

ZAŠTITA MATERIJALA I ŽIVOTNE SREDINE

MATERIAL AND ENVIRONMENT PROTECTION



ČASOPIS: ZAŠTITA MATERIJALA I ŽIVOTNE SREDINE

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UTICAJ GUSTINE STRUJE NA MORFOLOGIJU ELEKTROHEMIJSKI DOBIJENOG BAKARNOG PRAHA

INFLUENCE CURRENT DENSITY ON THE MORPHOLOGY ELECTROCHEMICAL OBTAINED COPPER POWDER

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Izvod

U radu je ispitivan uticaj gustine struje na morfologiju elektrohemski dobijenog bakarnog praha. Vršeno elektrohemski taloženje bakarnog praha iz sulfatnih elektrolita. Korišćeni su elektroliti sa tri koncentracije Cu^{2+} ($7 \text{ g}/\text{dm}^3$, $18 \text{ g}/\text{dm}^3$ i $33 \text{ g}/\text{dm}^3$) i svaka u kombinaciji sa tri koncentracije H_2SO_4 ($100 \text{ g}/\text{dm}^3$, $150 \text{ g}/\text{dm}^3$ i $200 \text{ g}/\text{dm}^3$), tako da je bakarni prah taložen iz devet elektrolita. Kao katoda je korišćena bakarna žica površine 1cm^2 , a bakarna anoda je bila priljubljena uz zid elektrohemiske laboratorijske celije zapremine 500cm^3 . Eksperimenti su rađeni na sobnoj temperaturi, a cirkulacija elektrolita vršena je pomoću magnetne mešalice.

Bakarni prah taložen je galvanostatski pri gustinama struje od: $j=1500A/\text{m}^2$, $j=2000A/\text{m}^2$ i $j=2500A/\text{m}^2$. Proizvedeni bakarni prah sa katode otresan je svakih tri minuta. Sve osobine praha zavise od oblika i dimenzije čestice (morfologije), od kojih je prah sačinjen i međusobno su povezane. Ispitivanje morfologije i veličine čestice vršeno je pomoću skenirajuće elektronske mikroskopije (SEM). Analizom dobijenih mikrofotografija utvrđeno je da se sa povećanjem gustine struje morfologija čestica bakarnog praha menja od kompaktnih, masivnih dendrita i masivnih čestica, do razgranatih, 3D dendrita koji imaju strukturu kao zrna kukuruza. Sa povećanjem gustine struje dobijaju se sitnija zrna bakarnog praha koja su pravilno raspoređena.

Ključne reči: kataliza, elektrokataliza, elektrohemski taloženje, prah bakra, morfologija, karakterizacija.

Abstract

The paper investigates the effect of current density on the morphology of copper powder obtained electrochemically. Copper powder from sulphate electrolytes was deposited electrochemically. The electrolytes used had three different concentrations of Cu^{2+} ($7 \text{ g}/\text{dm}^3$, $18 \text{ g}/\text{dm}^3$ and $33 \text{ g}/\text{dm}^3$) each combined with three concentrations of H_2SO_4 ($100 \text{ g}/\text{dm}^3$, $150 \text{ g}/\text{dm}^3$ and $200 \text{ g}/\text{dm}^3$), so that copper powder was deposited from nine electrolytes. The cathode was a copper wire with the surface of 1cm^2 , whereas the copper anode was attached to the wall of the electrochemical laboratory cell with the volume of 500cm^3 . The experiments were performed at room temperature and the circulation of electrolytes was conducted using a magnetic stirrer.

Copper powder was deposited galvanostatically at the following current densities: $j=1500A/\text{m}^2$, $j=2000A/\text{m}^2$ and $j=2500A/\text{m}^2$. The copper powder produced was shaken off from the cathode every three minutes. All the properties of the powder depend on the shape and size of the particles (morphology) which constitute the powder and they are in correlation. Investigation of the morphology of particles was performed using scanning electron microscopy (SEM). The analysis of the obtained microphotographs shows that the increase of current density changes the morphology of copper powder particles from compact, massive dendrites and massive particles to

branching 3D dendrites with the straucture of corn grains. The increase in current density results in smaller particles of copper powder which are evenly distributed.

Key words: catalysis , electrocatalysis , electrodeposition, copper powder , morphology , characterization .

