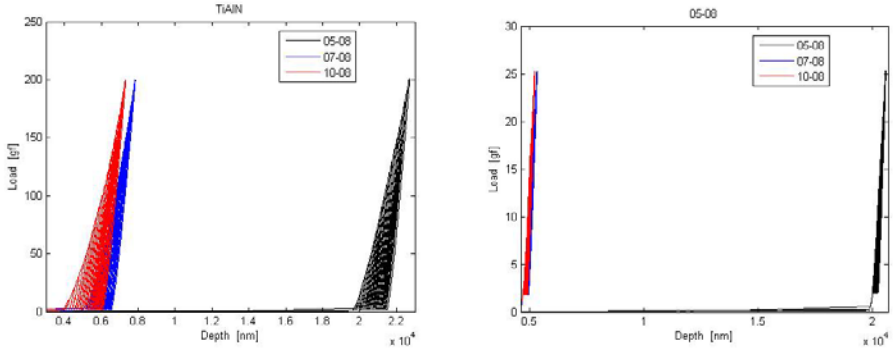

Fig. 6: Cyclic indentation curves on systems - different target – load 200 g and 25 g.

Here is presented cyclic indentation curves (fig. 6) for systéms differing in composition of target. The highest hardening of surface by deposition process is for composition of target 50% Al and 50 % Ti. Partly there is changed systém the first by cyclic indentation. The highest hardening by cyclic indentation is for system the third. With

decreasing normal force on 25 g indentation curves give resulted the highest hardening on systém the first, then systém the second. The least hardening is on systém the third.

X-ray fluorescent analysis

There is used this method for evaluation scratches after scratch indentation. Step by step spectrum is saved from measurement in the scratch in small area with increasing value of normal force acted during scratch indentation in the local place.

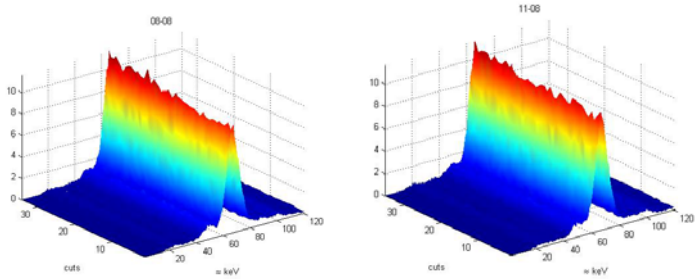

Fig. 7: Development of x-ray spectrums in the scratch on systém with different pressure

The changing of spectrums show (fig. 7) step by step decreasing of thickness in scratch. In the half of maximal normal force increasing failures is given from the result of spectrums. The failures enlarge area. The spectrums in the second systém (fig. 7) has similar changing but changing is irregular from start of scratch.

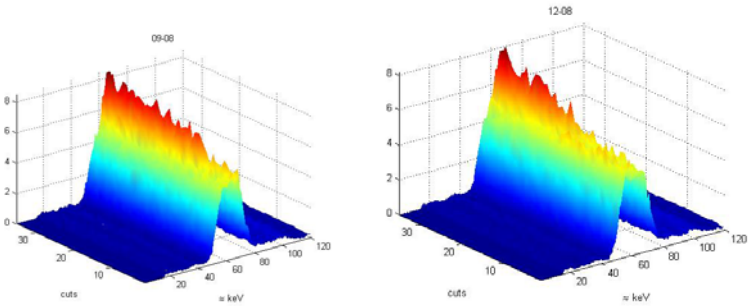

Fig. 8: Development of x-ray spectrums in the scratch on systém with different bias

The development of spectrums in the scratch on the first systém show (fig. 8) from start of scratch increasing of maximum for Fe as the result failuring in the scratch and decreasing of thickness of thin film in the scratch. The other development of spectrums show similar character as above mentioned samples, only slope is bigger. Development of spectrums in this scratch (fig. 8) on the second systém give higher resistance of this systém then systém in fig. 7. The end of scratch give bigger failures because create the large relaxation of stress generated by indentor.

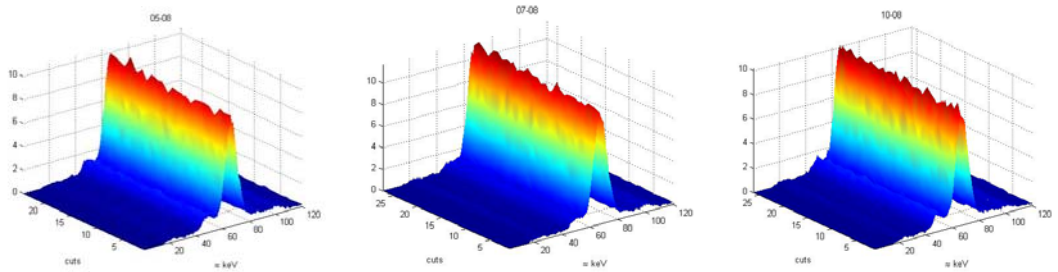

Fig. 9: Development of x-ray spectrums in the scratch on systém with different target for deposition

The development of spectrums in the scratch of the first systém (fig. 9) give results about decreasing of thisckness of thin films and/or peeling of thin films step by step from start of scratch. It is regulary process. Here is possible view (fig. 9) smaller failures on the second systém and with increasing normal force here is changing in mild steps then on sample 05-08. Development of spectrums in fig. 9 on the third systém is similar as above mentioned samples with step by step mild failuring and decreasing of thickness of thin film in scratch.

GDOES

This analysis is used for evaluation of depth profile of chemical composiition in above mentioned systems.

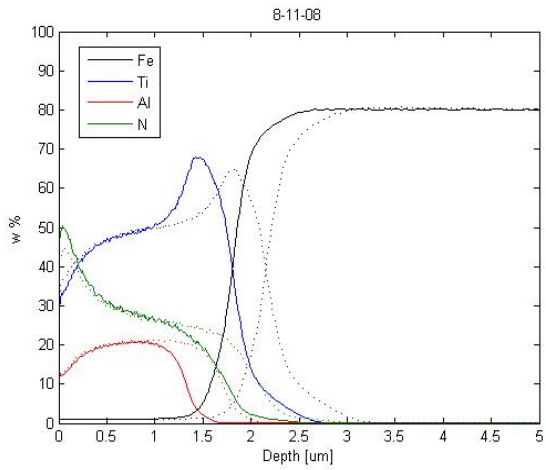

Fig. 10: Depth profile of chemical composition of systems with different pressure

The depth profile (fig. 10) give result in increasing of thickness by increasing of pressure during deposition. It is true if the other parameters was really the same for both deposition.

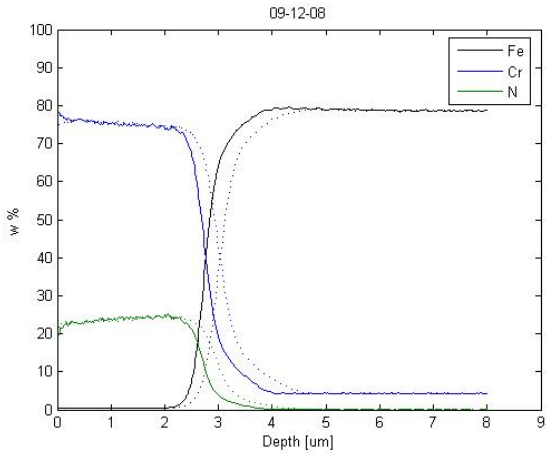

Fig. 11: Depth profile of chemical composition of systems with different bias voltage

Depth profile for samples with differences in bias voltage (fig. 11) give similar results. Thickness is a little smaller for lower bias, which can be done by higher energy of impacted ions to the surface.

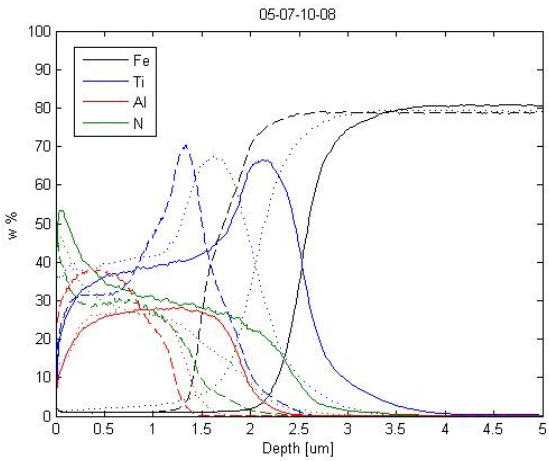

Fig. 12: Depth profile of chemical composition of systems with different target for deposition

The depth profile of systems created with target with different chemical composition (fig. 12) give similar amount of Ti. All systems has interlayer Ti. Samples 05-08 and 10-08 has similar chemical composition therefore are deposited from target with different chemical composition.

Conclusion

The analysed materials are systems thin film – substrate from HSS. Here are changed deposition parameter namely deposition pressure, bias voltage during deposition process and chemical composition of target for deposition. Increasing of deposition pressure give increasing surface hardness but increasing brittle of surface too and failures has bigger expansion. Increasing of bias voltage has influence on thin film by increasing brittle of failures and then decrease resistance to the scratch indentation. Changing of composition of target for deposition process do not have strong influence.

Optional conditions are for composition 50% Al and 50% Ti. Increasing among of Al give increasing nanohardness of thin films. Composition of target 60% and 70% Al give similar chemical composition of AlTiN thin films.

The paper is realised by financial support from state budget of Ministry of Industry and Trade of Czech Republic, project n. FT-TA4/082.

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ANALOGY BETWEEN CRYSTALS FORMS AND SHAPE OF ASSEMBLY DEVICES FOR MANUFACTURING OF SPATIALLY REINFORCED COMPOSITE STRUCTURES IN FOUR AND SEVEN DIRECTIONS

PODUDARNOST KRISTALA I OBLIKA ALATA ZA PROIZVODNJU PROSTORNO OJAČANIH KOMPOZITA U ČETIRI I U SEDAM PRAVACA

Jadran Šundrica[1], Tomislav Filetin[2]

Izvorni znanstveni rad / Original scientific paper

Abstract: The paper gives evidence of analogy between the crystals forms and the shape of assembly devices for preparing and casting of spatially reinforced composite structures by the presentation of computer and real models and the corresponding crystals. The spatially reinforcement structures are divided into simple and complex types obtained by the combination of the simpler ones. The arrangement schemata of reinforcing rods are given for simple structures as well as the calculations for the geometric parameters required for manufacturing. The analogy between a crystal of Diamond with the shape of the device for the manufacturing of reinforcement structures in four directions (4D) have been selected to illustrate the approach in simple spatially reinforced structures. Isotropic (completed) and anisotropic (uncompleted) complex spatially reinforced structures are obtained by a combination of the basic structures by employing the arrangement schemata of reinforcing rods and appropriate geometric parameters. In order to demonstrate the analogy, a comparison of a hexaoctahedron and Carolite with the model of a reinforcement structures in seven directions (7D) has been presented. It is concluded that the analogy of developing regular complex shapes that are found in crystals by combining simple geometric solids of parallelepipeds and pyramids gives the shape of the appropriate devices used for the assembling and casting of simple and complex structures of spatially reinforced composites.
Key words: spatially reinforced structures, crystals**,** composite manufacturing
Sažetak: U radu je prikazana podudarnost kristala i oblika alata za slaganje i lijevanje kompozita s prostornim rasporedom ojačala usporedbom odgovarajućih slika kristala te računalnih i realnih modela. Strukture prostornog ojačavanja podjeljene su na jednostavne ojačane u tri, četiri i šest pravaca i složene dobivene kombiniranjem jednostavnih. Za jednostavne strukture dane su sheme postavljanja krutih ojačala kao i rezultati izračuna geometrijskih parametara neophodnih za proizvodnju. Podudarnost dijamanta s oblikom alata za postavljanje ojačala u obliku štapova u četiri pravca je izabrana kao dokaz teze o analogiji kod jednostavnih prostorno ojačanih struktura. Izotropne složene prostorno ojačane strukture nastaju kombiniranjem jednostavnih u pogledu oblika, shema postavljanja ojačala i geometrijskih parametara za proizvodnju. Usporednim prikazom heksaoktaedra, modela strukture ojačane u sedam pravaca (7D) i kristala karolita pokazuje se analogija kod složenih prostorno ojačanih struktura. Iz sadržaja rada može se zaključiti da postoji analogija između oblika jednostavnih i složenih geometrijskih tijela i kristala s oblicima alata za postavljanje prostorno ojačanih struktura.
Ključne riječi: prostorno ojačane strukture, kristali**,** proizvodnja kompozita

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1. INTRODUCTION

The study of composite materials of different compositions and structures can show their relation to the material properties, including their application potential [1]. The application of *spatially* reinforced composite materials is lagging behind the application of conventional composite materials due to the complexity of the procedures involved in their manufacturing. This provides the context for an analysis of the models for space arrangement of the cylindrical rod reinforcements.

The manufacturing of spatially reinforced composites is preceded by the arranging of reinforcing rods according to the schema defined by the number of reinforcing directions. The intention is to eliminate one of the main reasons for the limited application of *spatially* reinforced composites by the systematisation of the porous structures necessary for the manufacturing of *spatially* reinforced composites, through the development of real and computer models of porous structures and by determining the shape of the casting devices.

The results of the study of advanced composite materials, in particular of all spatially reinforced composites, have been and still are unavailable, since these are carried out mainly by military institutions, which usually means that they are protected. On the other hand, the information on classical composite materials can be found in numerous publications and represents the basis of this paper.

The starting point for a literature review has been to examine the publications with references to available documents of the European Patent Office (EPO) on composites and reinforcing agents [2]. The principle source of reference to scientific papers and books in the field of composite materials is Hull and Clyne [3] who have studied the fundamentals required for an understanding of composite materials: matrices, fibres, contact surfaces and fibre orientation, their interrelations, manufacturing, and properties and behaviour in application. Matthews and Rawlings [4] extended their work to laminate and unidirectional composites and non-destructive testing methods.

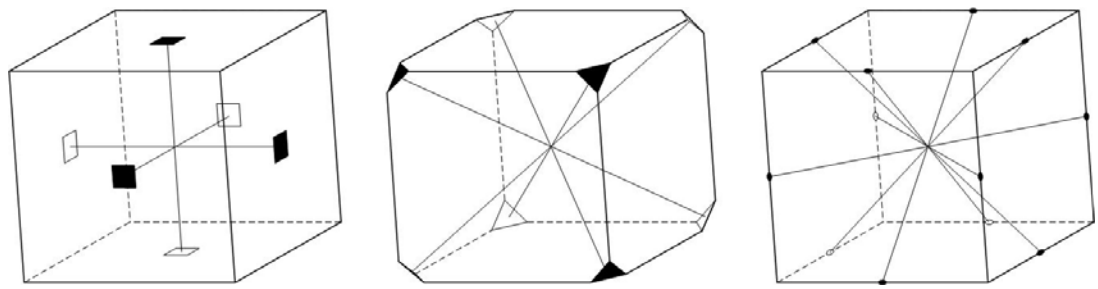
Erich Fitzer [5, 6] studied in particular carbon fibre-reinforced composites, including simple space-reinforced C-C composites. Tarnopol'skii, Zhigun and Polyakov [7] systematized the existing knowledge and published theoretical considerations in addition to test results for space-reinforced composites. The same authors make several mentions of the crystal analogy for spatially reinforced composites but do not provide a list of authors who dealt with this topic. This work uses the assumptions from [8] on the similarity between space and plane arrangement of atoms with regular geometric figures and solids as well as the results of authors' own research [9, 10].

2. STRUCTURES FOR THE MANUFACTURING OF SPATIALLY REINFORCED COMPOSITES

2.1 Simple structures and the composition of complex structures

Porous structures necessary for the manufacturing of spatially reinforced composites can be divided into simple and complex types. Simple reinforcement structures can be formed in the directions of three coordinate axes x, y and z (3D), presented in Figure 1a), reinforced in the directions of space diagonals of a cube t, u, v, w (4D) presented in Figure 1b), or reinforced in directions of the diagonals of the cube faces k, l, m, n, r, s (6D) presented in Figure 1c).

Complex structures result from the combination of simpler types. Complex structures for the manufacturing of spatially reinforced composites include a group of isotropic and anisotropic schemata. Regardless of the number of reinforcing directions, complex structures consist of two or more structures of reinforcement in one direction, reinforcement structures in the plane or structures of simple spatially reinforced composites.



a) *axes x, y and z (3D)* — *b)* *body diagonals t, u, v, w (4D)* — *c)* *diagonals of faces k, l, m, n, r, s (6D)*

Figure 1: Composite reinforcement directions

3.2 Isotropic complex structures for the manufacturing of space-reinforced composites

A group of isotropic complex structures used for the manufacturing of spatially reinforced composites consists of reinforcement structures in seven directions (7D), nine directions (9D), ten directions (10D) and thirteen directions (13D).

Table 1: Classification and ways of forming the complex structures from the combination of simpler types

Structures	Isotropic	Anisotropic	3D	4D	6D	Square	Hexagonal	Rhomb
7D	✓	✗	✓	✓	✗	3	4	✗
9D	✓	✗	✓	✗	✓	3	✗	6
10D	✓	✗	✗	✓	✓	✗	4	6
13D	✓	✗	✓	✓	✓	3	4	6

A reinforcement structure in seven directions (7D) is obtained by a combination of reinforcement structures in three directions (3D) and four directions (4D). The combination of reinforcement structures in three directions (3D) and six directions (6D) yields a reinforcement structure in nine directions (9D), and the combination of structures in four directions (4D) and six directions (6D) yields a structure in ten directions (10D). Unifying all three simple structures results in a reinforcement structure in thirteen directions (13D), which is the basis for the manufacturing of the most complex isotropic spatially reinforced composite.

3. ANALOGY BETWEEN CRYSTALS FORMS AND SHAPE OF ASSEMBLY DEVICES FOR THE MANUFACTURING OF SPATIALLY REINFORCED POROUS STRUCTURES IN FOUR (4D) AND SEVEN DIRECTIONS (7D)

3.1 Geometric parameters of basic structures

In order to manufacture a particular space structure it is necessary to determine the arrangement schema of the reinforcing rods in a single direction and the minimal gap under the condition of contact. Based on these data, the sides of the jig are made with bores laid out according to an appropriate scheme. For reinforcement structures in three directions the arrangement scheme is square, and the sides of the jig are in the form of a square. Reinforcement structures in four directions have jig faces in the form of equilateral triangles and a hexagonal arrangement scheme, whereas structures in six directions are arranged in a jig with faces in the shape of rhomb according to a rhombic scheme.

The required size of the end product determines the dimensions of the assembly device faces and the minimal length of the reinforcing agent L_{min}. For a unit cube the minimal lengths of the reinforcing rods are:- 1 for reinforcement in three directions (3D) and $\sqrt{3}$ for reinforcement in four directions (4D). The number of assembly device faces necessary to produce porous structures is double the number of reinforcement directions.

Table 2 gives the angles between different reinforcing directions and the theoretical maximum percentage of filled space f_{max} of simple structures for the manufacturing of spatially reinforced composites.

Table 2: Geometric parameters of simple nD structures for reinforcing agents of circular cross-section

GEOMETRIC PARAMETERS	NUMBER OF REINFORCEMENT DIRECTIONS		
	Three (3D)	**Four (4D)**	**Seven (7D)**
Scheme of the arrangement of reinforcing agent in each direction	Square	Hexagonal	Square & Hexagonal
Angles between reinforcement directions	3 x 90°	4 x 70.53°	3 x 90°, 4 x 70.53°
Theoretical maximum percentage of space filling f_{max}	0.5890	0.6802	0.4006

While developing the actual and computer models of simple structures necessary for the manufacturing of spatially reinforced composites a correspondence between the shapes of moulds, casting devices, regular geometric solids and crystal shapes has been posited.

3.2 Analogy between the octahedron and the shape of a device for the manufacturing of reinforcement structures in four directions (4D)

The starting points for the manufacturing of porous structure for composite reinforcement in four directions are the reinforcing rods set in the direction of one of the body diagonals of a cube t, u, v and w. The arrangement scheme of the reinforcement rods is hexagonal as presented in Figure 3.

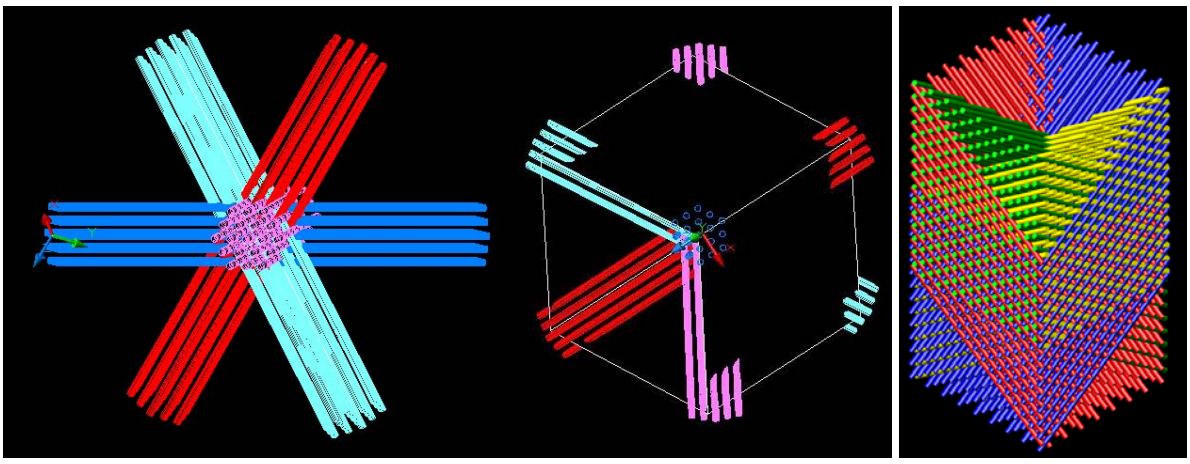


Figure 3: Models of structures for manufacturing of composite reinforced in four directions (4D)

However, for a clearer representation of the arrangement scheme and the shape of the devices for assembling, eight four-side pyramids can be put together, thus obtaining a solid with eight faces, an octaedron, as presented in Figure 4.

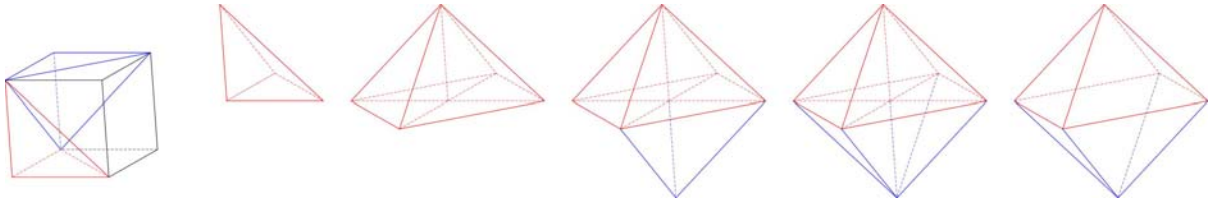


Figure 4: Obtaining an octahedron from a cube

The analogy of the diamond crystal with the shape of the devices for assembling models and real porous structures required for the composites reinforced in four directions (4D) is presented in Figure 5.

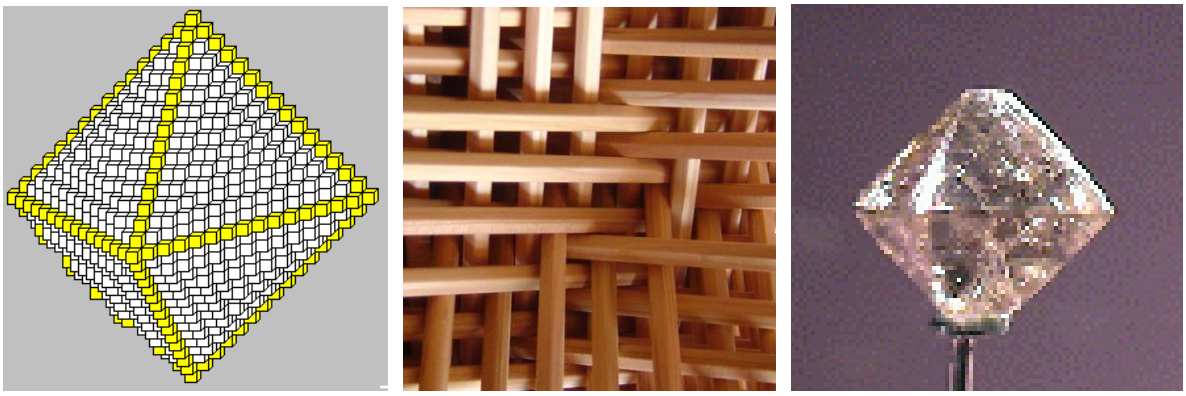


Figure 5: Structural model (left), actual porous structure for the manufacturing of a composite reinforced in four directions (4D) (centre) and diamond crystal (right)

3.3 Analogy between a hexaoctahedron and the form of a device for the manufacturing of reinforcement structures in seven directions (7D)

Complex structures necessary for the manufacturing of spatially reinforced composites are obtained by combining two or more simple reinforcement structures; thus, after closing the reinforcement planes, they form complex geometric shapes composed of a combination of hexahedron, octahedron, and rhombic dodecahedron, and in each case we can find equivalent shapes of crystals in nature.