Uvod

U zavisnosti od oblika i namene proizvoda, prahovi koji se koriste za njihovu proizvodnju moraju da zadovolje različite zahteve [1]. Postojanje različitih metoda za proizvodnju prahova posledica je ne samo raznovrsnosti zahteva koje treba da ispune prahovi koji se primenjuju u različitim oblastima, već i raznolikosti osobina samih metala. Za primenu metalnih prahova od važnosti su sledeće osobine: fizičke (veličina čestica, raspodela veličina čestica i specifična površina), hemijske (sadržaj metala, primesa, adsorbovanih ili rastvorenih gasova i koroziona otpornost) i tehnološke (nasipna masa, brzina tečenja, prividna gustina, mogućnost presovanja, itd.). Sve tehnološke osobine uglavnom zavise od oblika i veličine čestica, zbog čega je pri taloženju prahova od velike važnosti mogućnost dobijanja čestica odgovarajuće nasipne mase i morfologije. Elektrolitička metoda dobijanja prahova ima niz prednosti u poređenju sa drugim metodama proizvodnje praha. Tu se, pre svega, misli na visoku čistoću dobijenog praha i njegove izvanredne tehnološke karakteristike (moć presovanja i sinterabilnost). Elektrolizom je moguće proizvesti prahove oko 60 metala. Danas se elektrolizom vodenih rastvora i rastopa soli dobijaju prahovi bakra, srebra, železa, cinka, nikla, kadmiјuma, olova, kalaja, antimona, titana, cirkonijuma, vanadijuma, tantala, urana, torijuma i dr. Većina prahova dobija se primenom rastopljenih elektrolita, dok oko 20 metala može da se istaloži iz rastvora [1-4].

Poslednjih godina je pokazano [6-11] da je variranjem sastava elektrolita i režima elektrolize moguće dobiti prahove sa širokim dijapazonom osobina kao i

predvideti odlučujuće karakteristike prahova koji su od vitalne važnosti za kvalitet praha i odgovarajuću namenu. Industrijska proizvodnja bakarnog praha elektrolitičkim putem daleko je veća od proizvodnje bilo kog drugog metalnog praha [6,12]. Bakarni prahovi proizvedeni elektrolizom su visoke čistoće a moguće ih je proizvesti u širokom opsegu osobina tako da mogu da zadovolje mnoge zahteve. Čestice elektrolitičkog bakarnog praha imaju prvenstveno dendritični oblik. Specifična površina prahova je velika ($800-2500 \text{ cm}^2/\text{g}$), a nasipna masa se kreće u opsegu ($0.4-4.7 \text{ g/cm}^3$) [5]. Bez sumnje, najbolji elektroliti za dobijanje bakarnog praha elektrohemiskim putem su sulfatni [6,7,12-15], mada se u literaturi mogu naći i hloridni, koji do sada nisu našli primenu u industriji. Sulfatni elektroliti sadrže bakar-sulfat i sumpornu kiselinu, kao glavne komponente [$(5-45) \text{ g/dm}^3 \text{ Cu}^{2+}$ i $(120-250) \text{ g/dm}^3 \text{ H}_2\text{SO}_4$ respektivno], i ponekad hloridne jone (radi regulisanja dendritičnosti praha, kao sekundarnu komponentu).

Glavni parametri pri proizvodnji bakarnog praha elektrolitičkim putem su: katodna gustina struje, sadržaj bakra i sumporne kiselina u elektrolitu, temperatura elektrolita, brzina cirkulacije elektrolita, trajanje perioda rasta praha. Variranjem ovih parametra moguće je dobiti prahove bakra različitih morfoloških oblika, dimenzija i nasipnih masa.

Cilj ovog rada je da se ispita uticaj promene koncentracije Cu^{2+} jona i katodne gustine struje pri odgovarajućoj koncentraciji sumporne kiseline u elektrolitima na morfologiju elektrohemiski dobijenog bakarnog praha.

Eksperimentalni deo

Pri eksperimentalnom radu korišćeno je devet elektrolita čiji sastav i radni uslovi su prikazani u tabeli 2. Korišćene su tri koncentracije Cu^{2+} (7 g/dm³; 18 g/dm³ i 33 g/dm³) i svaka u kombinaciji sa tri koncentracije H_2SO_4 (100 g/dm³; 150 g/dm³ i 200 g/dm³), tako da je bakarni prah elektrolitički taložen iz devet različitih

elektrolita na sobnoj temperaturi i pri tri različite gustine struje (1500 A/m²; 2000 A/m² i 2500 A/m²).