This claim can be clearly illustrated by the complex space structure for the manufacturing of composites reinforced in seven directions (7D), which is defined by the directions of three coordinate axes x, y and z and the lines of the space diagonals of cube t, u, v, and w. It has already been demonstrated that reinforcing in seven directions can combine reinforcement structures in three (3D) and four directions (4D), and that the resulting structure is anisotropic.

One of the ways of defining the shapes of device for arrangements of reinforcements in seven directions is the insertion of three equal square prisms into a cube using the procedure presented in Figure 6.

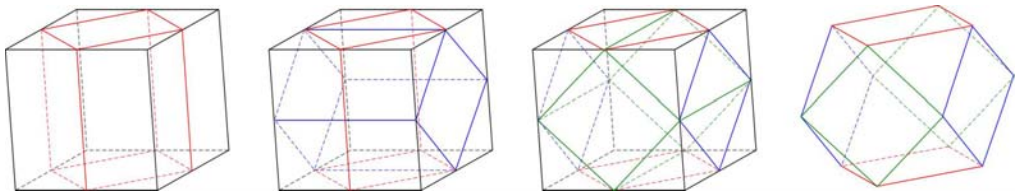


Figure 6: Obtaining a hexaoctahedron from a cube

The resulting solid, a hexaoctahedron, has fourteen faces of which six are the bases of three enclosed square prisms, and the remaining eight are equilateral triangles that close the surface between the base vertices. The reinforcing rods are arranged on the square faces in squares, and on the triangular faces in a hexagonal arrangement. The result of such a scheme is the model presented in Figure 7 and Figure 8 (centre).

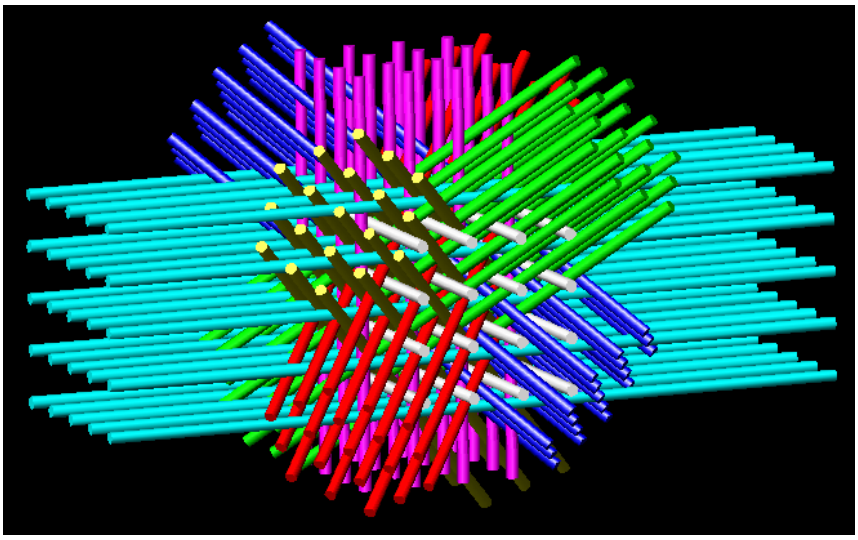


Figure 7: Model of structures for manufacturing composite reinforced in seven directions (7D)

The comparison of a hexaoctahedron and a Carolite crystal with the shape of the porous structure model for the manufacturing of composite material reinforced in seven directions (7D) presented in Figure 8 clearly confirms the proposed principle.

Figure 8: Analogy between hexaoctahedron (left), the model of composite structure reinforced in seven directions (7D) (centre) and Carolite (right)

A more detailed comparison of geometric solids, crystal forms and shapes of devices for assembling the porous structures necessary to manufacture other spatially reinforced composites is offered in recent publications [9, 10, 11].

4. CONCLUSIONS

This paper presents a systematisation of the porous structures required for the manufacturing of spatially reinforced composites.

For simple and complex spatially reinforced composite structures, the arrangement schemata, the results of calculations for the level of space fill, and computer and physical models of arranging cylindrical reinforcing rods have been provided. The suggestion of analogy between the forms of natural crystals with the shapes of the devices for assembling and casting the spatially reinforced composites has been illustrated by presenting the correspondence between the diamond crystal, octahedron, with the shape of the model and real porous structures necessary for the manufacturing of composites reinforced in four directions (4D) which has been presented in particular detail.

The comparison of the hexaoctehadron and Carolite with the porous structure model for the manufacturing of composite material reinforced in seven directions (7D) has confirmed the suggested analogy between the shapes of manufacturing devices for the complex spatially reinforced structures required for the manufacturing of composites with the forms of crystals.

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UTJECAJ PROCESNIH PARAMETARA NA IONSKU IZMJENU BAKRA NA ZEOLITU 13X

INFLUENCE OF PROCESS PARAMETERS ON COPPER ION EXCHANGE ON ZEOLITE 13X

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Izvorni znanstveni rad / Original scientific paper

Sažetak: U ovom je radu ispitivano uklanjanje bakra na sintetskom zeolitu NaX u kotlastom reaktoru pri temperaturi od 298 K. Ispitan je utjecaj brzine miješanja, veličine čestica i početne koncentracije bakra na brzinu uspostave ravnoteže i kapacitet ionske izmjene. Dobiveni eksperimentalni podaci iskorišteni su za određivanje najsporijeg koraka u procesu ionske izmjene te konstante brzine i efektivnog koeficijenta unutarfazne difuzije. Pri tome je korišten Weberov-Morrisov model.
Dobiveni rezultati ukazuju da svi ispitivani parametri imaju utjecaja na brzinu uspostave ravnoteže, te da vrijeme uspostave ravnoteže raste porastom veličine čestice i početna koncentracije, a opada porastom brzine miješanja. Na kapacitet izmjene utjecaj ima samo početna koncentracija bakra s tim da porastom početne koncentracije raste i kapacitet izmjene. Za čestice veličine 2.36 - 4.75 mm i brzinu miješanja od 240 okr/min unutarfazna difuzija je najsporiji korak, a izračunati efektivni koeficijenti difuzije reda 10^{-10} m^2/min.

Ključne riječi: bakar, zeolit 13X, difuzija

Abstract: The removal of copper ions from aqueous solutions using zeolite NaX on temperature of 298 K has been studied by a batch technique. The influences of agitation speed, particle size and solute concentration on the capacity of ion exchange and time to establish equilibrium were examined.
Obtained experimental data are used to identify the slowest on-going process and to calculate rate constant as well as diffusion coefficient of intraparticle diffusion using Weber-Morris model.
Rate of ion exchange of copper ions on the zeolite NaX is affected by: agitation speed, particle size and solute concentration. The ion exchange capacity is only affected by initial concentration. It is clear that the copper sorption capacity increased with initial concentration. For particles the size of 2.36 - 4.75 mm and the agitation speed of 240 rpm intraparticle diffusion is a slowest step, and diffusion coefficients are in range 1.164×10^{-10} to 1.871×10^{-10} m^2/min.

Keywords:copper, zeolite 13X, diffusion

1. UVOD

Prisustvo teških metala u ekosustavima velik je problem zbog njihovog negativnog utjecaja na žive organizme. Najvažnijim izvorom onečišćenja prirodnih vodenih tokova teškim metalima smatraju se industrijske otpadne vode. Stoga ih je prije ispusta u okoliš potrebno obraditi. Upravo iz ovog razloga primjena zeolita u obradi otpadnih voda postaje predmetom znanstvenih istraživanja.[1-3]

Bakar je jedan od elemenata iz skupine teških metala opasnih za žive organizme zbog svoje toksičnosti, stabilnosti i sklonosti nakupljanju u okolišu. U prirodne vodene tokove osim industrijskim otpadnim vodama može doći i uslijed primjene u poljoprivredi, te kao sastavni dio protuobraštajnih premaza korištenih u brodogradnji.

U ovom radu želi se ispitati utjecaj brzine miješanja, veličine čestica i početne koncentracije na ionsku izmjenu bakra na sintetskom zeolitu 13X.

2. EKSPERIMENT

2.1. Zeolit 13X

Zeolit 13X je sintetski oblik prirodnog zeolita faujasita. Jedinična ćelija ovog zeolita sastoji se od osam okruglih šupljina, osam β rešetki i šesnaest heksagonalnih prizmi. Promjer okruglih šupljina iznosi 1.3 nm, a do njih se može doći kroz dvanaestočlane prstenaste kanale promjera 0.74 nm, dok promjer šestočlanih prstena na β rešetki iznosi 0.25 nm.[4]

U radu korišteni zeolit karakterizira Si/Al omjer od 1.23 i pripadajuća formula - $Na_{86}(AlO_2)_{86}(SiO_2)_{106}$ x $220H_2O$ (Sigma Aldrich). Poznavanje ove formule te pretpostavka da su izmjenjivi ioni natrija vezani slabim vezama za anionsku zeolitnu rešetku, te da se svi mogu zamijeniti ionima bakra koji se nalaze u otopini omogućava izračunavanje teorijskog kapaciteta izmjene koji za korišteni zeolit, uzimajući u obzir činjenicu da je bakar bivalentan, iznosi 2.47 mmol/g.

BET specifična površina određena je na osnovu mjerenja provedenih na uređaju ASAP 2000 i prikazana u tablici 1.

Tablica 1. Veličine čestica zeolita i pripadajuća BET specifična površina

Veličina čestica mm	BET specifična površina m^2/g
2.36-4.75	494,821
0.4-0.5	499.339
0.1-0.125	573.956
0.071-0.09	576.804

2.2. Utjecaj brzine miješanja na ionsku izmjenu bakra na zeolitu 13X

Ispitivanje utjecaja brzine miješanja na brzinu ionske izmjene vršeno je na način da se 0.2 L otopine bakrovog (II) nitrata miješa sa 1 g zeolita 13X, veličina čestica 2.36-4.75 mm, pri brzinama okretaja miješalice od 60 - 240 okr/min. Kod ovih pokusa koristila se otopina bakra koncentracije 9.814 mmol/L koja je pripremljena otapanjem $Cu(NO_3)_2x3H_2O$ (Kemika) u destiliranoj vodi, a točna koncentracija otopine određena je korištenjem UV/Vis spektrofotometra.

2.3. Utjecaj veličine čestica zeolita na ionsku izmjenu bakra na zeolitu 13X
Utjecaj veličine čestica zeolita na brzinu izmjene proveden je pri istoj koncentraciji otopine i istoj masi zeolita kao i u eksperimentima iz poglavlja 2.2. uz brzinu miješanja od 240 okr/min. Pri tome je korišteno pet različitih raspona veličina čestica: 2.36-4.75 mm, 1.7-2.36 mm, 0.4.-0.5 mm, 0.1-0.125 mm te 0.071-0.09 mm. Čestice zeolita veličine od 0.4 do 0.071 mm dobivene su usitnjavanjem većih čestica.

2.4. Utjecaj početne koncentracije na ionsku izmjenu bakra na zeolitu 13X
Eksperimenti su izvedeni s otopinama različitih množinskih koncentracija (5.970-9.814 mmol/L). Ispitivani sustav dobiven je miješanjem 1 g zeolita, veličine zrna 2.36 - 4.75 mm i 0.2 L otopine bakrovog (II) nitrata pri brzini miješanja od 240 okr/min..

Svi pokusi provedeni su pri konstantnoj temperaturi od 298 K i promjenjivom pH. Da bi se mogla pratiti promjena koncentracije bakra u otopini u određenim vremenskim intervalima uzimani su uzorci otopine volumena 0.0015 L. Koncentracija bakra u otopini mjerena je na UV/Vis spektrofotometru.

Količina bakra na zeolitu određena je iz razlike koncentracije bakra u otopine prije i poslije ionske izmjene:

$$q = \frac{(c_0 - c_t)V}{m} \qquad (1)$$

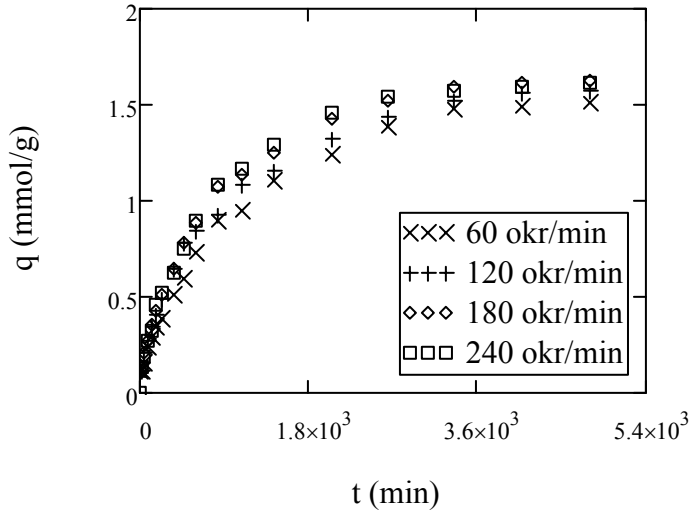
gdje je c_0 - koncentracija otopine metala u trenutku t=0, c_t - koncentracija otopine metala u trenutku t, V - volumen otopine metala, m - masa zeolita.

3. REZULTATI I RASPRAVA

Najvažnija značajka reakcija u heterogenom sustavu je prisutnost fizičkih procesa prijenosa tvari (difuzija) uz kemijsku reakciju (ionsku izmjenu). Brzina ionske izmjene će stoga ovisiti o brzinama fizičkog prijenosa tvari i same ionske izmjene. S obzirom na utjecaj brzina pojedinih procesa, razlikuju se tri reakcijska područja: područje međufazne difuzije kada je najsporiji proces upravo prijenos tvari do granične površine faza, područje unutarfazne difuzije kada je prijenos tvari u poroznoj krutini vrlo spor i kinetičko područje kada je ionska izmjena najsporija.

Utvrđivanje reakcijskog područja u pravilu se svodi na određivanje najsporijeg procesa koji određuje ukupnu brzinu heterogene reakcije. U ovom radu najsporiji proces je određen na osnovu eksperimentalnih istraživanja u kojima se izučavao utjecaj brzine miješanja i veličine čestica na izmjenu bakra.

3.1. Utjecaj brzine miješanja i veličine čestica na brzinu ionske izmjene bakra
Sa slike 1. na kojoj je prikazan utjecaj brzine miješanja na brzinu ionske izmjene može se vidjeti da se povećanjem brzine miješanja skraćuje vrijeme potrebno za uspostavu ravnoteže. Razlog tomu je što se povećanjem brzine miješanja smanjuje debljina filma oko čestice zeolita što dovodi do porasta količine izmijenjenih iona bakra u jedinici vremena. Kada daljnjim povećanjem brzine miješanja više ne dolazi do povećanja količine izmijenjenih iona, u jedinici vremena, postignuta je minimalna debljina filma te difuzija kroz film više nije najsporiji proces. [5,6] Kod ovih ispitivanja to je postignuto za brzine miješanja od 180 okr/min naviše.

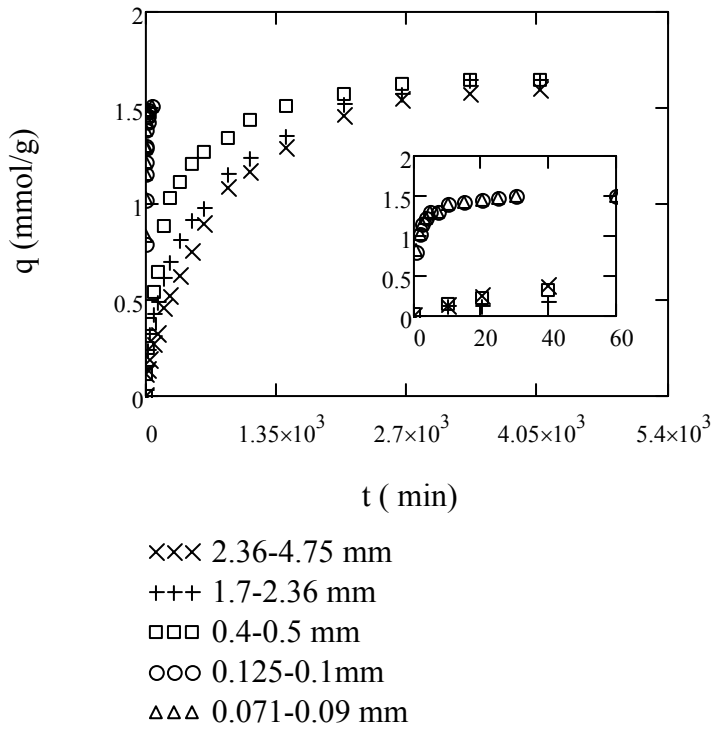


Slika 1. Utjecaj brzine miješanja na količinu izmijenjenih iona i brzinu ionske izmjene (c_0 = 9.814 mmol/L; T = 298 K, d = 2.36 -4.75 mm)

Sa slike 2. na kojoj je prikazan utjecaj veličine čestica zeolita na brzinu izmjene može se vidjeti da smanjenjem veličine čestica smanjuje se i vrijeme potrebno za uspostavu ravnoteže. Za uspostavu ravnoteže na česticama veličine 1.7-2.36 mm potrebno je 4080 min, a na česticama veličine 0.4-0.5 mm 3360 min. Razlog tomu je što se smanjenjem veličine čestica skraćuje difuzijski put iona kroz česticu zeolita te ubrzava ionska izmjena. U slučaju da se daljnjim usitnjavanjem čestica ne povećava brzina ionske izmjene postignuto je kinetičko područje izmjene odnosno sama izmjena je postala najsporiji proces.[5-7] Promjena reakcijskog područja, od unutarfazne difuzije na ionsku izmjenu, može se uočiti na česticama manjim od 0.125 mm. Za ove veličine čestica uspostava ravnoteže traje 30 min (manja slika) i daljnjim usitnjavanjem čestica se ne smanjuje se vrijeme uspostave ravnoteže.

Sama veličina čestice nama znatnog utjecaja na kapacitet ionske izmjene jer su kationska mjesta koja određuju kapacitet izmjene smještena u porama i kanalima zeolita, a ne na njegovoj površini.

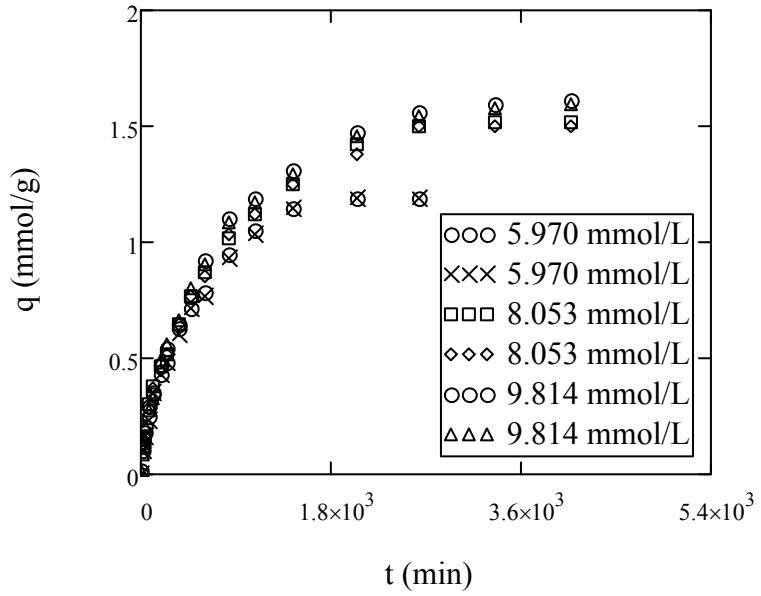
Iz ovih eksperimentalnih istraživanja utvrđeno je da se utjecaj otpora prijenosu tvari kroz film (međufazna difuzija) može zanemariti za brzine miješanja veće od 180 okr/min (slika 1.), a difuzija kroz česticu (unutarfazna difuzija) za čestice zeolita manje od 0.125 mm (slika 2.).



Slika 2. Utjecaj veličine čestica na količinu izmijenjenih iona i brzinu ionske izmjene (c_0 = 9.814 mmol/L; T = 298 K, N = 240 okr/min)

3.2. Utjecaj početne koncentracije na brzinu ionske izmjene te testiranje Weber-Morrisovog modela

Utjecaj početne koncentracije bakra u otopini na vrijeme uspostave ravnoteže i kapacitet izmjene bakra na zeolitu 13X prikazan je na slici 3. (za svaku koncentraciju prikazana je i ponovljivost rezultata, pa je prilikom izračuna konstanti brzine unutarfazne difuzije odnosno koeficijenata difuzije korištena srednja vrijednost dvaju istovjetnih pokusa).



Slika 3. Utjecaj koncentracije na količinu izmijenjenih iona i brzinu ionske izmjene (T = 298 K, N = 240 okr/min, d = 2.36 -4.75 mm)

Sa slike 3. se može vidjeti da vrijeme potrebno za uspostavu ravnoteže kao i kapacitet izmjene rastu porastom početne koncentracije. Za uspostavu ravnoteže, kod početne koncentracije od 5.97 mmol/L potrebno je 1440 minuta, a kod 9.814 mmol/L 3360 minuta dok kapacitet izmjene raste od 1.202 mmol/g na 1.559 mmol/g. Pri tome je potrebno napomenuti da maksimalni eksperimentalni kapacitet izmjene korištenog zeolita na 298 K iznosi 1.668 mmol/g (podaci se odnose na veličinu čestica od 0.06-0.1 mm i vrijeme kontakta od 48h).[8]

Sa slike 3. moguće je sagledati i utjecaj vremena kontakta na izmjenu bakra na zeolitu 13X pri čemu se može zaključiti da je izmjena bakra u početnom periodu brza, nakon čega nagli porast količine izmijenjenog bakra prelazi u postupan do uspostave ravnoteže. Ove promjene u brzini izmjene vjerojatno su posljedica duljine difuzijskog puta (uz pretpostavku da se izmjena odvija od površine čestice prema središtu), trenutačnog broja slobodnih mjesta na kojima se vrši izmjena kao i vrijednosti koncentracijskog gradijenta. Dobiveni rezultati su u suglasju s rezultatima istraživanja Kardaga i sur. te Du i sur. koji su između ostalog ispitivali utjecaj početne koncentracije na izmjenu NH_4^+ na turskom odnosno kineskom klinoptilolitu te s rezultatima Sheha i sur. koji su ispitivali utjecaj početne koncentracije kod izmjene Cr^{6+} na ionizmjenjivačkoj smoli.[9-11]

Weber-Morrisov model se temelji na linearnoj ovisnosti količine uklonjenog metala s drugim korijenom vremena (graf: q - $t^{1/2}$) tj.

$$q = I + k_{WM} t^{1/2} \qquad (2)$$

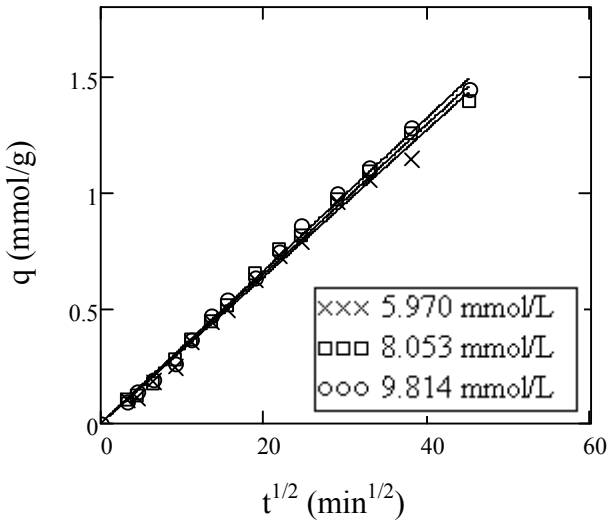
gdje je k_{WM} - konstanta brzine unutarfazne difuzije; t - vrijeme; I - odsječak pravca (I=0 - kontrolirajući mehanizam je difuzija kroz česticu, I>0 - kontrolirajući mehanizam je i difuzija kroz film i difuzija kroz česticu).[12]

Korištenjem Weber - Morrisova modela može se izračunati i efektivni koeficijent difuzije (Crank, 1975.): [12]

$$D_{WM} = \pi \left(\frac{d_p k_{WM}}{12 q_e} \right)^2 \qquad (3)$$

gdje je D_{WM} - efektivni koeficijent difuzije, d - promjer čestice; q_e - ravnotežni kapacitet izmjene.