Cirkulacija elektrolita vršena je pomoću magnetne mešalice. Kao katoda korišćena je bakarna žica površine ($S_{\text{elektr.}} = 1 \text{ cm}^2$), a bakarna anoda je bila priljubljena uz zid elektrohemiske laboratorijske celije zapremine 500 cm³.

Tabela 1. Sastav elektrolita i radni uslovi

Elektrolit	Sastav		Radni uslovi	
	Cu^{2+} (g/dm ³)	H_2SO_4 (g/dm ³)	Temperatura	Gustina struje (A/dm ²)
R I	7	100	sobna	$j = 1500 \text{ A/m}^2$ $j = 2000 \text{ A/m}^2$ $j = 2500 \text{ A/m}^2$
R II	7	150		
R III	7	200		
R IV	18	100		
R V	18	150		
R VI	18	200		
R VII	33	100		
R VIII	33	150		
R IX	33	200		

Pre svakog eksperimenta, elektrode su nagrizane u rastvoru HNO_3 (1:1), ispirane protočnom vodom, a zatim dva puta destilovanom vodom. Anoda je bila u svim slučajevima priljubljena uz zidove cilindrične celije, a katoda uronjena u sredinu celije. Proizvedeni bakarni prah sa katode otresan je svakih tri minuta. Otreseni prah ispiran je protočnom i dva puta destilovanom vodom i suspendovan u etanolu.

Za optičko ispitivanje praha u ovom radu korišćen je skenirajući elektronski mikroskop (SEM), koji predstavlja jedan od najboljih raspoloživih uređaja za

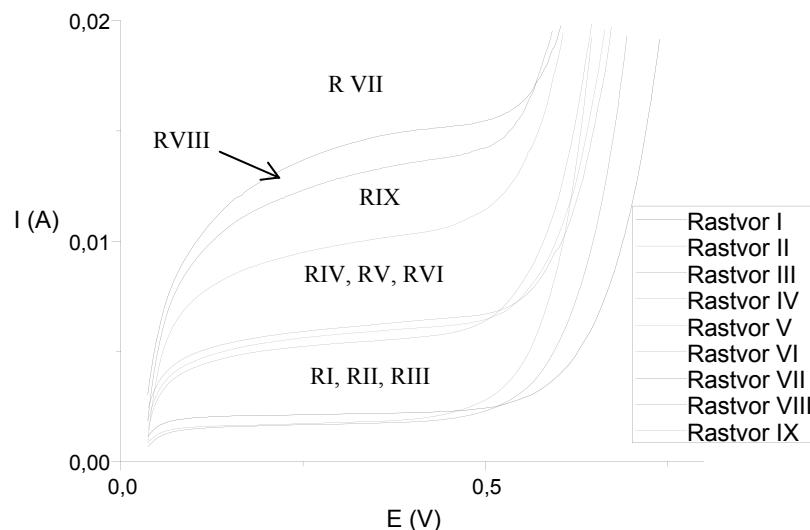
posmatranje diskretnih karakteristika metalnih prahova.

Morfologija čestica bakarnih prahova dobijenih pri navedenim uslovima praćene su primenom skenirajućeg elektronskog mikroskopa tipa Philips, model XL30, pri uvećanjima od 100x do 10 000x. Polarizacioni dijagrami snimljeni su pomoću potencijostata/galvanostata/ZRA Gamry Series GTM. Potencijostat/galvanostat/ZRA Gamry GTM 750 je veoma precizni istraživački elektrohemiski instrument koji je projektovan da bude ugrađen u kompjuter.

Rezultati i diskusija

Da bi se odabrala optimalna područja potencijala i struje za taloženje bakarnog praha, snimljene su katodne polarizacione