Metodom najmanjih kvadrata za linearne ovisnosti q - $t^{1/2}$ prikazane na slici 4., izračunat je nagib pravca tj. k_{WM}. Kao što se može vidjeti iz vrijednosti izračunatih koeficijenata determinacije, koji su prikazani u Tablici 2., kao i s grafova na slici 4., ovaj model dobro opisuje eksperimentalne podatke pa se može koristiti i za izračun efektivnog koeficijenta unutarfazne difuzije. Efektivni koeficijenti difuzije izračunati su korištenjem izraza (3) pri čemu je za promjer čestice zeolita uzeta srednja vrijednost.
Sa slike 4., može se uočiti i da regresijski pravci prolaze kroz ishodište (I=0) potvrđujući unutarfaznu difuziju najsporijim procesom na česticama veličine 2.36-4.75 mm uz dane radne uvjete. Ova provjera je potrebna za slučaj da je miješanje postiglo svoju graničnu hidrodinamičku efikasnost. Tada povećanje brzine miješanja neće utjecati na povećanje brzine izmijene iako je najsporiji proces i dalje difuzija kroz film.[13]



Slika 4. Procjena valjanosti Weber-Morrisova modela s eksperimentalnim podacima dobivenim pri različitim početnim koncentracijama bakrovog (II) nitrata (T = 298 K, N = 240 okr/min, d = 2.36 -4.75 mm)

Tablica 2. Konstanta brzine unutarfazne difuzije, efektivni koeficijenti unutarfazne difuzije i koeficijenti determinacije za izmjenu bakra na zeolitu 13X pri različitim početnim koncentracijama

Model	Parametar	Koncentracija		
		5.970 mmol/L	8.053 mmol/L	9.814 mmol/L
Weber Morrisov model	k_{WM} mmol/g $min^{1/2}$	0.0318	0.0325	0.0329
	$D_{WM}x10^{10}$ m^2/min	1.871	1.164	1.177
	R^2	0.992	0.977	0.988

4. ZAKLJUČAK

Cilj ovog rada bio je ispitati utjecaj brzine miješanja, veličine čestica zeolita i početne koncentracije na vrijeme uspostave ravnoteže i kapacitet ionske izmjene bakra na zeolitu 13X. Na osnovu dobivenih eksperimentalnih i računskih rezultata možemo zaključiti slijedeće:
Svi ispitivani parametri imaju utjecaja na brzinu uspostave ravnoteže.
Vrijeme uspostave ravnoteže raste porastom veličine čestice i početne koncentracije, a opada porastom brzine miješanja.
Na kapacitet izmjene utjecaj ima samo početna koncentracija bakra s tim da porastom početne koncentracije raste i kapacitet izmjene.
Za čestice veličine 2.36 - 4.75 mm i brzinu miješanja od 240 okr/min unutarfazna difuzija je najsporiji korak, a izračunati efektivni koeficijenti difuzije reda 10^{-10} m^2/min.

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KINETIC ANALYSIS OF CINK UPTAKE ON FIXED BED OF NATURAL ZEOLITE

KINETIČKA ANALIZA VEZANJA CINKA NA NEPOMIČNOM SLOJU ZEOLITA

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Izvorni znanstveni rad / Original scientific paper

Abstract: In this paper has been investigated the effect of zeolite bed depth on zinc removal from aqueous solutions by the column method. The zeolite bed depth in a column of defined diameter must be selected in such a way that it ensures good wetting and sufficient contact time of the zeolite – zinc solution at a constant flow rate and particles size. The experimental results indicate that the increase of bed depth delays the breakthrough point and exhaustion point. When bed depth increases and the flow rate remains constant, the contact time between the zinc solution and zeolite increases, also increasing the height of the mass transfer zone h_z and column efficiency η.
The bed depth/service time (BDST) model was used to evaluate the time at which the concentration of zinc in the effluent will not exceed the defined value, or defined cink removal percentage. For that purpose, experimentally obtained breakthrough curves were tested by the BDST model, for different zinc removal percentages of 95, 70, 50, 20, and 5 %. Slopes and intercepts of these BDST lines were used to calculate the characteristic parameters of the model, zinc removal capacity on zeolite and rate constant. The values obtained for capacity are of the same order of magnitude, and show good correspondence with experimental capacities in the exhaustion point.
Keywords: kinetic, zinc, natural zeolite, column method, BDST model.

Sažetak: U ovom radu ispitan je utjecaj visine sloja zeolita na uklanjanje cinka postupkom u koloni. Visina sloja zeolita u koloni određenog promjera mora biti tako odabrana da uz konstantan protok i veličinu čestica osigurava dobro kvašenje i dovoljno vrijeme kontakta zeolit - otopina cinka. Eksperimentalni rezultati pokazuju da s porastom visine sloja točke proboja i točke zasićenja se pomiču prema većim vrijednostima volumena i vremena. Porastom visine sloja uz isti protok povećava se vrijeme kontakta otopina cinka - zeolit, a visina zone prijenosa tvari h_z i efikasnost kolone η rastu.
Korištenjem BDST (engl. bed depth service time) modela može se procijeniti vrijeme rada kolone za koje se postiže odabrana koncentracija cinka u efluentu, odnosno odabran postotak uklanjanja cinka na zeolitu. U tu svrhu su eksperimentalno dobivene krivulje proboja testirane prema BDST modelu, i to za postotke uklanjanja cinka od 95, 70, 50, 20 i 5 %. Iz nagiba i odsječaka pravaca BDST modela su izračunati karakteristični parametri modela, kapacitet vezanja cinka na zeolitu i konstanta brzine. Dobivene vrijednosti kapaciteta su istog reda veličine, te pokazuju dobra slaganja s eksperimentalno određenim kapacitetima u točki iscrpljenja.

Ključne riječi: kinetika, cink, prirodni zeolit, postupak u koloni, BDST model.

1. UVOD

Industrijski procesi završne obrade metala i galvanizacije, rudarstvo, kemijska sredstva za zaštitu bilja, promet, komunalni otpad su tipični primjeri antropogenih izvora onečišćenja okoliša s teškim metalima. Kroz kontaminacijski lanac teški metali onečišćuju tlo, vodu i atmosferu. Stoga je nužna stalna kontrola industrijskih ispusta otpadnih voda i smanjivanje koncentracija metalnih iona do maksimalno dopuštenih vrijednosti. Pročišćavanje otpadnih voda onečišćenih s teškim metalima u visokim koncentracijama provodi se kemijskim taloženjem. Uklanjanje do vrlo niskih koncentracija postiže se postupcima trećeg stupnja obrade, poput ionske izmjene i adsorpcije, elektrodijalize, membranskih tehnika [1]. Znanstvena istraživanja posljednjih godina su usmjerena prema pronalaženju različitih jeftinih prirodnih materijala s dobrim adsorpcijskim i ionoizmjenjivačkim svojstvima. Upravo se prirodni zeolit pokazao efikasnim za uklanjanje teških metala, cinka, olova, bakra, kadmija, itd. iz vodenih otopina.

Rezultati naših prethodnih istraživanja ukazuju na mnoge prednosti primjene kontinuiranog postupka u koloni u obradi otpadnih voda [2]. Specifičnost izvedbe postupka u koloni je mogućnost regeneracije zeolita za više ciklusa izmjene. To dopušta višestruko korištenje iste mase zeolita, te obradu veće količine otpadnih voda.

Visina sloja zeolita utječe na vrijeme kontakta između otopine i zeolita, mogućnost stvaranja kanalića u sloju te na aksijalnu disperziju u sloju. Stoga su omjeri visine sloja prema promjeru kolone (H/D) i promjeru čestice zeolita (H/d) vrlo važni parametri pri dizajniranju kolone [3]. U ovom radu ispitan je utjecaj visine sloja zeolita na vezanje cinka postupkom u koloni. U primjeni, vrlo je važno predvidjeti vrijeme rada kolone u kojem se postiže odabran postotak uklanjana cinka na zeolitu. U tu svrhu su eksperimentalni podaci testirani prema BDST kinetičkom modelu.

2. EKSPERIMENT

Priprema uzorka zeolita

Prirodni zeolit porijeklom je iz nalazišta Vranjska Banja (Srbija). Uzorak je usitnjen i prosijan na frakciju veličine čestica 0.6-0.8 mm. Zatim je preveden u Na-oblik prema proceduri opisanoj u prethodnom radu [4].

Kemijski sastav Na-oblika uzorka zeolita određen je klasičnom kemijskom analizom alumosilikata [5]. Izražen u mas. % iznosi: SiO_2 – 65.15; Al_2O_3 –11.56; Fe_2O_3 - 1.35; MgO - 1.76; CaO – 0.91; K_2O - 0.72; Na_2O – 4.40; gubitak žarenjem -11.66.

Kvalitativna mineraloška analiza određena je rendgenskom difrakcijom, a izvedena je na difraktometru tipa “Philips-CubiX XRD” (CuKα , 2θ = 0-60, 0.03 2θ/s). Glavna zeolitna mineralna komponenta je klinoptilolit čiji je udio u uzorku ≈ 80 %.

Priprema otopina

Otopina cinka priprema se otapanjem odgovarajuće količine soli $ZnSO_4 \cdot H_2O$. Točna koncentracija cinka određena je kompleksometrijskom titracijom u kiselom mediju (pH =5-6), korištenjem visokoselektivnog indikatora 3,3 dimetildinaftidina [6], i iznosi $c_o(Zn)$ = 1.083 mmol/l.

Otopina sredstva za regeneraciju koncentracije od $c_o(Na)$ = 105.60 mmol/l priprema se otapanjem soli Na_2SO_4 u redestiliranoj vodi.

Izvedba postupaka u koloni

Radni ciklus

Eksperimenti su provedeni u staklenim kolonama unutarnjeg promjera 12 mm s visinom sloja zeolita od 120, 80 i 40 mm, uz istu početnu koncentraciju od c_o(Zn) = 1.083 mmol/l i protok otopine cinka od Q =1 ml/min. Postupak u koloni proveden je izotermno (T = 23 ^oC), propuštanjem otopine s vrha kolone kroz sloj zeolita (down flow mode). U izlaznoj se otopini (efluentu) u odabranim vremenskim intervalima određivao cink kompleksometrijski [6]. Postupak se prekidao kad se koncentracija cinka u efluentu izjednačila s početnom koncentracijom otopine (influentom). Stalnost protoka održavana je vakuum pumpom.

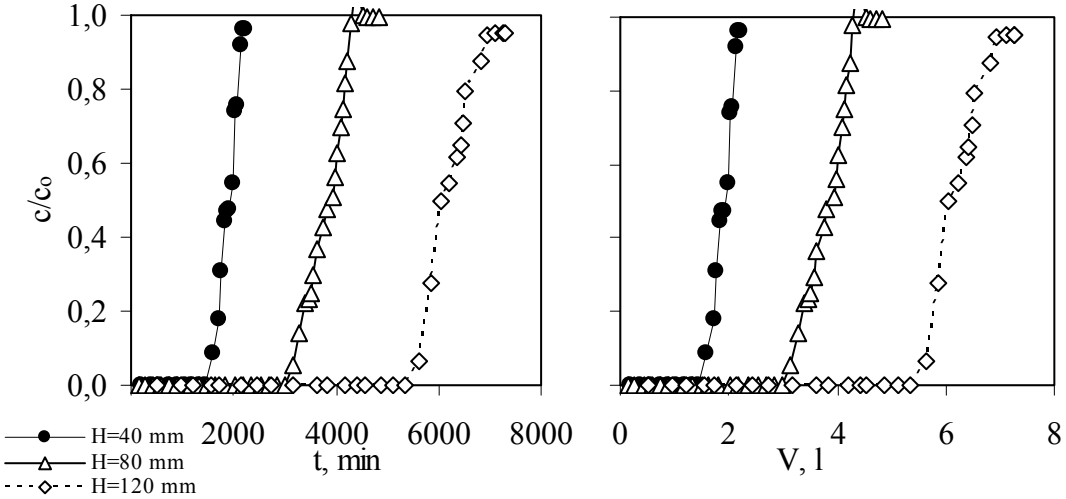
Ciklus regeneracije

Nakon svakog radnog ciklusa provodio se ciklus regeneracije s otopinom natrijeva suflata, početne koncentracije c_o(Na) = 105.60 mmol/l i protoka od Q = 1 ml/min, propuštanjem otopine također s vrha kolone kroz sloj zeolita (down flow mode).

3. REZULTATI I RASPRAVA

Utjecaj visine sloja

Odabir visine sloja u koloni određenog promjera, uz konstantan protok i veličinu čestica, mora biti takav da osigura dobro kvašenje i dovoljno vrijeme kontakta zeolit - otopina cinka, te smanji utjecaj aksijalne disperzije na prijenos tvari u koloni. Da bi se to postiglo, potrebno je da je odnos visine sloja prema promjeru čestica zeolita (H/d) veći od 20 [3]. U ovom radu su odabrane tri visine sloja zeolita od 40, 80 i 120 mm, a veličina čestica je takva da je u svim slučajevima odnos visine sloja prema veličini čestica zeolita (H/d) veći od 20.



Slika 1. Krivulje proboja vezanja cinka za tri različite visine sloja zeolita, prikazane kao ovisnost c/c_o o t i c/c_o o V.

Na slici 1. uočava se utjecaj visine sloja kako na vrijeme, tako i na volumen otopina efluenta do točke proboja i točke zasićenja. Sa smanjenjem visine sloja točke proboja i točke zasićenja se pomiču prema manjim vrijednostima vremena i volumena. Iz eksperimentalno dobivenih krivulja proboja izračunati su karakteristični parametri, a prema izrazima objavljenim u prethodnom radu [2]. Rezultati su prikazani u tablici 1.

Tablica 1. Karakteristični parametri krivulja proboja vezanja cinka na zeolitu za različite visine sloja zeolita.

H mm	V_B l	t_B h	q_B mg Zn /g	q_E mg Zn /g	η -	F -	h_z mm	EBCT min
120	5.360	89.33	39.51	45.25	0.87	0.445	34.2	13.56
80	3.150	52.50	37.80	51.36	0.74	0.636	20.8	9.04
40	1.595	26.58	38.78	45.98	0.84	0.520	12.3	4.52

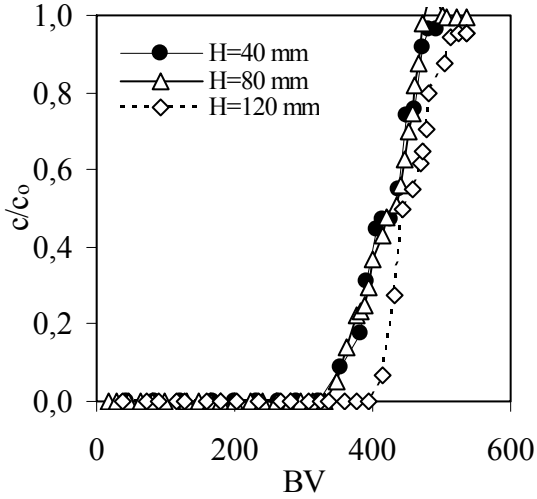
Napomena: V_B - volumen u točki proboja; t_B - vrijeme u točki proboja; q_B – kapacitet u točki proboja, q_E – kapacitet u točki zasićenja, η - efikasnost (q_B/q_E), F –parametar simetrije krivulje proboja, h_z - visina zone prijenosa tvari, EBCT - vrijeme kontakta (engl. empty bed contact time).

Na slici 2. su prikazane krivulje proboja kao ovisnost c/c_o o BV, pri čemu je BV:

$$BV = \frac{V}{V_S} \tag{1}$$

gdje je:

BV- broj volumena sloja, -
V - volumen efluenta, l
Vs - volumen sloja zeolita, l.



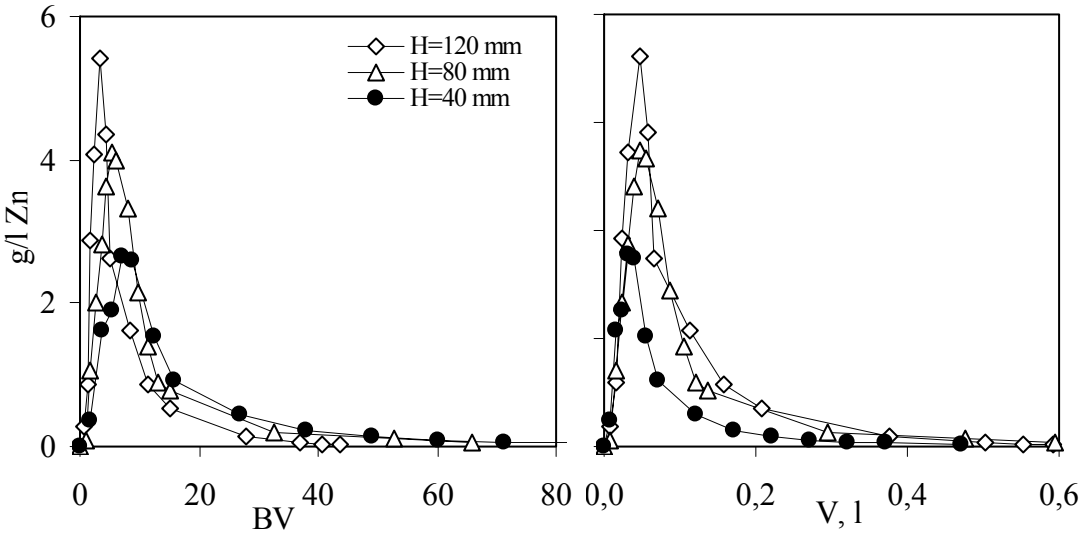
Slika 2. Krivulje proboja prikazane kao ovisnost c/c_o o BV.

Iz slike 2. i podataka u tablici 1. uočava se da s porastom visine sloja, točke proboja izražene preko BV vrijednosti neznatno rastu (352.9, 384.3 i 395 BV). To znači da s porastom visine sloja proporcionalno raste i volumen otopine cinka obrađen do točke proboja, pa su i razlike u vrijednostima kapaciteta u točki proboja (q_B) i točki iscrpljenja (q_E) pri tri visine sloja neznatne.

Veća visina sloja zeolita odražava se na duže vrijeme kontakta, EBCT [2], te porast visine zone prijenosa tvari h_z i efikasnosti kolone η. S porastom visine sloja, uz istu veličinu čestica zeolita u sloju, smanjuje se utjecaj aksijalne disperzije na prijenos tvari u koloni, a krivulja je strmija (Slika 2).

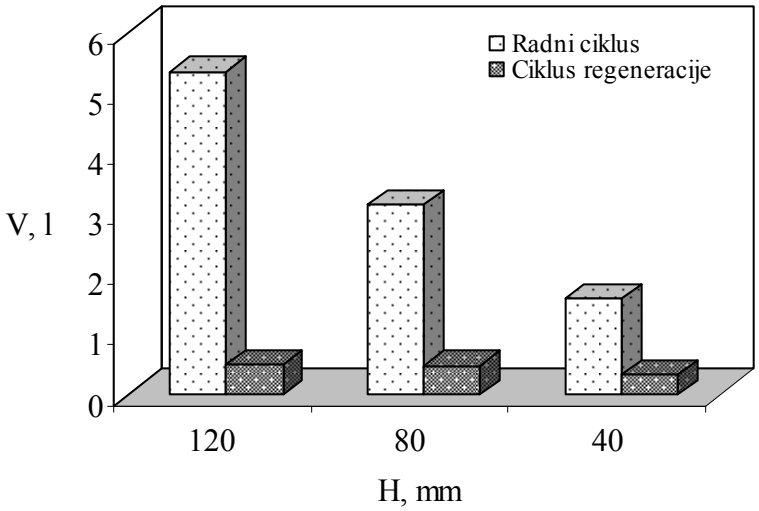
Na slici 3. prikazane su krivulje regeneracije za tri različite visine sloja. Uočava se da su krivulje regeneracije vrlo slične. Prvo pokazuju nagli skok u koncentraciji cinka u efluentu, a zatim nagli pa lagani pad. Skok u koncentraciji cinka u efluentu raste s porastom visine sloja zeolita u koloni, jer se i veća količina cinka vezala na zeolitu u radnom ciklusu.

Volumeni otopine za regeneraciju potrebni za potpunu regeneraciju sloja zeolita rastu s porastom visine sloja, sa 0.332 l na 0.476 l i 0.502 l. Preračunato na BV, ti volumeni iznose 71 BV, 52 BV i 37 BV, tj. opadaju s porastom visine sloja.



Slika 3. Krivulje regeneracije za tri visine sloja zeolita, izražene kao g Zn/l o BV i g Zn/l o V.

Na slici 4. data je usporedba volumena otopine cinka obrađene u radnom ciklusu do točke proboja s volumenom otopine dobivene regeneracijom. Uočava se da je za sve tri visine sloja volumen regenerata za oko 7 puta manji od volumena obrađene otopine cinka, pa se za isti iznos povećava i koncentracija cinkovih iona.



Slika 4. Usporedba volumena otopine obrađene u radnom ciklusu i volumena otopine dobivene regeneracijom, za tri visine sloja.

Kinetička analiza krivulja proboja prema BDST modelu

Eksperimentalne točke krivulja proboja testirane su prema BDST modelu. BDST model su izvorno izveli Bohart & Adams za adsorpciju na aktivnom ugljenu. Temelji se na pretpostavci da je brzina adsorpcije određena površinskom reakcijom između adsorbata i neiskorištenog kapaciteta adsorbensa, i data je sljedećom jednadžbom [7, 8]:

$$\ln(\frac{c_o}{c_t} - 1) = \ln(e^{(k_a \cdot q_{BA} \cdot \frac{H}{v})} - 1) - k_a \cdot c_o \cdot t \,. \qquad (2)$$

Kako je član $e^{(k_a \cdot q_{BA} \cdot \frac{H}{v})}$ znatno veći od 1, to se jednadžba (2) može pojednostaviti u oblik:

$$\ln(\frac{c_o}{c_t} - 1) = \ln e^{(k_a \cdot q_{BA} \cdot \frac{H}{v})} - k_a \cdot c_o \cdot t \qquad (3)$$

gdje je:

- t - vrijeme, h
- c_o – početna koncentracija otopljene tvari u influentu, mmol/l
- c_t – koncentracija otopljene tvari u efluentu u vremenu t, mmol/l
- q_{BA} – količina adsorbirane tvari u vremenu t, mmol/l
- H – visina sloja adsorbensa u koloni, m
- k_a – konstanta brzine, l / mmol h.
- v – linearna brzina otopine kroz sloj, m/h.

Jednadžba (3) primijenjena je na sustav zeolit-otopina cinka, i njenim rješavanjem po vremenu t, dobije se:

$$t = \frac{q_{BA}}{c_o \cdot v} \cdot H - \frac{1}{k_a \cdot c_o} \ln (\frac{c_o}{c_t} - 1) \qquad (4)$$

gdje je:

- c_o – početna koncentracija cinka u influentu, mmol/l
- c_t – odabrana koncentracija cinka u efluentu u vremenu t, mmol/l
- q_{BA} – kapacitet vezanja cinka na zeolitu, mmol/l
- H – visina sloja zeolita u koloni, m.

Pri tom se vrijednost q_{BA} preračunava na vrijednost q prema sljedećoj jednadžbi:

$$q = \frac{q_{BA} \cdot V_S \cdot M_{Zn}}{m} = \frac{q_{BA} \cdot M_{Zn}}{\rho} \qquad (5)$$

where:

- q - kapacitet vezanja cinka na zeolitu, mg/g
- m - masa sloja zeolita u koloni, g
- M_{zn} - molrna masa cinka, mg /mmol
- ρ - gustoća sloja zeolita, g/l.

Rješavanjem jednadžbe (4) po visini H, i za vrijednost t = 0, dobije se:

$$H_o = \frac{v}{k_a \cdot q} \ln(\frac{c_o}{c_t} - 1) \qquad (6)$$

gdje je:

H_o - kritična visina sloja, odnosno minimalna visina sloja zeolita u koloni koja je potrebna da koncentracija cinka u efluentu ne prijeđe vrijednost c_t u vremenu t = 0 [9].

Jednadžba (4) se pojednostavljeno može prikazati:

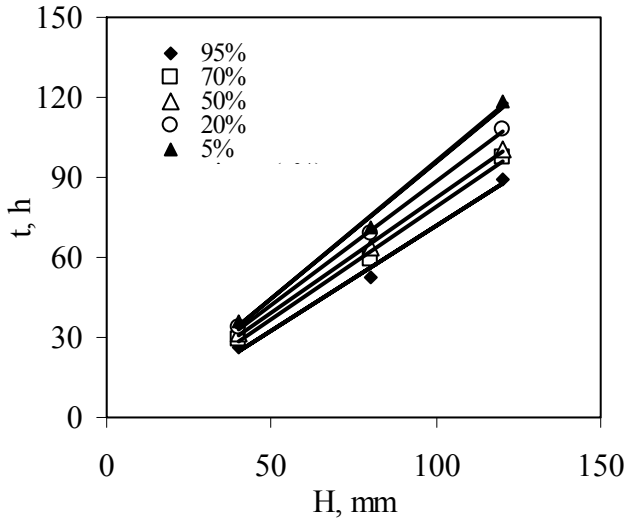
$$t = a \cdot H - b \tag{7}$$

u kojoj su a i b nagib, odnosno odsječak pravca:

$$a = \frac{q}{c_o \cdot v} \tag{8}$$

$$b = -\frac{1}{k_a \cdot c_o} \ln\left(\frac{c_o}{c_t} - 1\right) . \tag{9}$$

Jednadžba (4) omogućava određivanje vremena t za koje se, pri datoj visini sloja H, postiže odabrana koncentracija c_t u efluentu, odnosno odabran postotak uklanjanja. Vrijednosti q i k_a se trebaju odrediti eksperimentalno za što širi interval protoka, odnosno linearnih brzina otopine kroz sloj. U tu svrhu bilo bi potrebno za svaku visinu sloja odrediti krivulje proboja za tri protoka otopine, što znači da bi trebalo provesti devet radnih ciklusa. To je vremenski dugotrajno i skupo. Hutchins [7] je predložio proceduru prema kojoj se primjena Bohart-Adamsove jednadžbe može provesti uz samo tri eksperimenta pri tri visine sloja uz isti protok. U skladu s tim su iz krivulja proboja prikazanih na slici 1. očitane vrijednosti vremena za postotke uklanjanja cinka na zeolitu od 95, 70, 50 i 30 i 5 % za svaku visinu sloja zeolita 40, 80, 120 mm. Iz očitanih vrijednosti vremena za svaku visinu sloja su provučeni pravci, a prikazani su na slici 5.



Slika 5. Pravci dobiveni obradom krivulja proboja prema BDST modelu.

U tablici 2. su prikazane jednadžbe pravaca. Dobivene vrijednosti korelacijskog koeficijenta R^2 veće od 0.990 ukazuju na pouzdanost primjene BDST modela na sustav vezanja cinka na zeolitu postupkom u koloni. Iz nagiba BDST pravaca korištenjem jednadžbe (8) izračunat je kapacitet vezanja cinka na zeolitu q. Konstanta brzine (k_a) izračunata iz odsječka BDST pravca korištenjem jednadžbe (9) predstavlja konstantu brzine vezanja cinka na zeolitu (tablica 2).

Tablica 2. Parametri BDST modela.

% uklanjanja	H=40 mm	H=80 mm	H=120 mm	BDST jednadžba	R^2	k_a, l/mmol h	q_{BA} mmol/l	q mg/g	H_o, mm
	Vrijeme, h								
95	26.58	52.50	89.33	t = 0.784 H -6.61	0.990	0.410	452.56	44.22	8.43
70	29.58	59.33	97.50	t = 0.849 H -5.78	0.995	0.221	489.84	47.86	6.81
50	31.33	63.50	100.58	t = 0.885 H -4.11	0.998	0.009	499.41	48.80	4.75
20	33.83	68.83	107.92	t = 0.926 H - 3.90	0.999	-	531.72	51.96	-
5	36.33	71.33	118.50	t = 1.027 H -6.78	0.993	-	592.59	57.90	-

Napomena: za postotak uklanjanja od 20 i 5 %, izračunate vrijednosti za k_a i H_o poprimaju negativne i nerealne vrijednosti.

Uočava se da su za sve postotke uklanjanja cinka na zeolitu dobivene vrijednosti kapaciteta istog reda veličine, i da pokazuje dobra slaganja s eksperimentalno određenim kapacitetima u točki iscrpljenja, q_E (tablica 2.). To ukazuje da se temeljem izračunatih parametra modela mogu procijeniti krivulje proboja pri drugim radnim uvjetima bez dodatnog provođenja eksperimenta.

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DETERMINATION OF THERMAL CONDUCTIVITY BY TRANSIENT HOT WIRE METHOD

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Abstract

Thermal property data are important for the engineering solutions of the heat transfer problems. There are many cases in which thermal conductivity of the studied material is not available, eg. cement materials of different compositions during setting and hardening. Furthermore, these materials are wet and porous and in order to prevent development of humidity gradients under imposed thermal gradients, one finds transient measurement methods as preferable.

This work describes a developed apparatus and a transient Hot Wire (HW) method to obtain the thermal conductivity of dry and wet materials. Single, thin platinum wire is used as both a constant power heater and temperature sensor. The result obtained from measurement is the temperature development of the HW during heating period, which is described by a theoretical model. The thermal conductivity of the material under study is obtained by the solution of the parameter estimation problem, utilizing the Levenberg-Marquardt method of optimization. The results of the method evaluation on reference materials indicated an accuracy of 3% and a uncertainty of 0.7% (for 95% confidence). The reference materials used were gelatinous water (Agar gel 0.7%), glycerol and Ottawa (quartz) sand. The values of the thermal conductivity for fresh calcium aluminate cement pastes with water to cement mass ratio of 30 and 40 % are documented. The systematic error arising due to the measured sample electrical conductivity is calculated to be less than 0.5% for the experimental configuration used.

Keywords: thermal conductivity, hot wire method, reference materials, electrical conductivity, calcium aluminate cement.

1. Introduction

Material thermal property data are important for the engineering solutions of the heat transfer problems. Measurements of thermal properties of heterogeneous, wet and porous materials by conventional steady-state methods are subject to large errors. In order to avoid water migration during the run-time of the thermal tests, transient measurement methods are preferable [**1**, **2**]. The determination of thermal conductivity is very challenging since it belongs to a class of inverse problems where an estimated parameter is very sensitive to measured quantities necessary for its calculation. The hot wire method [**1**] involves an ideal line heat source, infinitely long with zero mass, immersed in an infinite sample. As the parallel wire method is very sensitive to the uncertainty of measuring the radial distance of a thermocouple from a heater, a resistance technique is employed. Furthermore, by this method, where the wire acts as both a heater and a resistance thermometer, the influence of local non-homogeneities of measured materials is minimized. Thermal conductivity is determined by inverse solution of the differential equation for radial heat conduction. In order to minimize errors due to an approximation of the used model and effects of the experimental setup a critical design of an experimental configuration is necessary.

This work describes a developed apparatus and a method to obtain a thermal conductivity of dry and wet materials. The systematic error due to a electrical conductivity of cement paste is minimized by the used experimental configuration. The values of the thermal conductivity for fresh calcium aluminate cement (CAC) pastes are documented to the best of our knowledge for the first time and compared to the available literature data on portland cement. Research on thermal properties of CAC is particularly interesting due to rapid heat generation during hydration and development of significant temperature gradient in material [**3**, **4**].

2. Hot wire model

When a heat generation is applied to the line heat source, its temperature response is based on an analytical solution [**5**] to the heat conduction model given in cylindrical coordinates:

$$\Delta T\left(r,t\right)_{t=0}^{t=t} = \frac{q}{4\pi\lambda}\left[-E_i \cdot \left(-\frac{r^2}{4at}\right)\right] \qquad (1)$$

where λ is the thermal conductivity of sample ($Wm^{-1}K^{-1}$), r is the radius of the wire (m) a is thermal diffusivity of sample (m^2s^{-1}), t is time (s), q is rate of heat generation (W/m) and E_i is the exponential integral computed as:

$$E_i(-z) = \gamma + \ln z + z - \frac{z^2}{2!} + \frac{z^3}{3!} - \frac{z^4}{4!} + ... \qquad (2)$$

in which $\gamma = 0.5772...$ is Euler's constant and $z = r^2/(4at)$.

3. Experiment

3.1. Materials

The reference materials used to evaluate the used apparatus and method are gelatinous water (Agar gel 0.7%) and Ottawa sand. For detailed discussion on reference materials used please see further in **3.3** and **4.2.**

Furthermore, this paper documents the thermal conductivities of cement pastes obtained with sample of commercial CAC ISTRA 40 taken from a regular production of Istra Cement International, Pula, Croatia. The cement has the oxide mass fraction composition listed in **Table 1**. Physical properties of used cement are given in **Table 2**. All mixes were prepared with deionized water. The main compounds are CA (cement notation: C=CaO, A=Al_2O_3, F=Fe_2O_3, S=SiO_2, H=H_2O) and ferrite phase (C_4AF-C_6AF_2), with mayenite, $C_{12}A_7$, gehlenite, C_2AS and β-C_2S as minor compounds. Cement pastes with water to cement mass ratio of 0.3 and 0.4 were prepared.

Table 1. Chemical composition of investigated CAC.

CaO	Al_2O_3	Fe_2O_3	FeO	SiO_2	TiO_2	MgO	SO_3	Na_2O	K_2O	Sum
37.10%	38.47%	14.39%	2.90%	4.43%	1.05%	0.90%	0.20%	0.14%	0.17%	99.8%

Table 2. Physical properties of investigated CAC.

>90 µm, %	Blaine, cm^2/g	Specific gravity, g/cm^3	Setting time, min		Standard consistency, %	Bulk density, kg/m^3	
			initial	final		Loose	Compacted
3.76	3401	3.20	298	329	24.0	950	1776

3.2. Measuring device

The thermal conductivity is determined from the time dependant temperature rise of an electrically heated wire. The wire used is 99.99+% platinum (Aldrich) with a diameter $2r$ = 76 µm and length of l = 176 mm. It is desired to have a wire with as small a diameter as possible because the theory assumes a true line heat source. The wire is heated by placing a constant voltage across the bridge, as suggested by Glatzmaier and Ramirez [**6**]. The supplied voltage has an output range of 0 – 25V and is stable to within ±10µV. Change in the wire electrical resistance is determined by measuring the unbalanced voltage of a precision Wheatstone bridge during heating period. This voltage is read by a computer via an 8 channel 10-bit A/D converter. Measuring apparatus is connected to the PC via RS232 protocol that provides the sampling rate of 15ms. Specially designed programs provide control of the automatic measuring apparatus and easy usage. The core of the measuring apparatus is a microcontroler PIC 16F877 which was programmed in MPLab by a direct RISC instructions and ICD-2 programmer/debugger. From the previously obtained resistance versus temperature calibration (least-squares regression) of the used Pt wire the change of the temperature is deduced.

The low temperature rise of hot wire, obtained by applying low input voltage, is desirable in terms of minimizing the effects of natural convection, radiation and/or gas evolution. On the other hand, higher voltage reduces the effect of noise and allow for a more precise temperature measurement. In this work the applied voltage gave temperature rise of 5°C (during 2 min). Only for measurements on glycerol the temperature rise was reduced to 3°C in order to minimize the natural convection effect.

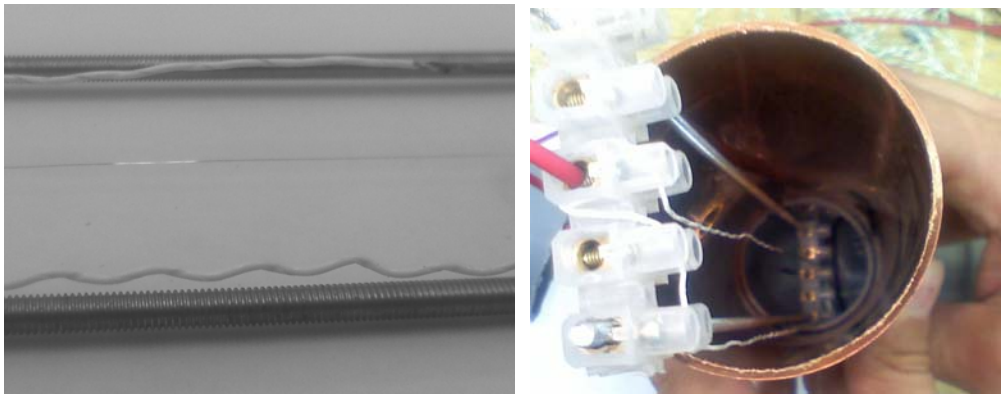

Figure 1. Thermal conductivity measuring setup.

3.3. Experimental setup

The mould containing the investigated sample is obtained in the following manner. The specimens were cast in cylindrical copper containers with inner diameter $2R$ = 51 mm, length 250 mm and thickness of 1 mm. The Pt wire was placed in the center of the tube. A Pt wire supported by a tensioning system is placed in the tube, the frame being next to the inside surface of the copper pipe, **Figure 1**. Also the thermocouple is placed near the tube axis to monitor the temperature of the sample. The copper tube was carefully filled with the sample continuously applying vibrations in order to minimize air entrapment. Copper tube is sealed with styropore and rubber stoppers and placed in the temperature controlled water bath (±0.03°C).

Thermal conductivities of reference materials were determined at 20 °C. Prior to loading the Ottawa sand to mould, it was dried at 105°C. The gelatinous water was prepared by mixing 0.7 % of agar powder by weight with hot (85 °C) deionized water in a laboratory glass. The mixture was heated and stirred vigorously using a magnetic stir hot plate. Once the gel was melted, it was poured into a mold by tapping it to help the air bubbles rise to the surface. The mold was put in a water bath at 20 °C and waited for at least 4 h to attain uniform temperature. The fresh pastes were tested at temperature 20 °C during the period of 1.5 – 2.5 hours after mixing.

4. Results and discussion

4.1. Thermal conductivity determination

Deviations from the idealized model in Eq. (**1**), classified as inner and outer, can be minimized by a proper selection of experimental conditions. Inner deviations arise from the non-ideality of the wire that has finite length, mass and heat capacity. These deviations, which depend on the properties of the wire, have significant impact only on the initial temperature response ($t < t_{min}$). Outer deviations are due to the finite dimensions of the sample and have impact at longer times ($t > t_{max}$) when the outer boundary conditions (of the sample) influence the wire temperature response. The so-called time window defines representative temperature response corresponding to the sample thermal properties. It is estimated by numerical simulation supposing a systematic error of 0.1 % to be between t_{min} = 0.5 s and t_{max} = 120 s. For simulations a numerical model of one dimensional radial heat conduction was built for the used experimental configuration and solved by using

MATLAB®'s built-in solver *"pdepe"* [**7**, **8**]. The model employed two coupled partial differential equations of energy conservation: one for the wire and one for the sample [**9**].

The thermal conductivity was calculated by fitting the experimental results to a theoretical expression (**1**) by using literature values for thermal diffusivity [**10-12**], listed in **Table 3**, and eight terms for calculating the exponential integral according to the Eq. (**2**). This parameter estimation problem was solved by the Levenberg-Marquardt method of optimization [**13**, **14**]. In order to investigate the sensitivity of thermal conductivity and thermal diffusivity a simulation analysis was performed by plotting predicted responses by Eq. (**1**) with ± 10 % change in the investigated parameters. The results on parameter sensitivity analysis, shown in **Fig. 2**, indicate a low impact of thermal diffusivity and good sensitivity of thermal conductivity onto the temperature response (ΔT). Therefore, an uncertainty of value on thermal diffusivity has little impact to estimation of thermal conductivity. Data on thermal diffusivity of fresh cement pastes are taken from independent transient measurements conducted in our laboratory [**15**].

Table 3. Literature data on thermal conductivity and thermal diffusivity at T = 20 °C.

Material	λ / W m^{-1} K^{-1}	a 10^{7} / m^{2}s^{-1}
Ottawa sand	0.306 [**17**]	2.33 [**11**]
Gelatinous water (Agar)	0.5985 [**10**]	1.433[**10**]
Glycerol	0.285 [**12**]	0.962 [**12**]
Fresh cement paste w/c = 0.4	-	2.97 [**15**]
Fresh cement paste w/c = 0.3	-	3.30 [**15**]

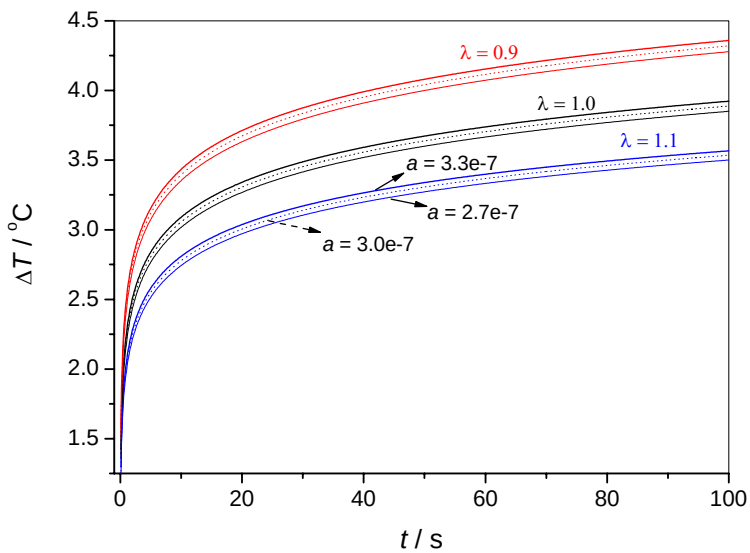

Figure 2. Parameter sensitivity analysis. Impact of ± 10 % change in values of thermal conductivity and thermal diffusivity onto the theoretical temperature response.

4.2. Evaluation on reference materials

The reference materials used to evaluate the used apparatus and method are gelatinous water (Agar gel 0.7%) and Ottawa sand. Ottawa sand consists of spherical grains (high purity silica) with an accurately graded particle size distribution to pass an 850-μ (US Standard No.

20) sieve and to be retained on a 600-μ (US Standard No. 30) sieve. Data on the thermal conductivity of Ottawa sand in air is readily available from several sources, although no specific standard exists for this property.
The solid density of the Ottawa sand was measured by submerging a known mass of sand in water and measuring the volume change of the liquid. The solid density was found to be 2.69 g/cm^3, which is very close to the published value of 2.65 g/cm^3 [**16**]. Knowledge of the bulk density is important because the thermal conductivity can change based on how tightly the sand particles are packed. Measured bulk density of investigated Ottawa sand of 1.650 g/cm^3 is close to the published value of 1.615 g/cm^3 [**17**]. The thermal diffusivity data on Ottawa sand were not readily found in literature. Hence, the used value in Eq. (**1**) is taken for sand in general [**15**]. The density and thermal conductivity of investigated Ottawa sand are 2.64 g/cm^3 and 0.31 Wm^{-1} K^{-1}, which is close to the published value of 2.6 g/cm^3 and 0.3 Wm^{-1}K^{-1} [**15**].

Agar is gel-forming polysaccharide, widely used in industry and in scientific applications. Agar form gels at approximately 35°C and once formed does not melt below 85°C. Gelation occurs when a chain of macromolecules forms a network capable of entrapping the dispersing medium. Such gel has a composition close to a pure liquid but resemble a solid. In that way heat transfer through agar is by conduction solely, excluding natural convection.

A repeatability analysis was conducted on samples by repeating the measurements 10 times. The mean values of the thermal conductivities and estimated precision at a 95 % confidence level are listed in **Table 4**. Very good agreement was found between the results of the experimental investigation and sources of available data. This finding validates the accuracy of the measurement apparatus and provides confidence that further results are accurate. It can be concluded that the results of the method evaluation on reference materials indicated an accuracy of 3 % and uncertainty of 0.7 % (for 95 % confidence).

4.3. Effect of cement paste electrical conductivity

The electrical conductivity of cement paste was measured by conductivity meter (Lab 960 Schott instruments) 0.5 h after mixing cement and water. For cement pastes with water to cement ratio 0.4 and 0.3 the measured electrical conductivities are 1287 μScm^{-1} and 1098 μScm^{-1}, respectively. The resistance of the cement paste sample in a defined geometry (see **3.3**) is calculated by referring to the values of the obtained electrical conductivity. The deviation of the overall electrical resistance (of the parallel system of sample and Pt resistance), R_{II} from the Pt resistance is calculated to be less than 0.5 %.

Hence, in the experimental configuration the systematic error due to the electrical conductivity of cement paste can be assumed to be less than 0.5 %.

4.4. Thermal conductivity of fresh cement pastes

Cement based material is a complex heterogeneous, multiphase and polydisperse system. Through such a material the heat is transferred by a combination of different modes. They include conduction through the solid particles, conduction and convection through the gaseous and liquid phases, evaporation – condensation mechanism [**2**], and radiation at the particle surfaces. However, this overall process is practically modelled solely by a heat conduction model considering the conduction parameters as apparent. Therefore, one should bear in mind that the physical parameters measured in this paper for cement paste and Ottawa sand are more properly called apparent thermal conductivity [**2**]. The values of the thermal

conductivity for fresh calcium aluminate cement pastes obtained show good agreement with the literature values for Portland cement (PC) [**18**], **Table 4**.

Table 4. Measured and published data on thermal conductivity at T = 20 °C.

	λ / W m^{-1} K^{-1}			
Material	Measured	Uncertainty	Reported	Accuracy
Ottawa sand	0.315	0.5 %	0.306 [**17**]	3 %
Gelatinous water (Agar)	0.615	0.7 %	0.5985 [**10**]	3 %
Glycerol	0.290	0.6 %	0.285 [**12**]	2 %
Fresh cement paste w/c = 0.4	0.98	0.7 %	(PC)0.97[**18**]	-
Fresh cement paste w/c = 0.3	1.06	0.6 %	(PC) 0.99 [**18**]	-

An example of a result for estimation of thermal conductivity based on the measured temperature response (cement w/c = 0.4) and the radial heat conduction model (1) is given in **Fig. 3**. A good fit with a standard deviation of 1.9 10^{-2} °C validates the appliance of the heat conduction model used for describing the heat transfer of investigated wet porous materials.

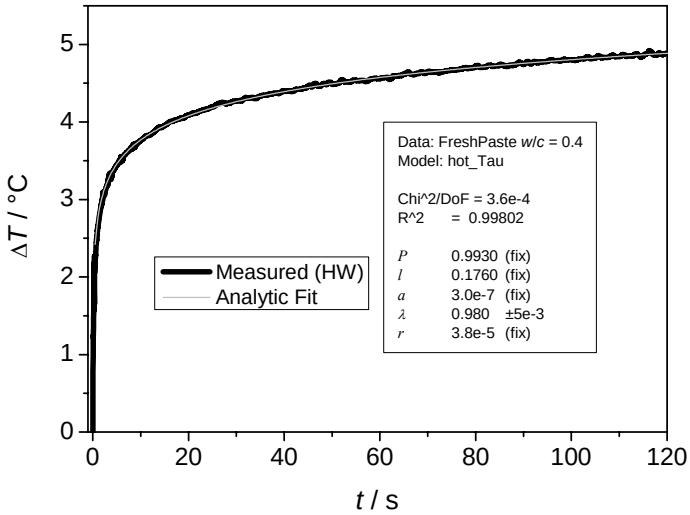

Figure 3. An example of a result for determination of thermal conductivity based on a measured temperature response and the heat conduction model (**1**).

5. Conclusion

In order to minimize errors due to an approximation of the used model and effects of the experimental setup a critical design of an experimental configuration is necessary. The results of the method evaluation on reference materials indicated an accuracy of 3% and uncertainty of 0.7% (for 95% confidence). The values of the thermal conductivity for fresh calcium aluminate cement pastes with water to cement mass ratio of 30 and 40 % are 0.98 W m^{-1} K^{-1} and 1.06 W m^{-1} K^{-1}, respectively.

6. Acknowledgement

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INFLUENCE OF TRANSITION METAL - CHLORIDE SALTS ON CAC HYDRATION

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Abstract: Duration of suitable workability of cement based materials during placement is defined by setting time. The use of adequate set regulators for each application is subject of great practical and financial interest. From the practice, it is known that even a small amount of different organic and inorganic compounds show pronounced influence on setting time of cement materials. In this paper the influence of transition metals in the form of chlorides salts, on the hydration of calcium aluminate cement (Istra 40 manufactured by Istra Cement, Pula, Croatia) had been investigated. The effect has been studied at two temperatures, 14 and 20 ^{o}C with a water to cement mass ratio of 0.25 and 0.40. A simple method of analyzing cement hydration based on the measurement of temperature rise of cement pastes is presented. Times of initial and final sets were established from the obtained time-temperature curves. The results of the setting time obtained from the measured temperature rise of cement pastes were compared to the standard Vicat needle measurements. The composition of cement and hydrates formed had been investigated by powder X-ray diffraction (XRD). Interesting regularity was observed upon plotting the obtained results on setting times vs. atomic number of added cation.

Keywords: setting time, set regulators, calcium aluminate cement, hydration, metal chloride salts, transition metals, X-ray diffraction, temperature measurement.

1. Introduction

In comparison to PC, calcium aluminate cements (CAC) show relatively slow setting but rapid hardening characteristics. As the setting time defines suitable time for workability during placement, the use of adequate set regulators presents potential of practical and financial consequences. An important characteristic of CAC hydration is that the rate of hydration decreases and the setting time increases with increasing temperature up to 30 ^{o}C, above which the hydration accelerates rapidly [**1**]. The set of CAC may be considerably influenced by addition of small quantities of alkali metal salts [**2**]. These additions can interfere with hydration of cement in a variety of ways. A number of different mechanisms have been suggested [**2-4**] to explain the action of set regulators on CAC, mainly with respect to the dissolution of anhydrous cement, and the nucleation and precipitation processes for the main hydration products.