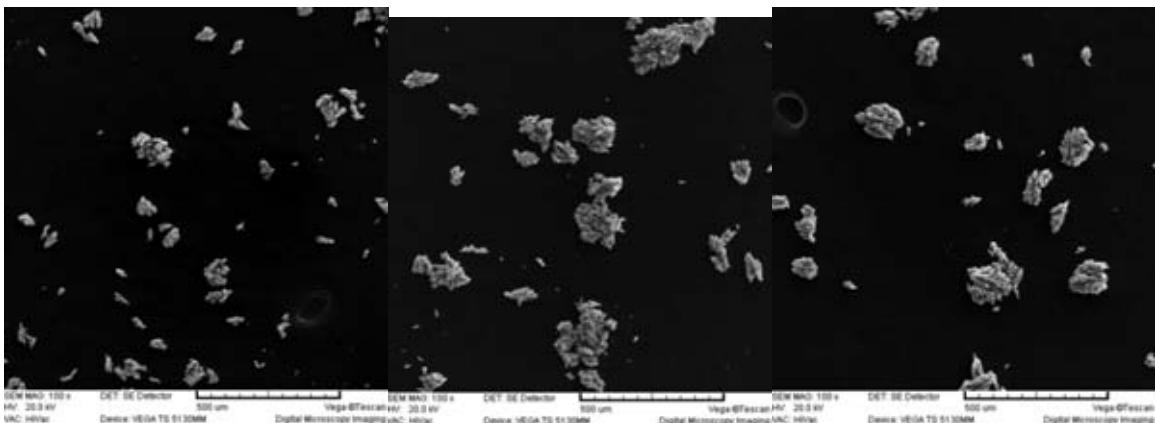
krive za svih devet pripremljenih elektrolita. Na slici 1. prikazane su katodne polarizacione krive za proces taloženja bakra iz pripremljenih elektrolita (I – IX).



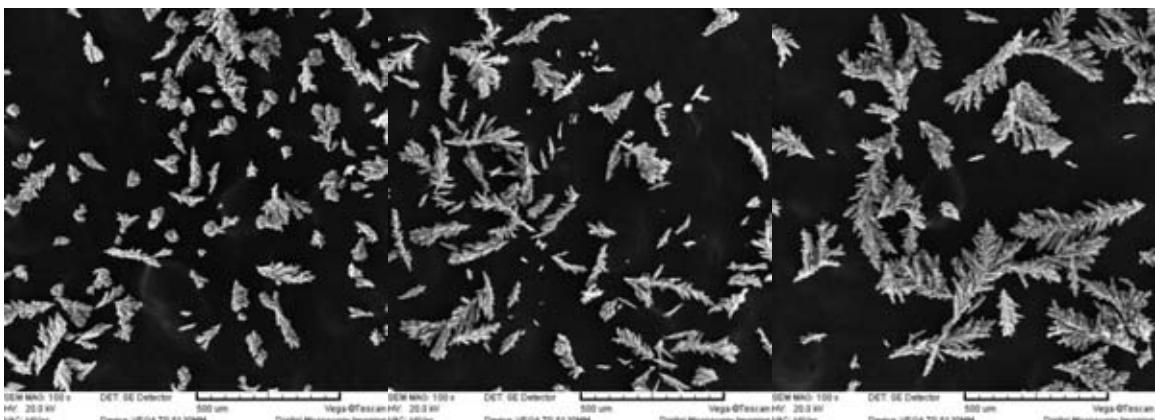
Slika 1. Polarizacione krive za katodni proces taloženja bakra

Sa slike 1. se može videti velika podudarnost polarizacionih krivih u oblasti platoa za rastvore R_I-R_{III} ($Cu^{2+} = 7\text{ g}/\text{dm}^3$), bez obzira na promenu koncentracije H_2SO_4 . Takođe, to se može primetiti i za rastvore R_{IV}-R_{VI} ($Cu^{2+} = 18\text{ g}/\text{dm}^3$) uz pomeranje platoa u oblast veće gustine

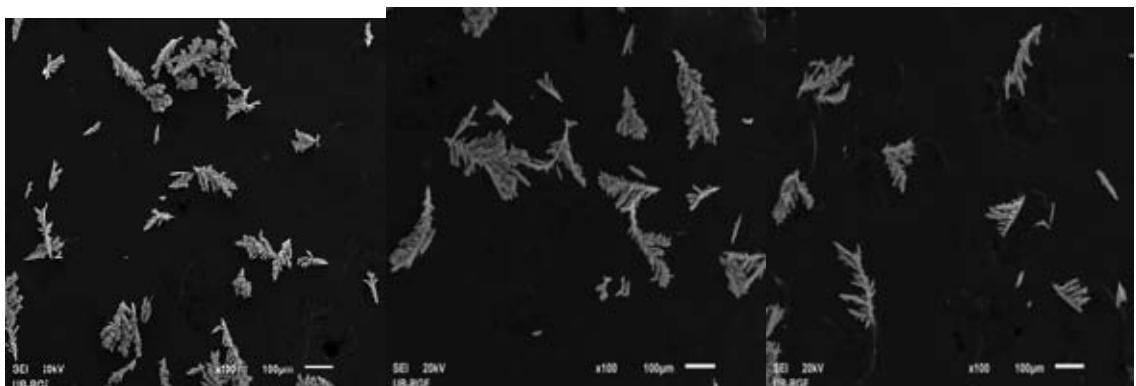
struje. Međutim, za rastvore R_{VII}, R_{VIII} i R_{IX} nema podudarnosti polarizacionih krivih u oblasti platoa, što ukazuje na veći uticaj H_2SO_4 pri koncentraciji $Cu^{2+} = 33\text{ g}/\text{dm}^3$ na elektrohemski proces i dobijanje bakarnog praha.