Hydraulic hardening of CAC is primarily due to the hydration of CA (cement notation: C=CaO, A=Al_2O_3, F=Fe_2O_3, S=SiO_2, H=H_2O), but other compounds may also participate in the hardening process especially in long term strength development [**1**, **3**]. The hydration of CAC is highly temperature dependent [**5-7**], yielding following main morphologically different hydration products at approximate temperature ranges:

$$CA + 10\ H \rightarrow CAH_{10} \qquad T < 20°C \qquad (\mathbf{1})$$

$$2\ CA + 11\ H \rightarrow C_2AH_8 + AH_3 \qquad T \sim 30\ °C \qquad (\mathbf{2})$$

$$3\ CA + 12\ H \rightarrow C_3AH_6 + 2\ AH_3 \qquad T > 55\ °C \qquad (\mathbf{3})$$

At ambient temperature metastable hydrates, CAH_{10} and C_2AH_8 [**8**] convert to the more stable C_3AH_6 and AH_3 [**2**] with consequent material porosity and permeability increase and loss of strength:

$$2\ CAH_{10} \rightarrow C_2AH_8 + AH_3 + 9\ H \qquad (\mathbf{4})$$

$$3\ C_2AH_8 \rightarrow 2\ C_3AH_6 + AH_3 + 9\ H \qquad (\mathbf{5})$$

Conversion is accelerated in warm and moist conditions. During the hydration of CAC a large quantity, typically 70-90% of total heat is liberated in a short period (first 24 h) [**1**, **9**].

Rodger and Double investigated the chemistry of hydration of CAC in the presence of accelerating and retarding admixtures. Upon plotting the results of Rodger and Double [**4**] against the added metalic atomic number, a well defined trend was observed on the influence of transition metals onto the setting behaviour, shown in **Fig 1**.

In order to clarify this finding, previously not addressed in literature, in this paper the influence of transition metals in the form of chlorides salts, on the hydration of CAC has been investigated. The effect has been studied at two temperatures, 14 and 20 ^{o}C with a water to cement mass ratio of 0.25 and 0.40.

Though less traditional and indirect, preferable techniques for measuring setting time are isothermal calorimetry, temperature rise and solution conductivity measurements [**10**]. Therefore, in this work a simple method of analyzing cement hydration based on the measurement of temperature rise of cement pastes is presented.

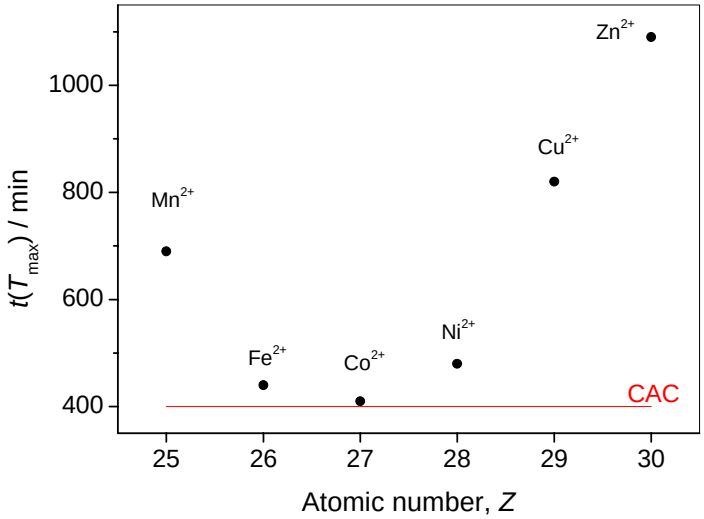


Fig 1. Time of maximum temperature rise of CAC samples, *w*/*c*=0.5 with 2.5 mmol Me^{2+}/100gCAC, in semiadiabatic conditions (plotted upon published data [**8**]).

2. Experimental

2.1. Materials

This paper examines the hydration of sample of commercial CAC ISTRA 40 taken from a regular production of Istra Cement International, Pula, Croatia. The cement has the oxide mass fraction composition listed in **Table 1**. Physical properties of used cement are given in **Table 2**. The main compounds are CA and ferrite phase (C_4AF-C_6AF_2), with mayenite, $C_{12}A_7$, gehlenite, C_2AS and β-C_2S as minor compounds. The QXRD analysis of investigated CAC gave the mass proportions of CA and $C_{12}A_7$ to be 39 % and 7 %, respectively. Specimens with water to cement mass ratio of 0.25 and 0.40 were prepared. The salts used as additives were commercial Analar grade reagents: $MnCl_2$ H_2O, $CoCl_2$ $6H_2O$, $CuCl_2$ $2H_2O$, and $ZnCl_2$.

To prepare the samples of pastes the additives were weighed into deionized water (according to a specified molar mass concentration) and than hand mixed with 100 g of cement. The plan of experiment is shown in **Table 3**.

Table 1. Chemical composition of investigated CAC.

CaO	Al_2O_3	Fe_2O_3	FeO	SiO_2	TiO_2	MgO	SO_3	Na_2O	K_2O	Sum
39.12	37.78	13.17	2.46	4.42	1.80	0.91	0.30	0.18	0.17	100.3

Table 2. Physical properties of investigated CAC.

>90 µm, %	Blaine, cm^2/g	Specific gravity, g/cm^3	Setting time, min		Standard consistency, %	Bulk density, kg/m^3	
			initial	final		Loose	Compacted
3.71	3563	3.20	216	246	25.0	950	1776

Table 3. The plan of experiment.

Method	$\gamma(Me^{2+})$ / mmol/(100gCAC)	*w*/*c*	*T* / °C
Temperature rise	1; 2 and 10	0.40	14
	1	0.40	20
Vicat	1	0.25	20

2.2. CAC temperature rise measurement setup

The specimens were cast in HDPE containers with inner diameter $2R$ = 31 mm, height 50 mm and thickness of 0.7 mm. The HDPE container was fully filled with the cement paste w/c = 0.4, continuously applying vibrations in order to minimize air entrapment. The thermocouple measuring end was placed exactly at the center of the container (r=0 and z=h/2 as shown in **Fig. 2**). This was designed by fixing thin (1.3 mm) wooden support at the axis of the container. Specimens are carefully sealed with lids and insulating tape and placed vertically in the temperature controlled water bath (±0.03°C). K-type thermocouples 0.2 mm thick with grounded twisted-shielded wiring were used. An 8 channel data logger with a 20 bit resolution is used to collect the temperature measurements. It stores the entire set of temperatures once every second. The experimental data is simultaneously transferred to a PC. Cold junction temperature held at room temperature is sensed by a precision thermistor in good thermal contact with the input connectors (on thermal block) of the measuring instrument. In order to have accurate cold junction compensation a change of its temperature is kept as slow as possible.

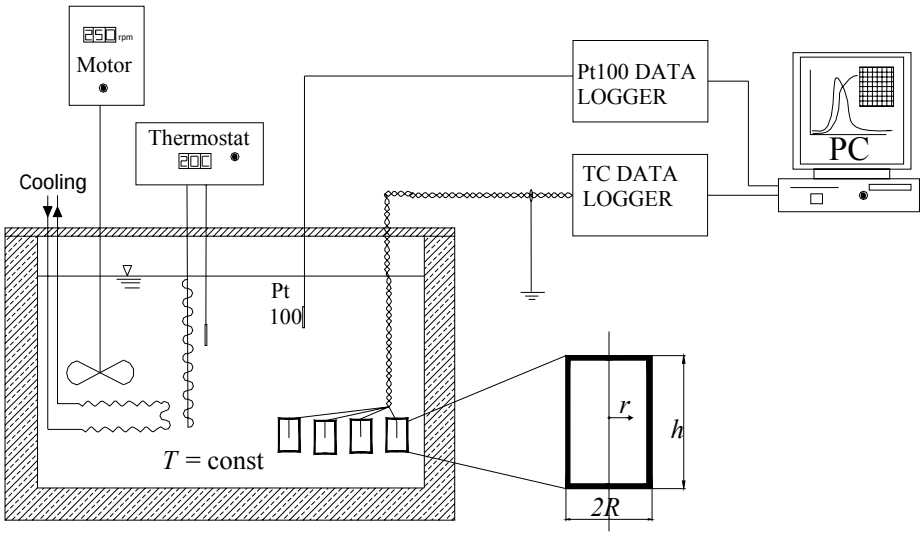


Figure 2. Scheme of the CAC temperature rise measurement setup.

2.3. Setting time measurement

The setting time was determined using the American Society for Testing Materials (ASTM) method C 804-75. The experiments used a standard consistency CAC paste given in **Table 2**.

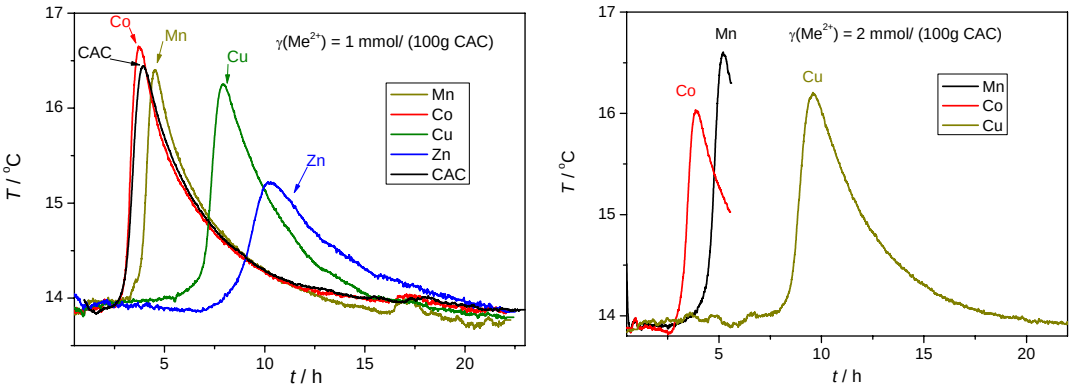
2.4. X-ray diffraction

The composition of cement and hydrates formed was investigated by X-ray diffraction (XRD). Philips diffractometer PW1830 with Cu Kα radiation was used, the scan step was 0.02° with collection time of 2 s.The hydration was blocked and free water removed by addition of acetone (2-propanon). This was done by grinding and mudding the sample in three doses with acetone in agate mortar.

3. Results and discussion

Results of temperature rise measurements for CAC, w/c = 0.4 cured at T = 14°C and 20 °C are given in **Figs 3** and **4**, respectively. No significant temperature rise is observed during the induction period due to a small and constant rate of heat

generation (~1 J(h g)$^{-1}$) [**9**]. Induction period is followed by the onset of the accelerated stage of reaction due to massive precipitation of hydrates. The maximal temperature rise is reached in only few hours after the onset of the accelerated stage. Interestingly, after the onset of the main peak the hydration rate is faster for the samples with added Co^{2+} salt. Furthermore, the flatter and longer main peak of the temperature rise curve for samples with added Zn^{2+} and Cu^{2+} salts supports the notion of slow growth and crystalisation of hydrates.



a) **b)**

Fig 3. Temperature rise of CAC cured at T = 14°C w/c = 0.4: **a)** $\gamma(Me^{2+})$ = 1 mmol/(100g CAC); **b)** $\gamma(Me^{2+})$ = 2 mmol/(100g CAC).

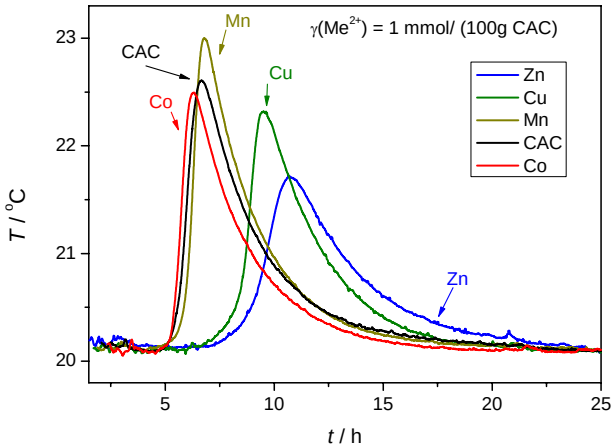


Fig 4. Temperature rise of CAC cured at T = 20°C w/c = 0.4, $\gamma(Me^{2+})$ = 1 mmol/(100g CAC).

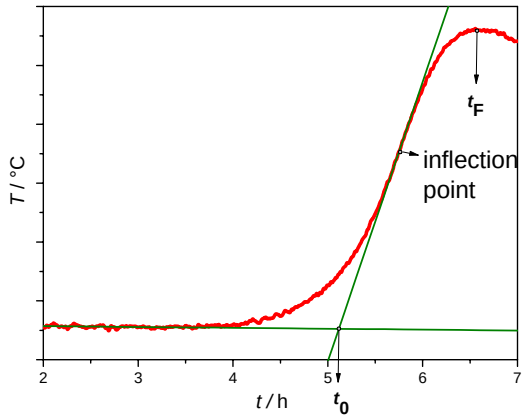


Figure 5. The method of acquiring the initial, t_0 and final, t_F setting time.

Times of initial, t_0 and final, t_F sets were established from the obtained time-temperature curves, as illustrated in **Fig 5**. Initial set is acquired from the intersection of two straight lines [**12**]: one fitted through the induction period of the curve and the other fitted through the inflection point of the rising slope of main peak. The final set was approximated as the point of maximal heat generation [**13**].

The X-ray analysis of hydrated samples, *w/c* = 0.4 cured at 14 °C and 20 °C for 30 h is shown in **Fig 6**. At 14 °C primarily CAH_{10} with an appreciable quantity of C_2AH_8 and AH_3 appeared. Higher amount of C_2AH_8 at 14 °C than expected from the literature [**1**, **5-7**, **10**], and a relatively short setting time can be attributed to a higher amount of $C_{12}A_7$ phase in the used cement (7 %). In authors previous work on CAC with lower content of $C_{12}A_7$ (3%) [**9**, **14**] the main hydrate observed below 20 °C was CAH_{10} with barely detectable quantity of C_2AH_8 and AH_3. At 20 °C more quantity of C_2AH_8 and AH_3 with a higher degree of reacted CA could be detected in comparison to 14 °C. Diffractograms on pure pastes were compared to those with salts additions, and concluded that no significant differences on diffractograms could be detected (therefore not shown in this paper).

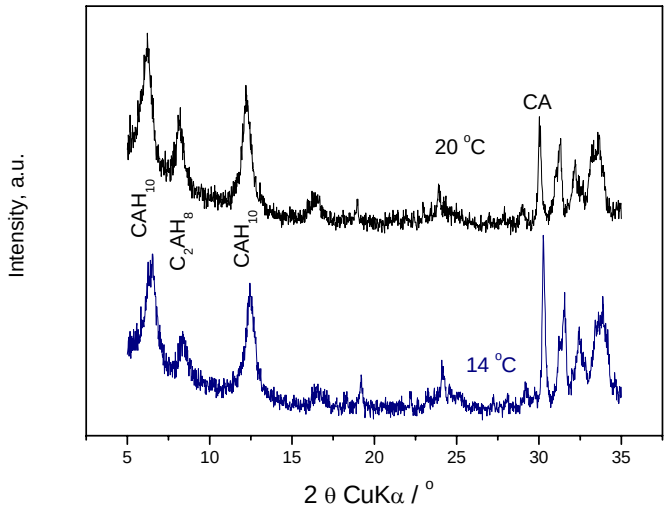


Figure 6. X-ray analysis of hydrated samples *w/c* = 0.4 cured at 14 and 20 °C for 30 h.

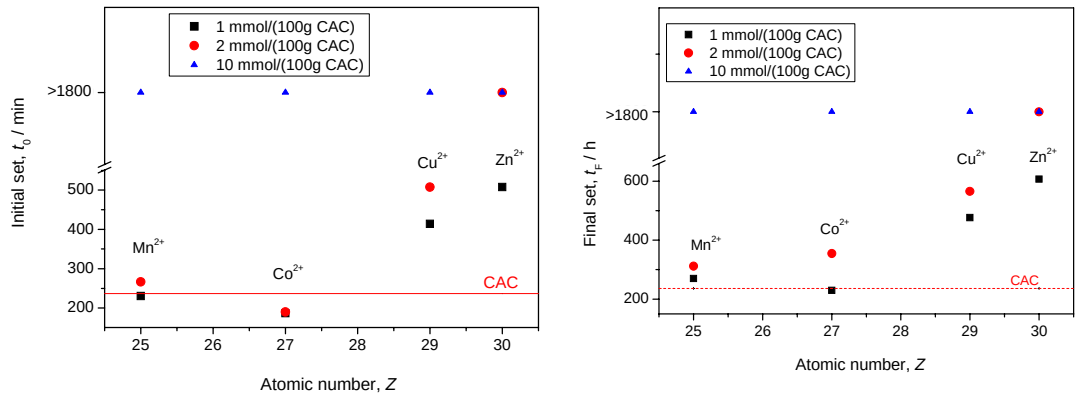
Results on setting times for hydration at 14 °C, *w/c* = 0.4 with different salt concentrations are given in **Fig 7.** Concentrations of 2 mmol/100gCAC exhibit longer setting time than 1 mmol/100gCAC, while 10 mmol Me^{2+}/100gCAC and 2 mmol Zn^{2+}/100gCAC showed no setting behavior in 30 h. Results on setting times for hydration at 20 °C with salt addition of 1 mmol/100gCAC are given in **Fig 7**. Comparison of initial setting times obtained by Vicat (*w/c* = 0.25) and temperature rise measurements (*w/c*=0.4), is shown in **Fig 8 a)**.

Setting can be attributed to the loss in mobility of water in the aqueous phase as hydrate formation takes place appreciably. Unlike calorimetry or temperature rise measurements, the Vicat initial setting time is significantly affected by *w/c* due to the consistency of the paste being tested [**11**]. This reflects the fact that the setting time is an arbitrarily defined parameter. In a more fluid paste longer time is needed to reach the required resistance to penetration.

A well defined trend could be observed upon plotting the setting times against added cation's atomic number, shown in **Fig 7 and 8**. Similar trend of the setting times vs. atomic number is observed for both methods of measurements. Furthermore the

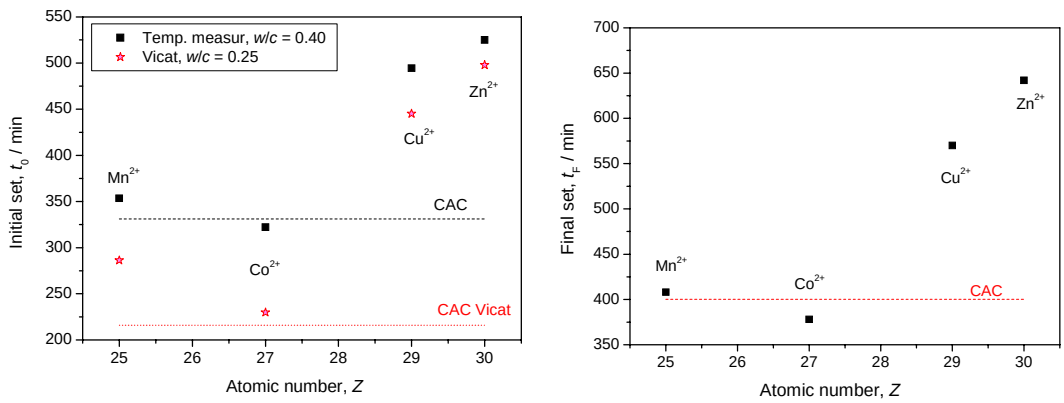
observed trend is similar for all investigated concentrations, except the highest and both investigated temperatures, as seen from comparison of **Figs 7 and 8**.

Retarded setting times and hydration rate observed at 20 °C in comparison to 14 °C can be explained by a low level of supersaturation, sluggish nucleation of CAH_{10} and the massive gel formation [**12**]. This is valid for all the concentrations of salt additions used.



a) **b)**

Figure 7. Setting times for hydration at 14 °C *w/c* = 0.4 with different salt concentrations: **a)** Initial setting time and **b)** Final setting time.



a) **b)**

Figure 8. Setting times for hydration at 20 °C with salt addition of 1 mmol/100gCAC: **a)** Vicat and temperature rise initial setting time, and **b)** Final setting time.

4. Conclusion

A simple method of analyzing cement hydration based on the measurement of temperature rise of cement pastes is presented. Times of initial and final sets were established from the obtained time-temperature curves.

A well defined trend was observed upon ploting the obtained results on setting times vs. added cation's atomic number. The relative effect of the additions is similar at the two investigated temperatures, 14 and 20 °C and concentrations 1 and 2 mmol/100gCAC, but the absolute induction time is retarded by increasing temperature and concentration. No setting behavior was observed during 30 h of hydration for adding 10 mmol Me^{2+}/100gCAC or 2 mmol Zn^{2+}/100gCAC.

Higher amount of C_2AH_8 at 14 °C than expected from the literature, and a relatively short setting time was attributed to a higher amount of $C_{12}A_7$ phase in the investigated cement (7 %).

5. Acknowledgement
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INHIBICIJA KOROZIJE CuNiFe SLITINE p-IDROKSIBENZOJEVOM KISELINOM

CORROSION INHIBITION OF CuNiFe BY MEANS OF p-IDROXYBENZOIC ACID

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Izvorni znanstveni rad / Original scientific paper

Sažetak: U radu je ispitana mogućnost inhibicije korozije CuNiFe slitine u kloridnoj otopini pomoću p-hidroksibenzojeve kiseline. Navedena kiselina pripada skupini fenolnih kiselina, spojeva koji su prisutni u biljnom materijalu. Ispitivanja su provedena praćenjem potencijala otvorenog strujnog kruga te elektrokemijskim metodama, kao što su metoda linearne polarizacije i potenciodinamička polarizacijska metoda. Kao osnovni elektrolit korištena je 0.5 mol dm^{-3} otopina NaCl bez i u prisustvu p-hidroksibenzojeve kiseline u koncentracijama od 1×10^{-6} do 1×10^{-3} mol dm^{-3}. U radu je također ispitan i utjecaj povišenja temperature elektrolita na koroziju i inhibiciju navedene slitine. Rezultati ispitivanja su pokazali da p-hidroksibenzojeva kiselina djeluje kao katodni inhibitor korozije CuNiFe slitine. Adsorpcijsko ponašanje ove fenolne kiseline može se opisati Freundlichovom adsorpcijskom izotermom, a dobivena vrijednost standardne slobodne energije adsorpcije ukazuje na fizikalnu adsorpciju. Porastom temperature elektrolita dolazi do intenzivnije korozije CuNiFe slitine, te smanjenja inhibicijskog djelovanja p-hidroksibenzojeve kiseline.
Ključne riječi: CuNiFe slitina, inhibicija korozije, p-hidroksibenzojeva kiselina.

Abstract: This study examined the possibility of inhibition of corrosion of the CuNiFe alloy in NaCl by means of p-hidroxybenzoic acid. This acid belongs to the group of phenolic acids, compound that are common present in plant material. Examinations were conducted by open circuit potential measurements, linear polarisation measurements and potentiodynamic polarisation measurements. The basic solution was 0.5 mol dm^{-3} NaCl without and in the presence of p-hidroxybenzoic acid in concentrations of 1×10^{-6} mol dm^{-3} to 1×10^{-3} mol dm^{-3}. The influence of temperature on corrosion and corrosion inhibition of CuNiFe alloy was also examined. The results have shown that p-hidroxybenzoic acid act as a cathodic corrosion inhibitor of the CuNiFe alloy. The adsorption behaviour of this phenolic acid can be described by the Freundlich adsorption isotherm, and the values determined for standard free adsorption energies indicate physical adsorption process. Increasing the temperature of electrolyte causes stronger corrosion of CuNiFe alloy and decreasing inhibiting efficiency of p-hidroxybenzoic acid.
Keywords: CuNiFe alloy, corrosion inhibition, p-hidroxybenzoic acid.

1. UVOD

Zbog svojih dobrih osobina, kao što su zadovoljavajuća čvrstoća, visoka toplinska i električna vodljivost, dobra obradivost te visoka otpornost prema koroziji, Cu-Ni slitine nalaze široku primjenu u proizvodnji kondenzatorskih cijevi, brodskih cjevovoda, dijelova postrojenja koji rade pod visokim tlakom, postrojenja za desalinaciju i sl. [1-3]. Dvije najčešće korištene Cu-Ni slitine sadrže 10 i 30 % Ni, a željezo je bitan sastojak ovih slitina jer povećava otpornost prema koroziji [4]. Optimalni sadržaj željeza u ovim slitinama je između 1.5 i 2.5 %. Korozijska otpornost slitina raste povećanjem sadržaja željeza sve do granice njegove topljivosti u krutoj otopini, a također raste i povećanjem sadržaja Ni [1,5].

Dobra otpornost slitina CuNiFe prema koroziji pripisuje se svojstvima zaštitnog filma koji se formira na površini slitine. Taj film se sastoji od različitih oksida kao što su Cu_2O, CuO, NiO, FeO, Fe_3O_4, Fe_2O_3 te dvostrukih oksida $FeCuO_2$ i $NiFe_2O_4$ [6,7].

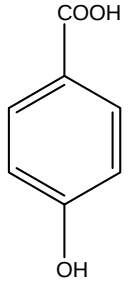
Jedan od načina poboljšanja zaštitnih osobina prirodno stvorenih, površinskih oksidnih slojeva je i primjena inhibitora korozije. Toksičnost većine komercijalnih inhibitora korozije bila je poticaj brojnim istraživanjima koja su imala za cilj pronalazak novih, netoksičnih inhibitora. Prirodni antioksidansi predstavljaju jeftine, dostupne i obnovljive spojeve koji se mogu koristiti kao inhibitori korozije. Ovi organski spojevi mogu se dobiti postupcima organske sinteze ili ekstrahirati i izolirati iz biljnog materijala [8].

U ovom radu ispitana je mogućnost inhibicije korozije CuNiFe slitine u 0.5 mol dm^{-3} NaCl otopini, pomoću p-hidroksibenzojeve kiseline. Navedena kiselina pripada skupini fenolnih kiselina, spojeva koji se prirodno nalaze u voću, povrću, sjemenkama i drugom biljnom materijalu [9-11]. Fenolne kiseline su prirodni antioksidansi, a neki od ovih spojeva pokazuju antibakterijsko i antigljivično djelovanje [12-14]. Ispitivanja na aluminijevim slitinama, te na čeliku pokazala su primjenjivost ovih spojeva kao inhibitora korozije [15,16].

2. EKSPERIMENTALNI DIO

Mjerenja su provedena s CuNiFe slitinom sastava Cu 87.7 %, Ni 9.9 % i Fe 2.4 %. Prije svakog mjerenja radna površina uzorka mehanički je obrađena brušenjem brusnim papirima različite finoće, odmašćena u etanolu i isprana redestiliranom vodom. U ovim ispitivanjima korišten je standardni elektrokemijski reaktor s protuelektrodom od platine te referentnom zasićenom kalomel elektrodom, koja je preko Lugginove kapilare bila u kontaktu s radnom elektrodom. Dvostruke stijenke reaktora omogućavale su termostatiranje otopine na željenim temperaturama.

Osnovna otopina bila je 0.5 mol dm^{-3} NaCl otopina bez i uz dodatak p-hidroksibenzojeve kiseline u koncentracijama od 1×10^{-6} mol dm^{-3} do 1×10^{-3} mol dm^{-3}. Na slici 1 prikazana je strukturna formula p-hidroksibenzojeve kiseline.

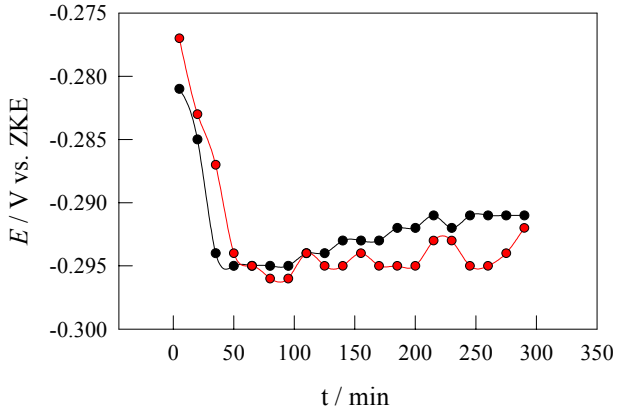


Slika 1. Strukturna formula p-hidroksibenzojeve kiseline.

Vremenska ovisnost potencijala otvorenog strujnog kruga CuNiFe slitine u 0.5 mol dm^{-3} NaCl otopini bez i u prisustvu najveće koncentracije p-hidroksibenzojeve kiseline praćena je pri T = 20 °C u vremenskom periodu od 300 minuta.
Potenciodinamička polarizacijska mjerenja provodila su se u području potencijala od -250 mV do + 200 mV prema potencijalu otvorenog strujnog kruga uz brzinu promjene potencijala od 0.2 mV s^{-1}.
Vrijednosti polarizacijskog otpora (R_p) određene su iz nagiba linearnih dijelova polarizacijskih krivulja dobivenih mjerenjima metodom linearne polarizacije u području potencijala ±15 mV prema potencijalu otvorenog strujnog kruga, uz brzinu promjene potencijala od 0.2 mV s^{-1}.

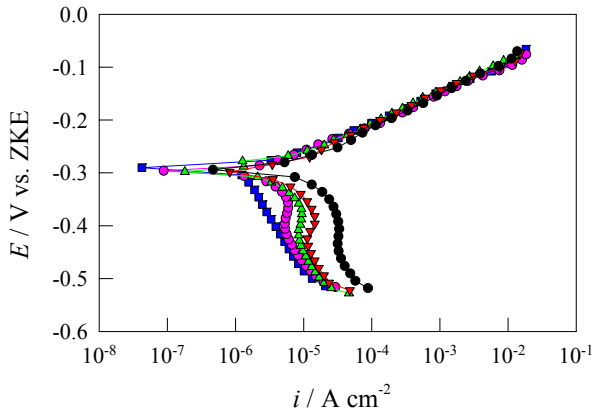
3. REZULTATI I RASPRAVA

Vremenska ovisnost potencijala otvorenog strujnog kruga za ispitivanu slitinu u 0.5 mol dm^{-3} NaCl otopini bez i u prisustvu p-hidroksibenzojeve kiseline prikazana je na slici 2.



Slika 2. Vremenska ovisnost potencijala otvorenog strujnog kruga za CuNiFe slitinu u 0.5 mol dm^{-3} NaCl otopini bez (●) i u prisustvu p-hidroksibenzojeve kiseline koncentracije 1×10^{-3} mol dm^{-3} (●).

Iz prikazanog dijagrama može se vidjeti da pri početku mjerenja dolazi do promjene potencijala otvorenog strujnog kruga u negativnom smjeru, a stabilna vrijednost potencijala uspostavlja se za otprilike 60 minuta. Dodatak p-hidroksibenzojeve kiseline nema značajniji utjecaj na vrijeme uspostavljanja ni na vrijednost potencijala otvorenog strujnog kruga.
Na slici 3 prikazane su potenciodinamičke polarizacijske krivulje za CuNiFe slitinu u 0.5 mol dm^{-3} NaCl otopini bez i u prisustvu različitih koncentracija p-hidroksibenzojeve kiseline.



Slika 3. Potenciodinamičke polarizacijske krivulje za CuNiFe slitinu u 0.5 mol dm^{-3} NaCl otopini bez (●) i u prisustvu p-hidroksibenzojeve kiseline koncentracija 1×10^{-6} mol dm^{-3} (▼), 1×10^{-5} mol dm^{-3} (▲), 1×10^{-4} mol dm^{-3} (●) i 1×10^{-3} mol dm^{-3} (■).

Iz slike se može vidjeti da dodatak p-hidroksibenzojeve kiseline izaziva značajno smanjenje katodnih gustoća struja, uz neznatan utjecaj na anodni dio krivulje. Vrijednost korozijskog potencijala CuNiFe slitine ne mijenja se dodatkom fenolne kiseline. Uzimajući u obzir navedene promjene može se zaključiti da p-hidroksibenzojeva kiselina djeluje kao katodni inhibitor korozije CuNiFe slitine. U tablici 1 dane su vrijednosti korozijskih parametara određenih iz polarizacijskih krivulja, kao i vrijednosti prekrivenosti površine, (Θ), i djelotvornosti inhibtora, (η), koje su izračunate prema jednadžbama (1) i (2):

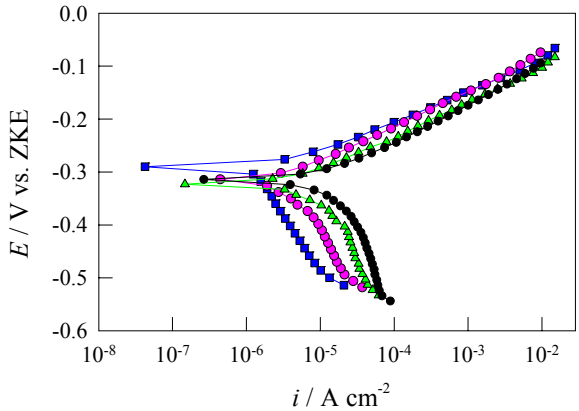
$$\Theta = \frac{i_{kor} - (i_{kor})_{inh}}{i_{kor}} \quad (1)$$

$$\eta = \Theta \times 100 \quad (2)$$

Tablica 1. Vrijednosti korozijskih parametara kao i prekrivenosti površine i djelotvornosti inhitora, određene iz potenciodinamičkih polarizacijskih mjerenja

c / mol dm^{-3}	i_{kor} / μA cm^{-2}	E_{kor} / V	θ	η / %
0	5.75	-0.295	-	-
1×10^{-6}	3.24	-0.296	0.4365	43.65
1×10^{-5}	2.80	-0.301	0.5130	51.30
1×10^{-4}	2.16	-0.306	0.6243	62.43
1×10^{-3}	1.27	-0.301	0.7791	77.91

Utjecaj povišenja temperature elektrolita na potenciodinamičke polarizacijske krivulje prikazan je na slici 4.



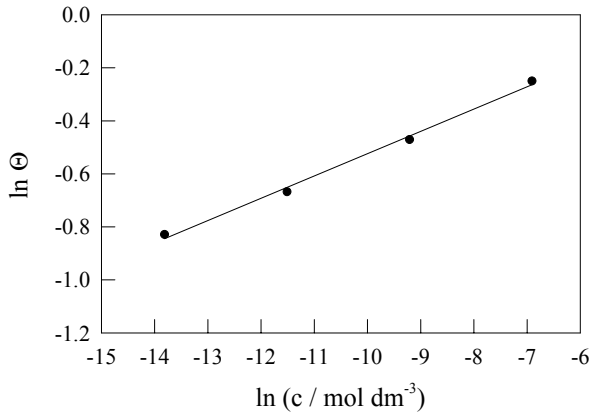
Slika 4. Potenciodinamičke polarizacijske krivulje za CuNiFe slitinu u 0.5 mol dm^{-3} NaCl otopini u prisustvu p-hidroksibenzojeve kiseline koncentracije 1×10^{-3} mol dm^{-3}, pri temperaturama elektrolita 20 °C (■), 30 °C (●), 40 °C (▲) i 50 °C (●).

Iz slike se može vidjeti da povišenje temperature elektrolita dovodi do povećanja katodnih i anodnih gustoća struja, dakle dolazi do intenzivnije korozije ispitivane slitine. Djelotvornost p-hidroksibenzojeve kiseline, kao inhibitora korozije CuNiFe slitine, smanjuje se s povećanjem temperature elektrolita što se može vidjeti iz tablice 2.

Tablica 2. Ovisnost djelotvornosti inhibitora o temperaturi za p-hidroksibenzojevu kiselinu

T / ºC	20	30	40	50
c (inhibitora) / mol dm^{-3}	η	η	η	η
1×10^{-3}	77.91	66.95	52.33	35.77

Ovisnost promjene vrijednosti prekrivenosti površine o koncentraciji p-hidroksibenzojeve kiseline prikazana je na slici 5.



Slika 5. Ovisnost promjene vrijednosti prekrivenosti površine o koncentraciji inhibitora.

Dobiveno ponašanje najbolje se može opisati Freundlichovom adsorpcijskom izotermom koja je dana izrazom:

$$\Theta = Kc^n \qquad \text{gdje je } 0 < n < 1, \tag{3}$$

ili u obliku jednadžbe:

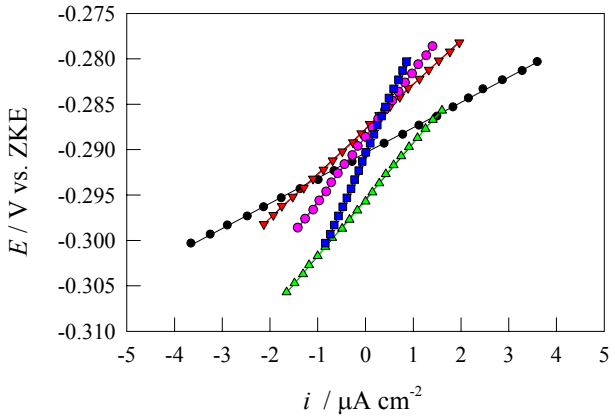
$$\ln\Theta = \ln K + n\ln c \tag{4}$$

K i c predstavljaju konstantu adsorpcijske ravnoteže i koncentraciju inhibitora. Dobivena je linearna ovisnost ln Θ - ln c, što ukazuje na primjenjivost Freundlichove izoterme.
Iz odsječka pravca određena je vrijednost konstante adsorpcijske ravnoteže, K, dok je standardna slobodna energija adsorpcije, ΔG°_{ads}, izračunata prema jednadžbi (5).

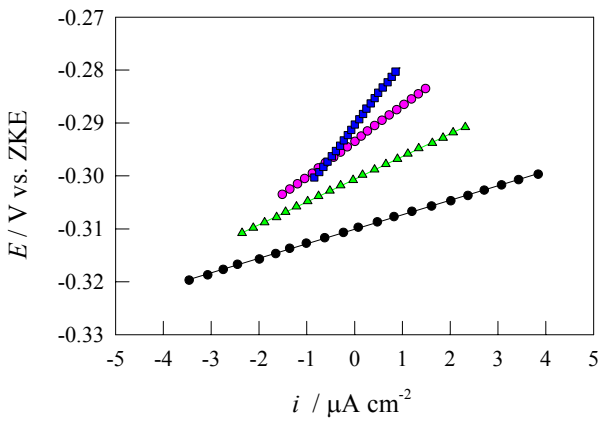
$$K = \frac{1}{55.5}\exp\left(-\frac{\Delta G^{0}_{ads}}{RT}\right) \tag{5}$$

Dobivena vrijednost konstante K iznosi 1.38 dm^3 mol^{-1}, a vrijednost ΔG°_{ads} iznosi -10.57 kJ mol^{-1}. Negativna vrijednost ΔG°_{ads} ukazuje da se adsorpcijski proces odvija spontano, a njen iznos ukazuje na fizikalnu adsorpciju p-hidroksibenzojeve kiseline na površini metala.

Na slikama 6 i 7, te u tablici 3 prikazani su rezultati dobiveni metodom linearne polarizacije. Na slici 6 može se vidjeti da dodatak p-hidroksibenzojeve kiseline dovodi do povećanja nagiba linearnih dijelova krivulja tj. do povećanja vrijednosti polarizacijskog opora. Najveća vrijednost polarizacijskog otpora dobivena je s najvećom ispitivanom koncentracijom p-hidroksibenzojeve kiseline, pri temperaturi 20 ºC. Iz slike 7 može se vidjeti da povećanjem temperature elektrolita dolazi do smanjenja nagiba linearnih dijelova polarizacijskih krivulja, što znači da dolazi do opadanja vrijednosti polarizacijskog otpora.



Slika 6. Krivulje linearne polarizacije za CuNiFe slitinu u 0.5 mol dm^{-3} NaCl otopini bez (●), i u prisustvu p-hidroksibenzojeve kiseline koncentracija 1×10^{-6} mol dm^{-3} (▼), 1×10^{-5} mol dm^{-3} (▲), 1×10^{-4} mol dm^{-3} (●) i 1×10^{-3} mol dm^{-3} (■).



Slika 7. Krivulje linearne polarizacije za CuNiFe slitinu u 0.5 mol dm^{-3} NaCl otopini u prisustvu 1×10^{-3} mol dm^{-3} p-hidroksibenzojeve kiseline, pri temperaturama otopine 20 ºC (■), 30 ºC (●), 40 ºC (▲) i 50 ºC (●).

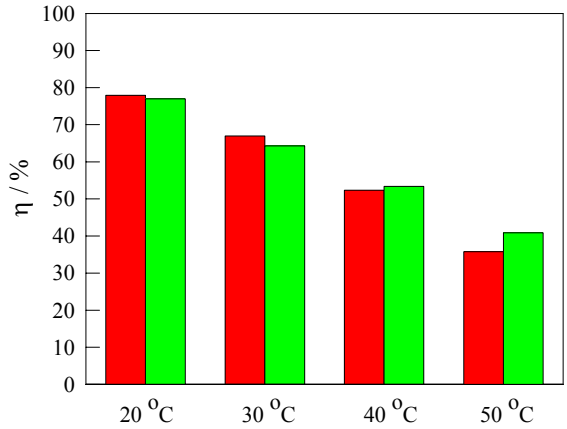
Vrijednosti djelotvornosti inhibitora izračunate su iz vrijednosti polarizacijskog otpora pomoću jednadžbe (6) i prikazane su u tablici 3.

$$\eta = \left(\frac{R_{pi} - R_p}{R_{pi}} \right) \times 100 \qquad (6)$$

Tablica 3. Vrijednosti polarizacijskih otpora i djelotvornosti inhibitora za p-hidroksibenzojevu kiselinu u 0.5 mol dm^{-3} NaCl otopini, određene iz mjerenja metodom linearne polarizacije

c / mol dm^{-3}	*Rp* / kΩ cm^2	η / %
0	2.787	-
1×10^{-6}	4.876	42.84
1×10^{-5}	6.185	54.94
1×10^{-4}	7.164	61.09
1×10^{-3}	12.100	76.97

Vrijednosti djelotvornosti inhibitora korozije dobro se slažu s vrijednostima izračunatim iz gustoća korozijskih struja dobivenih potenciodinamičkim polarizacijskim mjerenjima. To se može vidjeti i iz dijagrama prikazanog na slici 8, a koji prikazuje opadanje djelotvornosti inhibicije povišenjem temperature elektrolita.



Slika 8. Ovisnost djelotvornosti inhibitora o temperaturi elektrolita, dobivena metodom potenciodinamičke polarizacije (■) i metodom linearne polarizacije (■).

4. ZAKLJUČCI

Rezultati polarizacijskih mjerenja pokazali su da p-hidroksibenzojeva kiselina djeluje kao katodni inhibitor korozije CuNiFe slitine u 0.5 mol dm^{-3} NaCl otopini.
Inhibicijsko djelovanje fenolne kiseline može se objasniti fizikalnom adsorpcijom kiseline na površini CuNiFe slitine. Adsorpcijsko ponašanje može se opisati Freundlichovom adsorpcijskom izotermom.
Povišenje temperature elektrolita dovodi do povećanja vrijednosti korozijskih struja, smanjenja vrijednosti polarizacijskih otpora i smanjenja djelotvornosti p-hidroksibenzojeve kiseline kao inhibitora korozije ispitivane slitine.

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FIZIKALNA KARAKTERIZACIJA TEKUĆIH PENETRANATA

PHYSICAL CHARACTERISATION OF LIQUID PENETRANTS

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Prethodno priopćenje / Preliminary note

Sažetak: U radu je opisan postupak u kojemu se prati dinamika kapilarnog učinka tekućih, obojenih i fluorescentnih penetranata koji se uobičajeno rabe u ispitivanju penetrantima kao dijelu nerazornih ispitivanja. Geometrijski, kapilarni učinak prati se u planarnom i prizmatičnom procijepu. To je geometrija koja u bitnim crtama reprezentira neka važna svojstva realistične geometrije znatno uvećane površinske pukotine. Pripadna idealizacija očituje se u modifikaciji oblika poprečnog presjeka reprezentirane pukotine.
U razmatranim slučajevima mjerena je brzina uspinjanja penetranta u procijepu. Dodatno je bilježena i analizirana dinamika kapilarnog učinka. Rezultati za fluorescentni i obojeni penetrant uspoređivani su s rezultatima za vodu.

Ključne riječi: tekući penetranti, kapilarni učinak

Abstract: The paper describes the procedure for analying dynamics of cappilary action of liquid, colour and fluorescent penetrant, which are regularly exploited in penetrant non-destructive testing. Geometrically, the cappilary effect is analysed in the planar and prismatic gap. That geometries in substantial elements represent some characteristics of realistic geometries of considerably augmented cracks. The idealisation is seen in the modification of the shape of the cross section of the represented crack.

In the cases considered, we measured the rate of ascending of the penetrant in the gap. Furthermore, the dynamics of that process was registered. The results for fluorescent and coloured penetrant are compared with the corresponding results for water.

Key words: liquid penetrant, capilarry effect

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1. UVOD

Ispitivanje penetrantima jedna je od metoda nerazornih ispitivanja kojima se, bilo tijekom proizvodnje, ili tijekom eksploatacije, utvrđuje funkcionalnost ispitivane konstrukcije na temelju utvrđene prisutnosti površinskih indikacija, posebice pukotina.

Odluka o stanju ispitivane cjeline povlači za sobom znatne posljedice. Radi pouzdanosti donesene odluke, potrebno je između ostalog prethodno osigurati ispravnost svih komponenti rabljenih tijekom ispitivanja. U ovom radu razmatra se mogućnost provjere stanja penetranta, čije međudjelovanje s ispitivanom cjelinom je temelj za utvrđivanje prisutnosti površinskih indikacija.

Penetrant je fluid vrlo velike močivosti materijala ispitne plohe, npr. površine ispitivanog čeličnog objekta. Zbog močenja, on nastoji maksimizirati površinu u kontaktu s ispitivanim objektom, tj. razlijeva se po površini i dodatno ispunjava strukture otvorene na površinu poput pora i pukotina neovisno o tome nalaze li se na većoj, jednakoj, ili manjoj visini od plohe na koju je nanesen penetrant. Pukotina se sastoji od relativno bliskih, nepravilnih ploha koje penetrant također moči jer time povećava veličinu površine koja mu je u kontaktu s objektom. Dakle, penetrant ulazi u pukotinu, neovisno o tome da li pritom povećava, ili smanjuje potencijalnu energiju. Navedena pojava je kapilarni učinak, suštinski jednaka uobičajenom prikazu kapilarnog učinka u kojemu se voda u posudi uspinje unutar staklene kapilare (cijevi malog unutarnjeg promjera) iznad razine vode u posudi.

Prilikom ispitivanja penetrantima, ispitivana se ploha poslije tretira tako da se omogući uočavanje dijela penetranta koji je ispunio dio pukotine. Količina penetranta koji se nalazi unutar pukotine ovisi o nizu čimbenika. S jedne strane, geometrija pukotine utječe na tu količinu – u širim i povezanijim pukotinama bit će veća količina penetranta. Kroz područja manje širine u pukotinama penetrant prolazi sporije. Nadalje, penetrant manje viskoznosti u jednakom će vremenskom intervalu ispuniti veći dio volumena pukotine nego penetrant veće viskoznosti. Kako je viskoznost temperaturno ovisna veličina, veličina dijela pukotine ispunjenog penetrantom ovisi i o temperaturi penetranta i o temperaturi ispitivanog objekta. Dodatno, neka svojstva penetranata se mogu promijeniti tijekom njihovog skladištenja, posebice dugotrajnog. Zaključno, svojstva penetranata potrebno je provjeravati u određenim razmacima radi osiguravanja maksimalne pouzdanosti nerazornih ispitivanja u kojima se rabe penetranti. Ispravnost penetranta i cijelog postupka ispitivanja uobičajeno se provodi pomoću referentnih uzoraka. Njihove su indikacije poznate, a nakon ispitivanja penetrantima sve trebaju biti uočene ako je ispitivani penetrant dostatne kvalitete. Takva je provjera integralna za cijeli ispitni sustav koji uz penetrant uključuje i ostale komponente, kao i osposobljenost ispitivača. Zbog toga se, u slučaju neuočavanja svih indikacija, ne može jasno izdvojiti dio ispitnog sustava odgovoran za nedostatni rezultat. Slijedom navedenog ne može se jasno iskazati da li je penetrant nedostatne kvalitete, ili nije.

U ovom radu preliminarno je razmotren pristup određivanju radne kvalitete penetranta tako da se dobije izdvojena informacija o statusu penetranta. U razvijanom pristupu razdvajaju se svojstva penetranta od utjecaja ostalih komponenti ispitnog sustava. Pristup

se temelji na vizualizaciji djelovanja penetranta u geometriji koja je vjerna reprezentacija pukotine. To djelovanje penetranta je njegovo močenje ploha objekta kojim je reprezentirana pukotina, tj. uspinjanje duž pukotine zbog kapilarnog učinka.

U sljedećem odjeljku rada opisani su ispitni postav, bilježene veličine i načini njihovog bilježenja. Treći odjeljak sadrži rezultate ispitivanja i njihovu diskusiju. Završni, zaključni, odjeljak sadrži razmatranja o smjernicama potrebnog daljnjeg razvoja pristupa za određivanje radne kvalitete pentetranta.

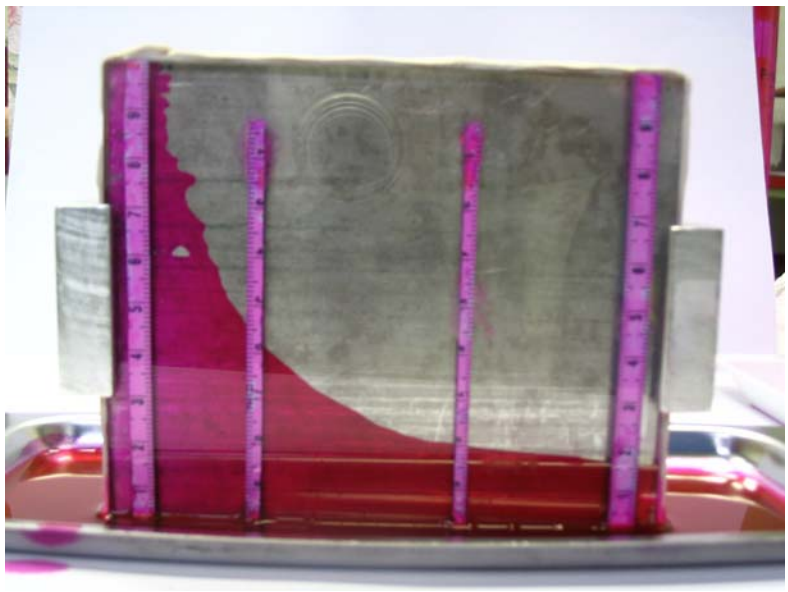
2. METODA I REZULTATI

Ispitni postav sastojao se od posude u koju se mogla uliti dostatna količina penetranta, metalne ploče određene hrapavosti na jednoj plohi i staklene ploče, slika 1. Poprečne dimenzije staklene ploče odgovaraju poprečnim dimenzijama metalne ploče. Za mjerenje su potrebni zaporni sat i mjerne trake.