a) $j=1500 \text{ A/m}^2$; $\text{Cu}^{2+}=7 \text{ g/dm}^3$ b) $j=2000 \text{ A/m}^2$; $\text{Cu}^{2+}=7 \text{ g/dm}^3$ c) $j=2500 \text{ A/m}^2$; $\text{Cu}^{2+}=7 \text{ g/dm}^3$



a) $j=1500 \text{ A/m}^2$; $\text{Cu}^{2+}=18 \text{ g/dm}^3$ b) $j=2000 \text{ A/m}^2$; $\text{Cu}^{2+}=18 \text{ g/dm}^3$ c) $j=2500 \text{ A/m}^2$; $\text{Cu}^{2+}=18 \text{ g/dm}^3$

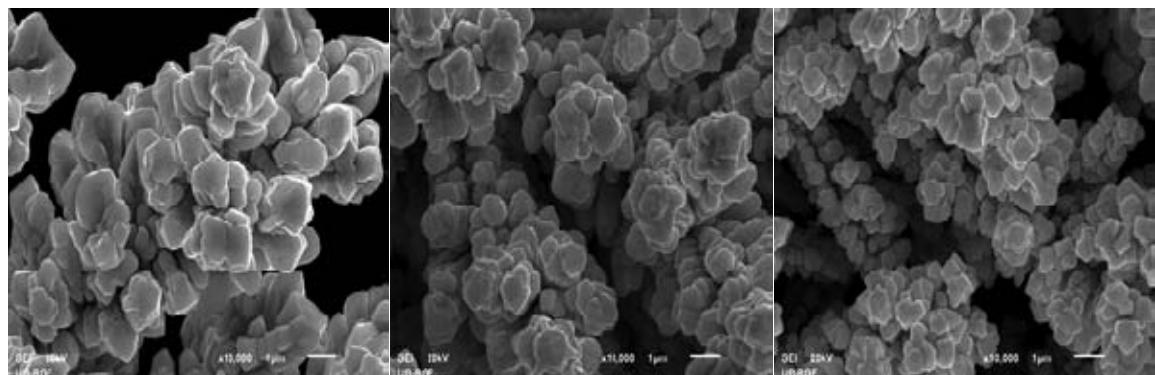
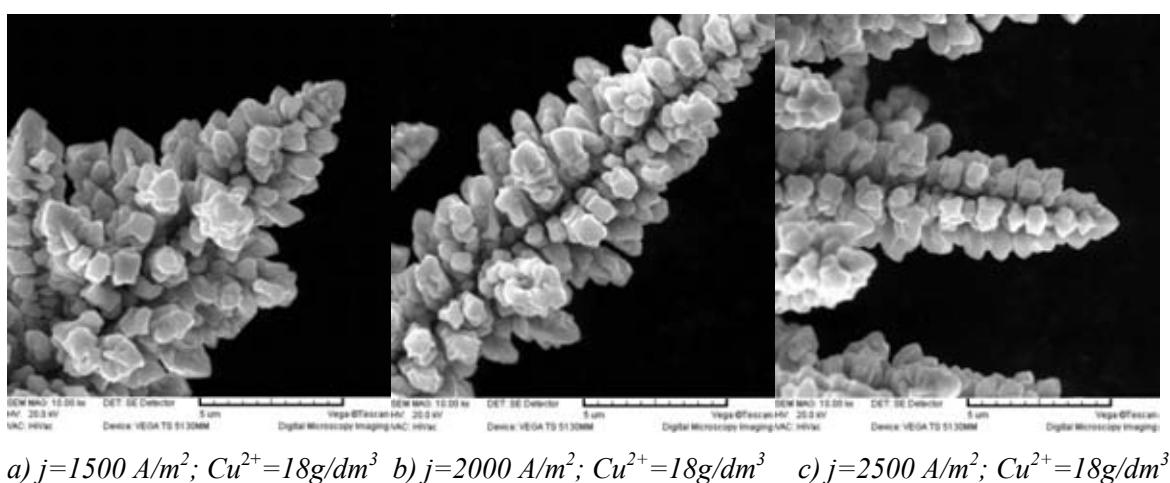
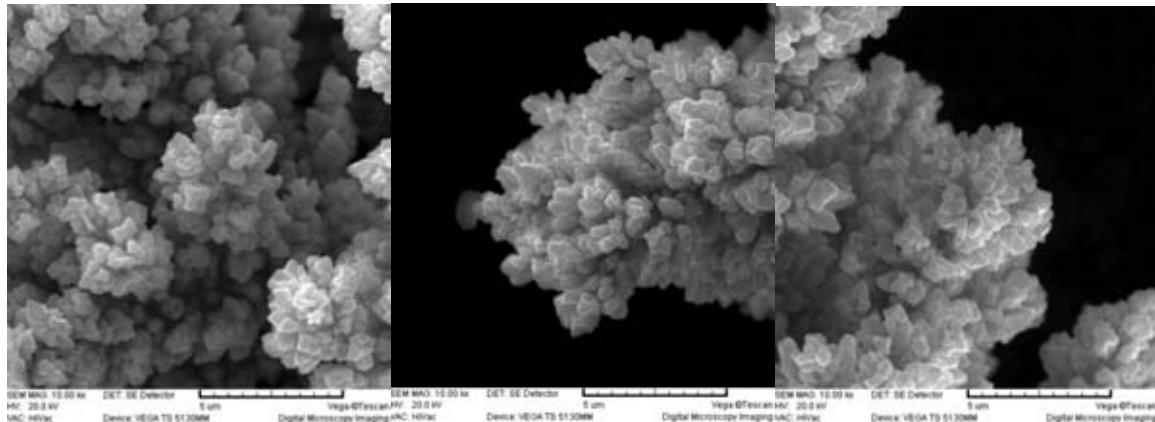