Slika 1. Prikaz ispitnog postava.

Staklena i metalna ploča postave se na relativno malu srednju udaljenost čime se postižu uvjeti za izraženi kapilarni učinak, odnosno za reprezentiranje pukotine. Ploče su u jednoj grupi ispitivanja bile planparalelne, a u drugima su tvorile klinove. Vrhovi klinova, bridovi spojenih ploča, bili su ili horizontalni, ili vertikalni. Promatrani proces je uspinjanje penetranta između ploča. Visina penetranta bilježi se kao funkcija vremena. Staklena i metalna ploča su udaljene od posude s penetrantom prije ispitivanja i njihovo (djelomično) uranjanje u posudu označava početak mjerenja vremena. Na slici 2 prikazana je tipična raspodjela penetranta u procijepu između ploha tijekom njegovog uspinjanja.

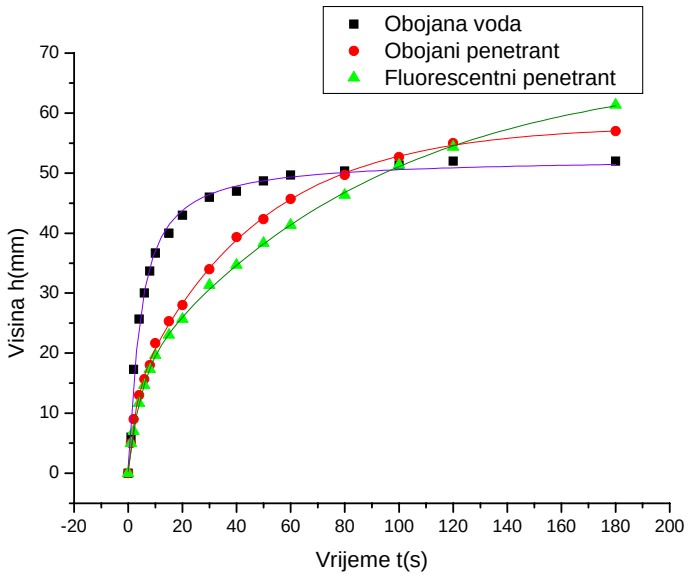
Odabirom stakla kao materijala jedne strane u reprezentaciji pukotine omogućena je jednostavna i sveobuhvatna vizualizacija procesa. S druge strane, time je umanjena sličnost reprezentacije pukotine s pravom pukotinom.



Slika 2. Uspinjanje obojanog penetranta između uspravne čelične i staklene ploče. Ploče su spojene na lijevom rubu.

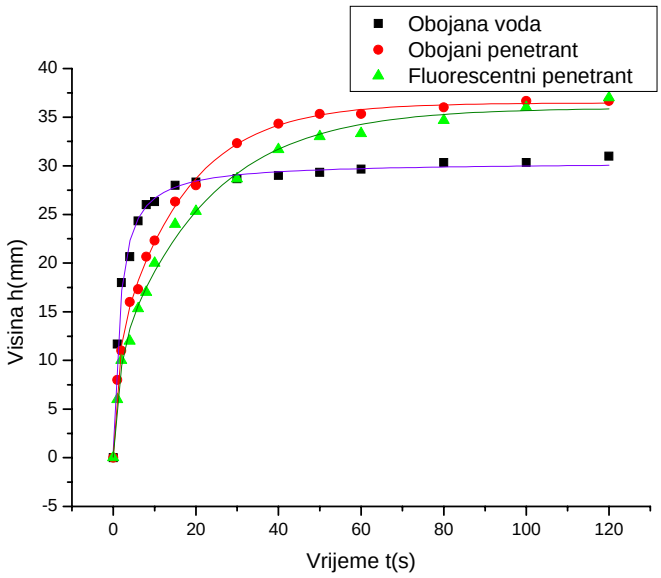
Vremenska ovisnost visine uspinjanja određivana je za nekoliko vrsta fluida: obojeni penetrant, fluorescentni penetrant i za obojanu vodu. Voda je bojana isključivo radi lakšeg uočavanja razine vode u određenom trenutku.

Uz staklenu plohu postavljeno je nekoliko mjernih traka. Za pojedini trenutak bilježi se položaj do kojeg se uspeo penetrant na svakoj od traka, a u grafičkim prikazima i daljnjim razmatranjima uzima se samo srednja vrijednost tog broja. To je zbog toga što se

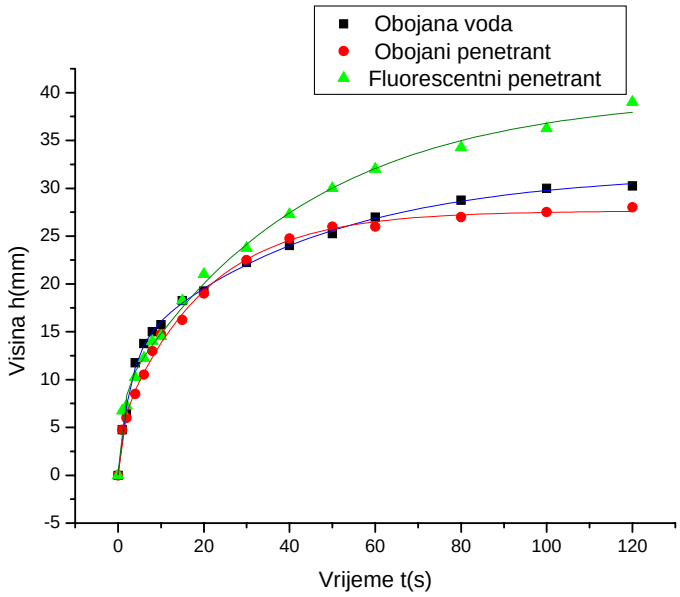


Slika 3. Vremenska ovisnost uspinjanja fluida između planparalelne čelične i staklene ploče razmaknute za 50 μm.

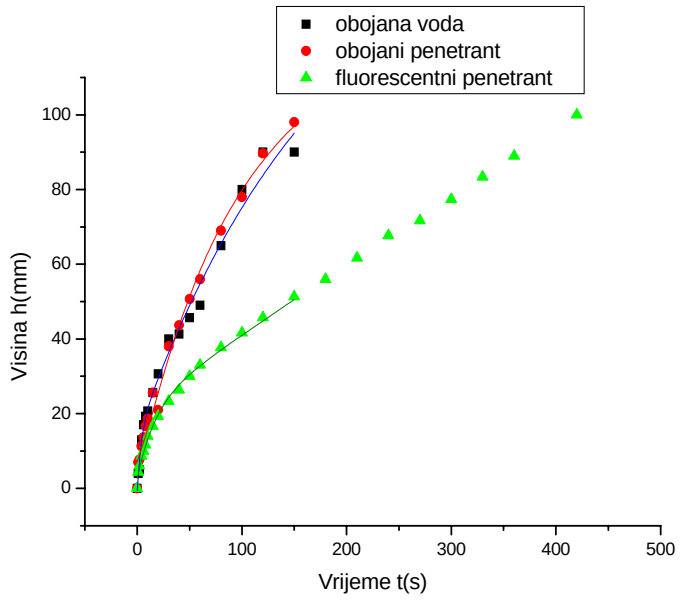
penetrant ne uspinje jednoliko duž cijele ploče, nego se pokraj rubova uspinje sporije. Dodatno, odstojnici kojima se osigurava određena udaljenost staklene i metalne ploče s donje strane djelomično sprečavaju protok penetranta, što se na manjim visinama uzima u obzir uprosječivanjem postignutih visina, da bi se na relativno većim visinama uspinjanja navedeno umanjilo.



Slika 4. Vremenska ovisnost uspinjanja fluida između planparalelne čelične i staklene ploče razmaknute za 100 μm.



Slika 5. Vremenska ovisnost uspinjanja fluida između planparalelne aluminijske i staklene ploče razmaknute za 100 μm.



Slika 6. Vremenska ovisnost uspinjanja fluida između čelične i staklene ploče postavljene u klin spojen s gornje strane. Razmak ploča na donjem rubu iznosi 50 μm.

3. DISKUSIJA REZULTATA

Grafovi vremenskih ovisnosti uspinjanja korištenih fluida kvalitativno su slični, sl. 3-6. Svi pokazuju nagli porast visine kratkom vremenskom intervalu nakon početka uspinjanja te prijelaz u zasićenje nakon nekoliko minuta uspinjanja. Postignute visine veće su za uže procijepe između ploča, sl. 3 i 4. Također, područje zasićenja koje se na grafovima zapaža kasnije se postižu u slučaju užih procijepa. Vrsta materijala ploča utječe na uspinjanje penetranta, npr. za ista vremena postignute visine znatno se razlikuju u geometrijski jednakim situacijama na koje se odnose sl. 4 i 5. Dodatno, za različite materijale relativni iznosi brzina uspinjanja se mogu mijenjati tijekom trajanja uspinjanja. Visine uspinjanja penetranata su veće nego visine koje dostiže destilirana voda. S druge strane voda, manje viskoznosti od penetranata, u kraćim razdobljima pokazuje veće brzine uspinjanja, a time i veće postignute visine. U području zasićenja, što se odnosi na zasićenje procijepa penetrantom, sile koje uzrokuju uspinjanje relativno su bliskih vrijednosti. Za određene geometrije, npr. klin na kojega se odnosi sl. 6, tijekom intervala bilježenja nije postignuto zasićenje. Kvalitativno, grafovi pokazuju očekivano djelovanje penetranta. Budući da je riječ o dvije vrste penetranta istog proizvođača, odnos zabilježenih visina uspinjanja, a onda i brzina uspinjanja, se ne može smatrati univerzalnim. Dakle, bez daljnjih ispitivanja drugih vrsta penetranata od različitih proizvođača ne može se zaključivati o odnosu dinamike uspinjanja različitih vrsta penetranata.

Među primijenjenim geometrijama, klin u kojemu se ploče spajaju na gornjoj strani najveće je sličnosti s pukotinama. U takvoj geometriji do izražaja dolazi da je uspinjanje penetranta sporije u užim procijepima (zbog viskoznosti), ali dugotrajnije (zbog jače rezultantne sile koja uzrokuje uspinjanje). Sa stajališta trajanja ispitivanja, geometrija

planparalelnih ploča je prikladnija jer se u kraćem vremenu postiže zasićenje procijepa penetrantima. To se vrijeme dodatno smanjuje za šire procijepe. Širina ne može biti po volji velika ako želimo uočljiv kapilarni učinak, tj. postignute visine koje su znatno veće nego njihove varijacije duž ploča i u uzastopnim ponavljanjima pokusa. Zbog toga je za provjeru radne kvalitete penetranta prikladnija geometrija planparalelnih ploča razmaknutih za oko 100 μm.

Budući da je radi lakše vizualizacije jedan objekt koji čini procijep uvijek bio staklena ploča, postignute visine u slučaju obje metalne ploče u određenoj bi se mjeri razlikovale. Iz postojećih ispitivanja nije moguće procijeniti za koji iznos i predznak bi se promijenila visini uspinjanja penetranta, odnosno vremenska ovisnost visine uspinjanja u slučaju kad su obje ploče od istog materijala.

4. ZAKLJUČAK

Metoda određivanja vremenske ovisnosti uspinjanja penetranta preliminarno pokazuje kvalitativno slaganje s uobičajenim svojstvima rabljenih fluida. Metoda je osjetljiva na čimbenike kojima se opisuju penetranti. Također se pokazuje i osjetljivost na neka svojstva okoline, npr. materijal stjenke procijepa. Navedeno upućuje na potrebu preciznog ispitivanja sposobnosti metode za razlikovanje penetranta iste nazivne vrste, ali različitih razina kvalitete za ispitivanje penetrantima.

U daljnjem radu pristupit će se ispitivanjima koja će obuhvaćati penetrante tijekom dužeg vremenskog razdoblja radi zahvaćanja i stanja njihove primjenjivosti i stanja njihove neprimjenjivosti za provedbu dijela nerazornih ispitivanja. Također, potrebno je povezati za istu vrstu penetranta rezultate za različite geometrije.

5. ZAHVALA

Ovaj rad izrađen je u okviru projekta MZOŠ “Pouzdanost metoda nerazornih ispitivanja”, br. 120-1201767-1763.

UTJECAJ OBRADE TALJEVINE NA MIKROSTRUKTURNE ZNAČAJKE AlSi10Mg LEGURE

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Izvorni znanstveni rad / Original scientific paper

Sažetak: U okviru ovoga rada utvrđen je utjecaj obrade taljevine AlSi10Mg legure sredstvima za usitnjavanje zrna i kemijskim modifikatorima na mikrostrukturne značajke i mehanička svojstva. Najčešće korištena sredstva za usitnjavanje su predlegure na bazi titana i bora u svrhu nukleacije što većeg broja primarnih zrna α_{Al}, od kojih je najpopularnija Al5Ti1B predlegura. Kemijskim se modifikatorima utječe na promjenu morfologije eutektičkog silicija iz igličastog (pločastog) u finiji vlaknasti oblik. Utvrđeno je da modifikacija natrijevim solima također poboljšava mehanička svojstva AlSi10Mg legure, posebno vlačnu čvrstoću. U ovom su radu ispitane fazna analiza, te mikrostrukturne značajke konstituenata poput srednje vrijednosti površine i srednje vrijednosti izduženja čestica pojedinih faza i razmak dendritnih grana (DAS) osnovne, cijepljene i modificirane taljevine AlSi10Mg legure. Zapaženo je da obrada taljevine cijepljenjem i modifikacijom općenito djeluje na usitnjavanje mikrostrukturnih konstituenata, odnosno kvantificiran je značajan učinak cijepljenja Al5Ti1B predlegurom na smanjenje primarnog aluminija, dok modifikacija natrijevim solima značajno smanjuje i morfološki mijenja eutektički silicij.

Ključne riječi: AlSi10Mg legura, obrada taljevine, mikrostruktura, mehanička svojstva.

Abstract: The influence of the melt treatment by the inoculants and chemical modificators on the microstructure characteristics and mechanical properties of the AlSi10Mg alloy has been examined in this work. The most common facilities for inoculation were master alloys on the titanium and boron base, with the most popular Al5Ti1B master alloy used for the purpose of the numerous primary grains of α_{Al} nucleation. Chemical modificators influenced the change of the eutectic silicon morphology form the needle (platelike) to finer lamellar shape. It has been determined that modification by the sodium salt also improves mechanical properties of the AlSi10Mg alloy, especially tensile strength. Phase analysis, microstructure characteristics of the constituents such as average surface area and elongation of the particles of particular phases, dendrite arm spacing (DAS) of the basic, inoculated and modificated melts of the AlSi10Mg alloy were determined in this work. It has been noticed that melt treatment by the inoculation and modification generally influences on the inoculation of the microstructural constituents, i.e. significant efficacy of the inoculation by the Al5Ti1B master alloy was established on the primary aluminum grain size decrease, while the modification by the sodium salt significantly influence and morphologically changes eutectic silicon.

Key words: AlSi10Mg alloy, melt treatment, microstructure, mechanical properties.

UVOD

Legura AlSi10Mg (EN AC 43000) spada u grupu široko primjenjivanih podeutektičkih Al-Si legura. Namijenjena je lijevanju odljevaka kompleksne geometrije u zrakoplovnoj, automobilskoj, kemijskoj i prehrambenoj industriji zbog dobrih mehaničkih svojstava i mogućnosti njihova povećanja umjetnim starenjem.

U tablici 1 prikazan je kemijski sastav AlSi10Mg legure namijenjene lijevanju u pijesak i lijevanju u trajne kalupe, dok su zahtijevana mehanička svojstva propisana normom EN 1706: 1998 [1] prikazana u tablici 2.

Tablica 1. Kemijski sastav AlSi10Mg legure namijenjene lijevanju u pijesak i kokilnom lijevanju [1]

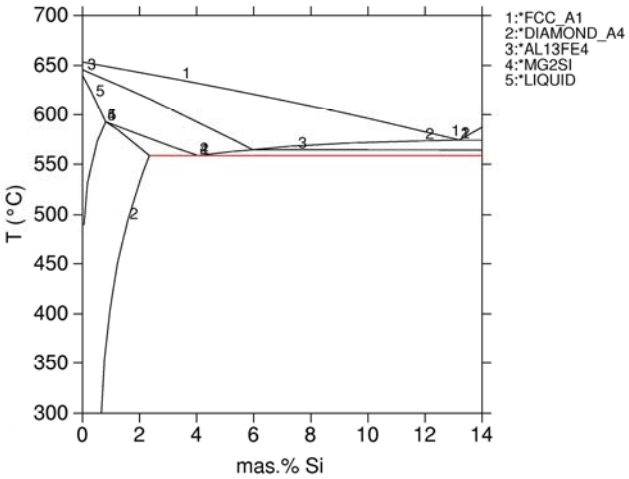
ELEMENT	Si	Fe	Cu	Mn	Mg	Ni	Zn	Pb	Sn	Ti	Ostale primjese
[mas. %]	9,0 – 11,0	0,55	0,005	0,45	0,20	0,005	0,10	0,05	0,05	0,15	0,15

Tablica 2. Mehanička svojstva lijevanih uzoraka prema EN 1706: 1998 [1].

Skupina legura	Postupak lijevanja	R_m, MPa	$R_{p0,2}$, MPa	$A_{50\ mm}$, %	HB
EN- AC 43000	Pijesak	150	80	2	50
	Kokila	180	90	2,5	55
EN-AC 43400	Visokotlačno lijevanje	240	140	1	70

Vlačna čvrstoća, granica razvlačenja $R_{p0,2}$ i tvrdoća tlačno lijevanih uzoraka su značajno više nego kod uzorka lijevanih u pijesak ili kokile. Samo istezanje je kod tlačno lijevanih odljevaka niže nego pri lijevanju u pijesak i kokilnom lijevanju. Razlog višim vrijednostima tvrdoće pri tlačnom lijevanju je sitnozrnata mikrostruktura, koja nastaje zbog uvjeta lijevanja.

Legura AlSi10Mg, obzirom na kemijski sastav tvori kompleksan dijagram stanja Al-Si-Mg proračunat pomoću ThermoCalc-a. Numeričko modeliranje ravnotežnog dijagrama stanja, nakon razvoja dendritne mreže primarnog α_{Al}, pretpostavlja izdvajanje faze na osnovi željeza $Al_{13}Fe_4$, te Mg_2Si ko – eutektičke faze.



Slika 1. Ravnotežni binarni dijagram stanja za leguru AlSi10Mg [2].

Interakcije pojedinih elemenata ukazuju na niz mogućih binarnih, ternarnih i kvaternarnih reakcija koje se tijekom skrućivanja mogu odvijati. Slijed skrućivanja podeutektičkih Al-Si legura općenito prati trend: stvaranje mreže dendrita α_{Al}, uz izlučivanje faza bogatih na željezu $Al_{15}(MnFe)_3Si_2$ i Al_5FeSi (ako je Fe>0,05%), te $Al_8Mg_3FeSi_6$ (ako je Fe>Mg), zatim eutektička reakcija $\alpha_{Al} + \beta_{Si}$, i naposljetku precipitacija sekundarne eutektičke faze Mg_2Si (Mg>0,2%) [3].

Obrada taljevine legure obuhvaća namjerne dodatke cjepiva i modifikatora s ciljem postizanja povoljnije veličine i morfologije mikrostrukturnih konstituenata.

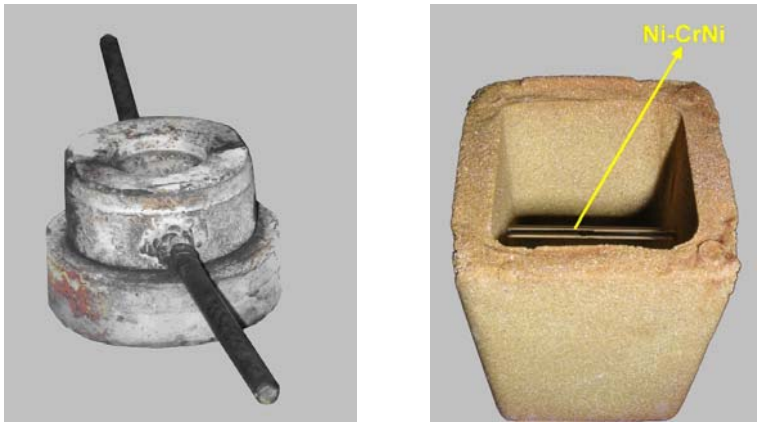
U inicijalnim stadijima skrućivanja cjepiva utječu na veličinu primarnih zrna stvarajući veliki broj potencijalnih centara kristalizacije, a samim tim i veći broj manjih, ujednačenih zrna. Primjenom sredstava za usitnjavanje zrna mogu se značajno poboljšati mehanička svojstva, napajanje odljevaka, smanjuje se poroznost, sastav taljevine podeutektičkih Al-Si legura postaje ujednačeniji, homogeniji čime se poboljšava kvaliteta odljevaka [4,5]. U industrijskoj proizvodnji najpopularnija metoda usitnjavanja zrna je upotreba sredstava za usitnjavanje zrna, čiji konstituenti djeluju kao podloge za stvaranje nukleusa prema mehanizmu heterogene nukleacije [4]. Ternarne legure na bazi bora su najčešće primjenjivano sredstvo za usitnjavanje zrna legura aluminija iz Al-Ti-B sistema na osnovu Al1Ti1B ili Al5Ti1B sastava. Predlegure dolaze u obliku žica, ploča, šipki, saća i tableta [6]. Količina predlegure koja se dodaje u taljevinu ovisi o kemijskom sastavu taljevine, sadržaju nečistoća i uvjetima lijevanja [6]. Stupanj pothlađenja neophodan za aktivaciju čestica predlegura je vrlo malen i iznosi 0,1 - 0,2 °C [4,7].

Modifikacija eutektika je postupak koji se koristi u industrijskoj proizvodnji proizvoda od Al-Si podeutektičkih legura u svrhu poboljšanja mehaničkih svojstava. Silicij u podeutektičkim Al-Si legurama skrućuje na fasetirani način što se manifestira igličastom ili pločastom morfologijom koja je tvrda i pogoršava mehanička svojstva. Postupkom modifikacije nastoji se prevesti silicij u povoljniji fini, vlaknasti oblik i postići njegovu ujednačeniju raspodjelu. Modifikacijom brzim hlađenjem ili putem dodatka kemijskih modifikatora poboljšavaju se mehanička svojstva i duktilnost Al-Si legura [8]. Prijelaz iz pločaste i igličaste u vlaknastu morfologiju povezan je s povećanjem pothlađenja [9,10]. Najviše se u industrijskoj proizvodnji koriste natrij i stroncij [9]. Antimon ne mijenja morfologiju silicija, već je usitnjava [6].

Utjecaj modifikatora na napajanje tijekom skrućivanja je kompleksan i zavisi od brzine hlađenja, sastava taljevine i njegovu dodatku u taljevinu. Dok sredstva za usitnjavanje zrna odgađaju razvoj dendritne mreže, modifikatori mijenjaju oblik fronta rasta eutektika. Natrij dozvoljava razvoj planarnog skrućivanja dendritne mreže i minimalno zarobljavanje tekućine u džepovima. Zbog kompleksnosti utjecajnih varijabli poput različitih namjernih dodataka u taljevinu uključujući i cjepiva i modifikatore postižu se različite mikrostrukturne značajke što kasnije izravno utječe na mehanička svojstva odljevaka.

METODOLOGIJA ISPITIVANJA

U okviru ovog rada ispitane su mikrostrukturne značajke osnovne cijepljene i modificirane taljevine AlSi10Mg legure lijevane u croning lončić (slika 2b) radi utvrđivanja utjecaja obrade taljevine. Preliminarno je ispitan kemijski sastav AlSi10Mg legure na spektrometru LABM3 787/86 na uzorcima osnovne, cijepljene i modificirane taljevine lijevanih u specijalnu bakrenu kokilu, prikazanu na slici 2a.



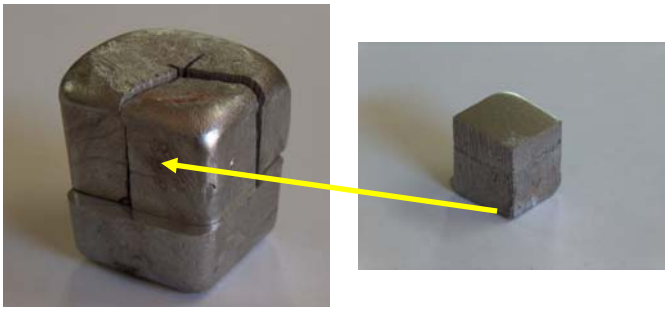
a) **b)**

Slika 2. Fotografije kalupa za lijevanje uzoraka AlSi10Mg legure:
a) bakrena kokila za lijevanje pločica namijenjenih kemijskoj analizi;
b) standardni croning lončić Quick Cup;

Jedan dio osnovne taljevine cijepljen je pomoću Al5Ti1B predlegure (1 [mas.%]), a drugi dio taljevine modificiran je dodatkom natrijeve soli $NaF+Na_2CO_3$ (0,77 [mas.%]). Uzorci osnovne, modificirane i cijepljene taljevine, lijevani su i u čeličnu kokilu, prikazanu na slici 3 iz kojih su izrađeni ispitni uzorci za određivanje vlačne čvrstoće.