a) $j=1500 \text{ A/m}^2$; $\text{Cu}^{2+}=33 \text{ g/dm}^3$ b) $j=2000 \text{ A/m}^2$; $\text{Cu}^{2+}=33 \text{ g/dm}^3$ c) $j=2500 \text{ A/m}^2$; $\text{Cu}^{2+}=33 \text{ g/dm}^3$

Slika 3. SEM mikrofotografije čestica bakarnog praha dobijene elektrohemijiski pri različitim gustinama struje a) $j=1500 \text{ A/m}^2$; b) $j=2000 \text{ A/m}^2$; c) $j=2500 \text{ A/m}^2$ iz rastvora I, IV i VII u kojima je koncentracija $\text{H}_2\text{SO}_4 100 \text{ g/dm}^3$. Uvećanje a), b) i c) 100x

Na slikama 3. i 4. dat je prikaz SEM mikrofotografije bakarnog praha dobijenog pri različitim gustinama struje $j=1500 \text{ A/m}^2$, $j=2000 \text{ A/m}^2$ i $j=2500 \text{ A/m}^2$ iz rastvora I, IV i VII u kojima je koncentracija Cu^{2+} jona 7 g/dm^3 , 18 g/dm^3

i 33 g/dm^3 , a koncentracija H_2SO_4 u sva tri elektrolita 100 g/dm^3 . Na slici 3. dat je prikaz elektrohemijiski dobijenog bakarnog praha pri tri različite korišćene gustine struje, a pri uvećanju 100x, a na slici 4. pri uvećanju 10 000x.