Slika 3. Čelična kokila za lijevanje ispitnih uzoraka za vlačna ispitivanja.

Utvrđivanje povezanosti mikrostrukturnih značajki uzoraka osnovne taljevine i taljevine s dodatkom cjepiva i modifikatora provedeno je pomoću mikrostrukturne analize, na uzorcima lijevanim iz osnovne taljevine AlSi10Mg legure, te taljevine cijepljene Al5Ti1B predlegurom i taljevine modificirane natrijevom soli u croning lončić, kako je prikazano slikom 4.



a) **b)**

Slika 4. Metodologija uzorkovanja za mikrostrukturnu analizu:
a) fotografija izrezanog uzorka lijevanog u croning lončić;
b) uzorak za mikrostrukturnu analizu.

Za svako stanje taljevine lijevano je 2-5 uzoraka. Metalografska analiza uzoraka provedena je na optičkom metalografskom mikroskopu Olympus GX51. Uzorci su snimani digitalnom kamerom Olympus DP70, dok je analiza provedena na računalu uz pomoć softvera Analysis®MaterialsResearchLab kod različitih povećanja. Fazna analiza čestica provedena je pri povećanju mikroskopa od 200X na 3 detalja svakog uzorka, dok je razmak dendritnih grana (DAS analiza) utvrđen na 3 detalja pri povećanju od 50X.

REZULTATI I DISKUSIJA

Kemijska analiza

Rezultati kemijske analize uzoraka – pločica osnovne taljevine ispitivane AlSi10Mg legure, cijepljene Al5Ti1B i modificirane $NaF+Na_2CO_3$, lijevanih u bakrenu kokilu prikazani su tablicom 3.

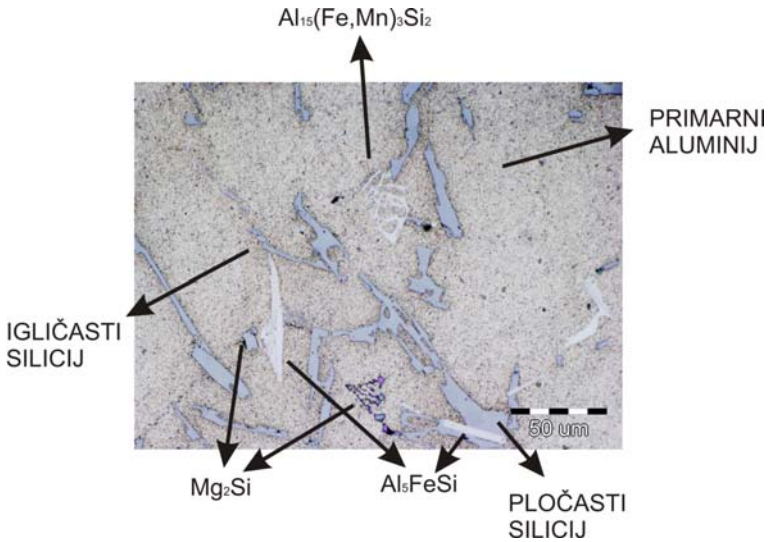
Tablica 3. Kemijski sastav uzorka taljevine AlSi10Mg legure.

KEMIJSKI SASTAV	ELEMENT [mas. %]									
	Si	Fe	Cu	Mn	Mg	Ni	Zn	Ti	B	Na
OSNOVNA TALJEVINA	9,8300	0,3180	0,0320	0,1180	0,3710	0,0023	0,1030	0,0120	0,0013	0,0009
CIJEPLJENA TALJEVINA (Al5Ti1B)	9,9000	0,2990	0,0370	0,0540	0,3620	0,0025	0,0870	0,0210	0,0021	0,0040
MODIFICIRANA TALJEVINA ($NaF+Na_2CO_3$)	10,180	0,3130	0,0380	0,0680	0,4200	0,0026	0,0900	0,0090	0,0011	0,0027

Maseni sadržaj osnovnog legirajućeg elementa Si nalazi se u normom propisanim granicama. Koncentracije Fe i Mn su nešto niže od normom propisanih maksimalnih vrijednosti što upućuje na čišći uložni materijal. Zapažene su očekivano više vrijednosti koncentracije Ti i B u cijepljenoj taljevini zbog dodatka 1 [mas.%] predlegure Al5Ti1B u odnosu na osnovnu taljevinu. U kemijskom sastavu modificirane legure uočen je povišen sadržaj Na u odnosu na osnovnu taljevinu radi dodatka natrijevih soli s ciljem modifikacije taljevine.

Identifikacija mikrostrukturnih konstituenata AlSi10Mg legure

Identifikacija intermetalnih faza provedena je na uzorku osnovne taljevine AlSi10Mg leguri, lijevanom u croning lončić, kako je prikazano slikom 5.

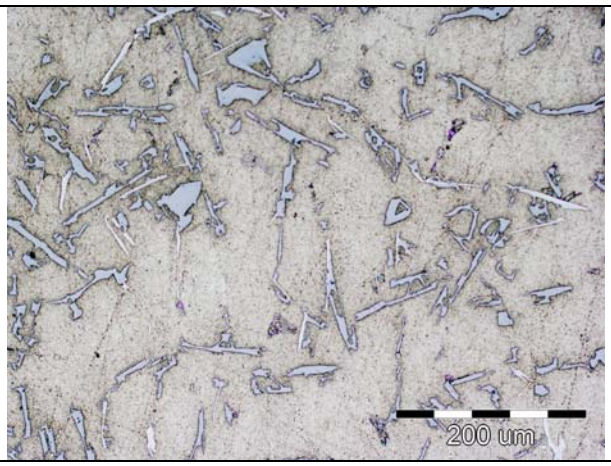
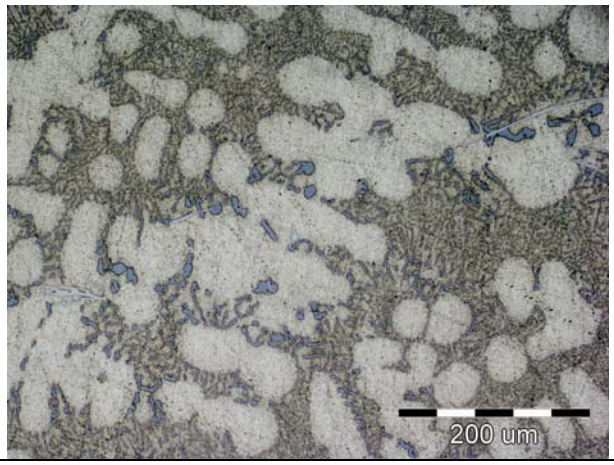


Slika 5. Mikrostruktura osnovne taljevine AlSi10Mg

Svijetlo siva podloga predstavlja primarni aluminij – α_{Al}. Silicij dolazi u obliku iglica i pločica, i sive je boje. Prikazana morfologija eutektičkog silicija nepovoljno utječe na mehanička svojstva. Intermetalne faze bogate željezom izlučuju se kao $Al_{15}(MnFe)_3Si_2$ u obliku kineskog pisma i Al_5FeSi u obliku iglica, i karakteristične su bijele boje. Uočeno je da je udio intermetalne faze $Al_{15}(MnFe)_3Si_2$ manji od udjela igličaste Al_5FeSi faze, što se može povezati s niskim brzinama hlađenja koje pogoduju izlučivanju morfologije iglica, ali i nižem masenom sadržaju Mn. Faza Mg_2Si je crne boje i izlučuje se na već razvijenom eutektičkom siliciju kao sekundarna eutektička faza. Udio Mg_2Si je relativno nizak zbog niskih koncentracija magnezija u ispitivanoj leguri.

Metalografska analiza uzoraka obzirom na obradu taljevine

Metalografska analiza uzoraka osnovne taljevine AlSi10Mg legure, legure cijepljene predlegurom, te analiza legure modificirane natrijevim solima, lijevanih u croning lončić, pri povećanju mikroskopa od 200X usporedno je prikazana slikom 6.

OBRADA TALJEVINE	MIKROSTRUKTURA
OSNOVNA TALJEVINA	
CIJEPLJENA TALJEVINA s Al5Ti1B	
MODIFICIRANA TALJEVINA s $NaF+Na_2CO_3$	

Slika 6. Usporedni niz mikrostruktura AlSi10Mg legure obzirom na obradu taljevine.

Metalografska analiza ukazuje na značajan utjecaj pojedinačne obrade taljevine cijepljenjem i modifikacijom na morfologiju i raspodjelu čestica. Intermetalne faze bogate željezom u značajnom su udjelu prisutne u mikrostrukturama uzoraka osnovne, cijepljene i modificirane taljevine i uglavnom

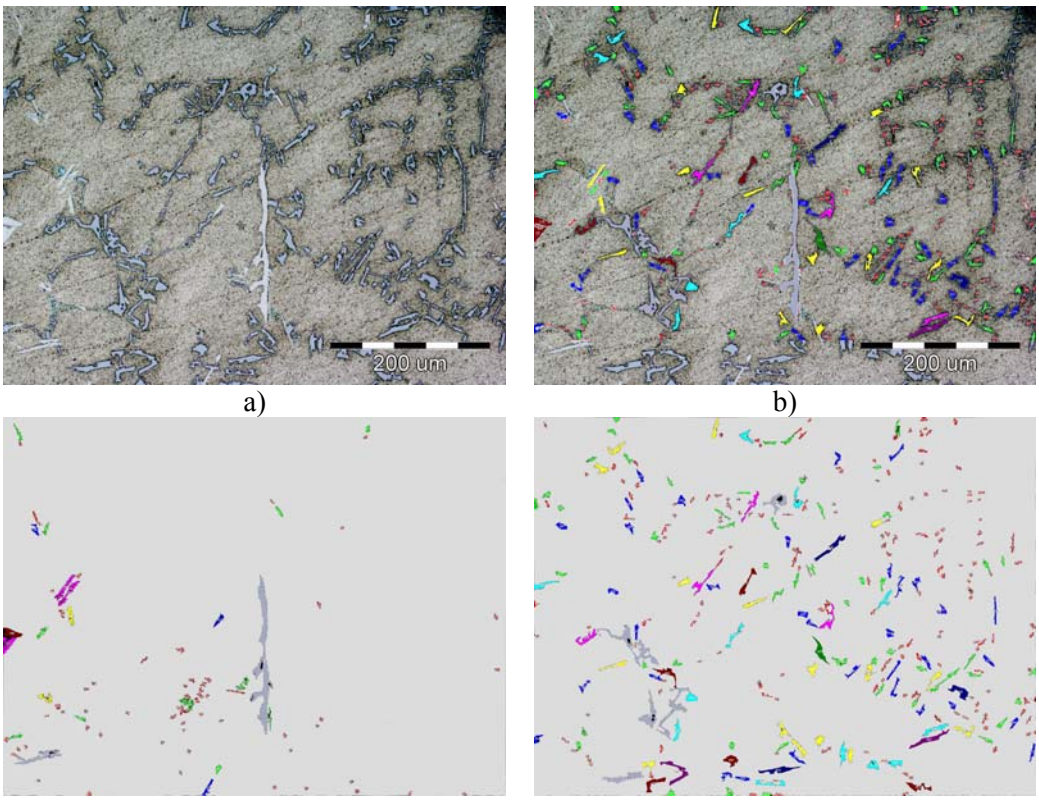
morfologije iglica karakterističnih za Al_5FeSi fazu, što se može pripisati sporom hlađenju taljevine u croning lončiću.

Cijepljenje Al5Ti1B predlegurom ima veći utjecaj na izlučivanje α_{Al}, što se manifestira većim područjima primarnih aluminijskih zrna. Zapaža se relativno grubi primarni α_{Al} i eutektički silicij. Metalografska analiza ukazuje na to da se cijepljenjem olakšava izlučivanje primarnog α_{Al}, odnosno povećava nukleacijski potencijal, uz pomoć dodataka koji iniciraju razvoj većeg broja visokotemperaturnih kristalizacijskih centara u taljevini i pritom omogućavaju postizanje istoosne mikrostrukture.

Dodatak natrija u taljevinu utječe na rast eutektičke faze tako da olakšava rast eutektičkog silicija, razvijanje planarne granične površine ukupnog rasta i prevođenje morfologije eutektičkog silicija u vlaknastu. Vlaknasti eutektički silicij je daleko sitniji u modificiranoj AlSi10Mg leguri u odnosu na igličastu morfologiju u osnovnoj i cijepljenoj AlSi10Mg leguri. U mikrostrukturi modificirane AlSi10Mg legure uočava se tendencija ka stvaranju eutektičkih kolonija silicija, te primarnog α_{Al} u izrazito usmjerenom, karakterističnom dendritnom obliku. Modifikacija ne odgađa razvoj dendritne mreže uslijed čega je metalografskom analizom ustanovljen daleko manji udio α_{Al}.

Mikrostrukturna fazna analiza uzoraka obzirom na obradu taljevine

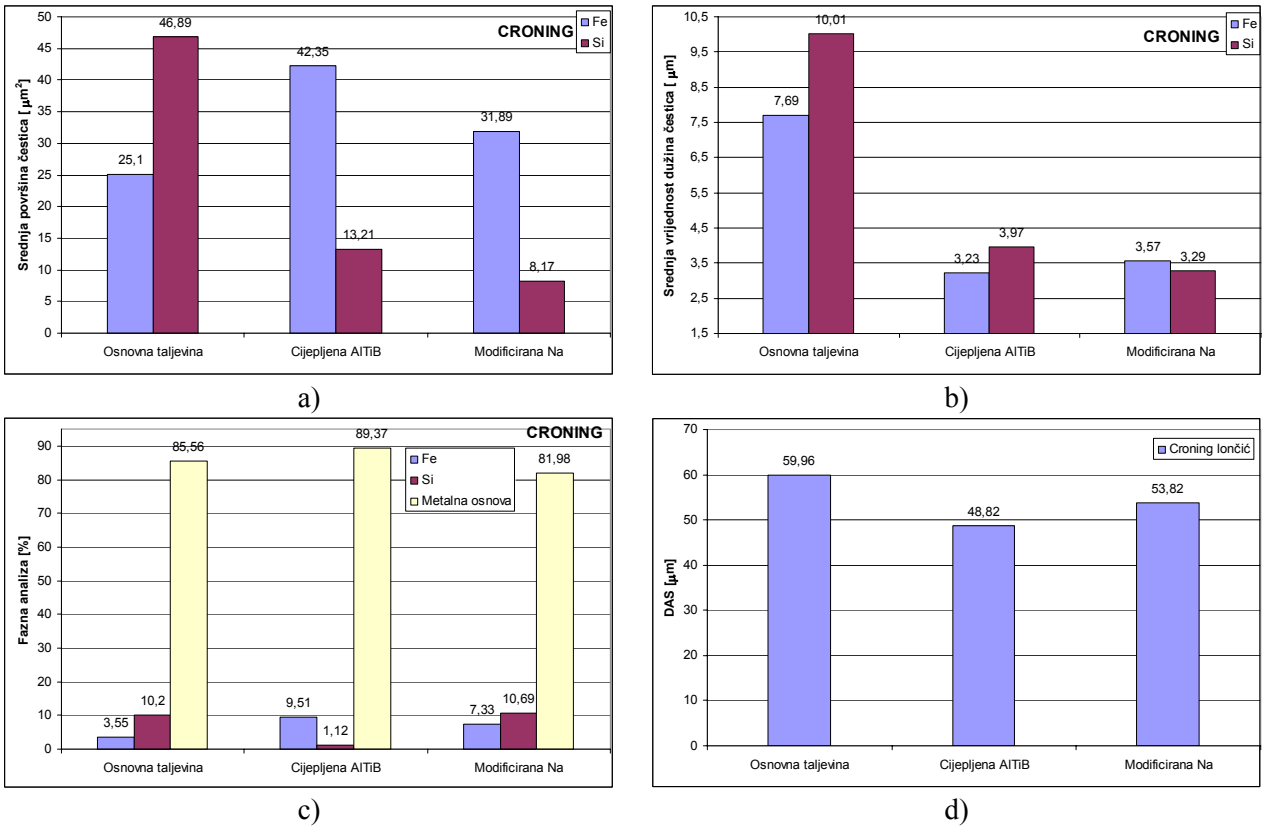
Mikrostrukturna analiza uzoraka AlSi10Mg legure provedena je radi identifikacije mikrostrukturnih konstituenata i utvrđivanja fazne analize uzoraka pri različitim načinima obrade taljevine. Slika 7 prikazuje primjer fazne analize čestica na mikrostrukturi uzorka osnovne taljevine AlSi10Mg legure.



a) b) c) d)

Slika 7. Mikrostrukturna fazna analiza uzorka AlSi10Mg legure:
a) analizirana mikrostruktura uzorka,
b) identifikacija pojedinih faza mikrostrukture,
c) intermetalne faze na osnovi željeza,
d) intermetalne faze na osnovi silicija.

Osim izdvajanja pojedinih faza određena je i srednja površina i dužina čestica pojedinih faza na osnovu željeza i silicija. Slika 8 prikazuje histograme povezanosti kvantificiranih mikrostrukturnih značajki pojedinih faza i načina obrade taljevine.



Slika 8. Prikaz ovisnosti mikrostrukturnih značajki od načina obrade taljevine AlSi10Mg legure.

a) ovisnost srednje površine čestica pojedinih faza od obrade taljevine,
b) ovisnost srednje dužine čestica pojedinih faza od obrade taljevine,
c) ovisnost fazne analize uzoraka od obrade taljevine,
d) ovisnost veličine DAS-a od obrade taljevine.

Očekivano je smanjenje površine čestica pojedinih faza cijepljenjem. Međutim srednja površina intermetalnih faza bogatih željezom povećava se cijepljenjem sa 25,1 μm^2 na 42,35 μm^2 što se pripisuje postojanosti željeznih faza pri visokim temperaturama (iznad likvidus temperature) pri kojima cijepljenje još nije učinkovito. Srednja površina čestica silicijeve faze smanjuje se cijepljenjem na 13,21 μm^2, a modifikacijom na 8,17 μm^2. Općenito, cijepljenje Al5Ti1B predlegurom i modifikacija natrijevim solima AlSi10Mg legure također značajno smanjuju srednju vrijednost dužine čestica intermetalnih faza na osnovi željeza sa 7,69 µm na 3,23 µm cijepljenjem i na 3,57 µm modifikacijom, a fazu eutektičkog silicija s 10,01 µm na 3,97 µm cijepljenjem i 3,29 µm modifikacijom. Iz navedenog možemo zaključiti da se čestice željeza usitnjavaju i zaobljavaju, a čestice silicija prevode u pogodniji vlaknasti oblik, što bi u pravilu trebalo pogodovati povećanju mehaničkih svojstva odljevaka. Cijepljenje značajno smanjuje sadržaj izlučene eutektičke silicijeve faze s 10,2 % na 1,12 %, i povećava sadržaj izlučenih intermetalnih faza bogatih željezom s 3,55% na 9,51 %, dok neznatno povećava sadržaj metalne osnove.

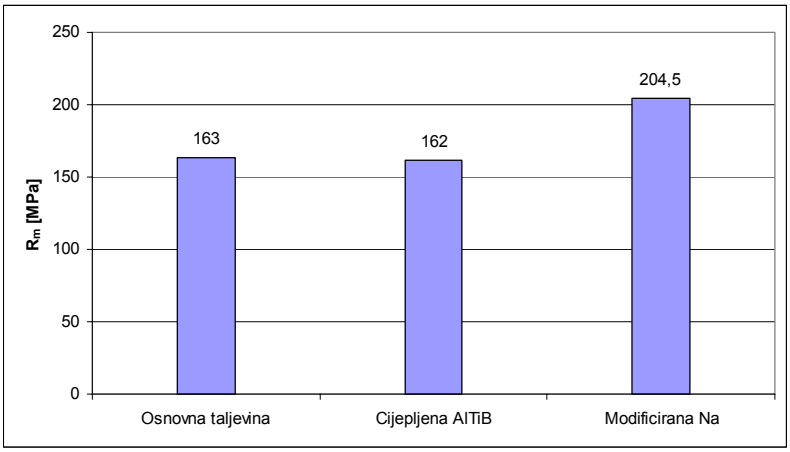
Modifikacija neznatno povećava sadržaj faze eutektičkog silicija i smanjuje sadržaj metalne osnove. Kako se i očekivalo modifikacija ne mijenja sadržaj faze eutektičkog silicija i smanjuje sadržaj metalne osnove. Razlog tome nalazimo u tome da natrij djeluje samo na fazu eutektičkog silicija, dok Al5Ti1B predlegura djeluje na izlučivanje odnosno sadržaj primarnog aluminija (metalne osnove). Cijepljenjem se povećava sadržaj metalne osnove odnosno primarnog i eutektički izlučenog

α_{Al}, dok se istovremeno potiskuje udio izlučenog eutektika odnosno silicija. Čini se da cijepljenje Al5Ti1B nema značajnijeg utjecaja na promjenu udjela izlučenih intermetalnih faza bogatih željezom.

Najveći utjecaj na razmak dendritnih grana (DAS) ima cijepljenje taljevine, što je i očekivano obzirom na porast nukleacijskog potencijala i olakšavanje razvoja α_{Al}.

Utjecaj obrade taljevine na mehanička svojstva ispitnih uzoraka AlSi10Mg legure

Slikom 9 prikazan je utjecaj obrade taljevine cijepljenjem i modifikacijom na vlačnu čvrstoću ispitnih uzoraka AlSi10Mg legure.



Slika 9. Utjecaj obrade taljevine na vlačnu čvrstoću uzoraka.

Cijepljenje Al5Ti1B predlegurom nema značajan utjecaj dok modifikacija značajno povećava vlačnu čvrstoću. Porast čvrstoće uzoraka modificirane taljevine pripisuje se vlaknastoj morfologiji eutektičkog silicija, dok bi razlog nepromijenjene vlačne čvrstoće uzorka cijepljene legure trebalo utvrditi daljnjim istraživanjima.

ZAKLJUČAK

Mikrostrukturna ispitivanja uzoraka osnovne i obrađene taljevine AlSi10Mg legure cijepljenjem Al5Ti1B predlegurom i modifikacijom natrijevim solima ($NaF+Na_2CO_3$) rezultirala su slijedećim zaključcima:

- Ispitivanjem mikrostrukture osnovne AlSi10Mg legure utvrđeno je prisustvo slijedećih faza: intermetalne faze bogate željezom većinom izlučene u obliku iglica - Al_5FeSi faza i nešto manje u obliku kineskog pisma $Al_{15}(MnFe)_3Si_2$, vjerojatno zbog nižeg sadržaja Fe i Mn u ispitivanoj leguri, te niskih brzina hlađenja. Sadržaj izlučene Mg_2Si faze je neznatan zbog niske koncentracije magnezija u ispitivanoj leguri.
- Cijepljenjem i modifikacijom dolazi do usitnjavanja i promjene morfologije rasta eutektičkih zrna, čime se smanjuje dendritna koherencija.
- Cijepljenje Al5Ti1B predlegurom prvenstveno utječe na izlučivanje primarnog aluminija što se manifestira smanjenjem DAS-a (za ~11 μm) na osnovu čega se može eksplicitno zaključiti o primarnoj učinkovitosti cijepljenja na usitnjavanje α_{Al}. Općenito dolazi do smanjenja srednje površine i dužine čestica pojedinih faza što ukazuje na povećanje nukleacijskog potencijala uslijed većeg broja centara nukleacije uvedenih cjepivom.
- Modifikacija s $NaF+Na_2CO_3$ značajnije smanjuje srednju površinu čestica eutektičkog silicija predvodeći ga u vlaknasti, morfološki povoljniji oblik, dok je njen učinak na dužinu čestica

obje faze približan onome od cijepljenja. U odnosu na osnovnu taljevinu, DAS je smanjen za ~6 μm.

- Cijepljenje Al5Ti1B predlegurom nije utjecalo na vlačnu čvrstoću ispitivane AlSi10Mg legure, dok ju je modifikacija natrijem značajno povećala. Razlog povećanju čvrstoće AlSi10Mg legure modificirane natrijem treba tražiti u promjeni morfologije eutektičkog silicija.

Pojedinačna obrada taljevine cijepljenjem i modifikacijom općenito pokazuje pozitivan učinak na mikrostrukturne značajke pojedinih faza jer se one prevode u sitniji, ujednačeniji i morfološki povoljniji oblik koji osigurava kompaktnost mikrostrukture i u konačnici povoljnija svojstva.

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