Slika 4. SEM mikrofotografije čestica bakarnog praha dobijene elektrohemski pri različitim gustinama struje a) $j=1500 \text{ A/m}^2$; b) $j=2000 \text{ A/m}^2$; i c) $j=2500 \text{ A/m}^2$ iz rastvora I, IV i VII u kojima je koncentracija H_2SO_4 100 g/dm^3 . Uvećanje a), b) i c) 10 000x

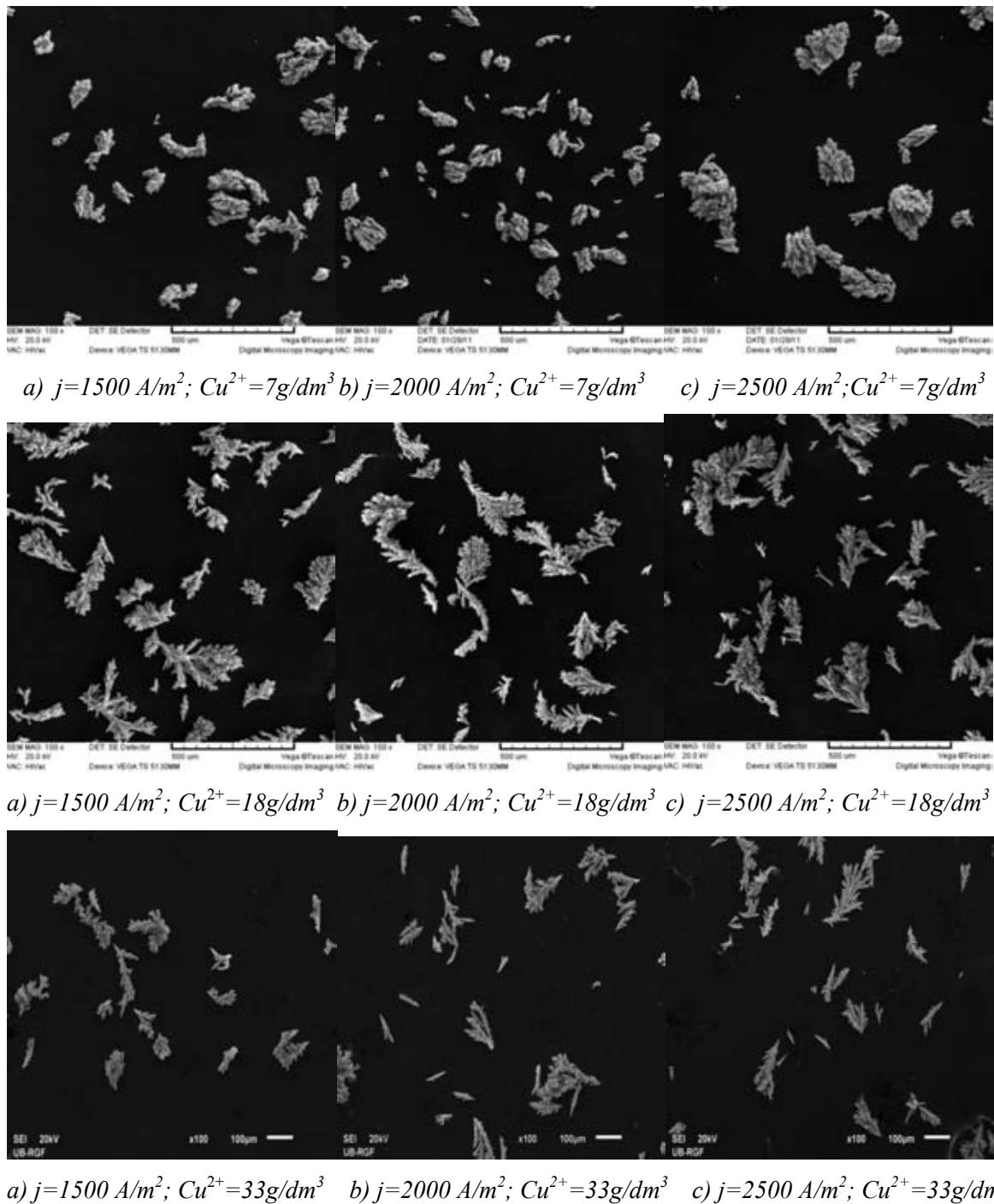
Slike 3. može se videti da sa povećanjem gustine struje dobijaju se veći (voluminozni) aglomerati čestica bakarnog praha. Takođe, nazire se dendritična struktura čestica bakarnog praha. Dendritičnost dobijenog praha se povećava sa povećanjem koncentracije Cu^{2+} jona ,

kao i povećanjem gustine struje. To je opšta slika na uvećanju od 100x.

Slike 4. pri uvećanju od 10 000x može se videti dendritična struktura bakarnog praha. Uočljiva je veoma mala razlika u strukturi zrna bakarnog praha, što navodi na zaključak da pri maloj koncentraciji

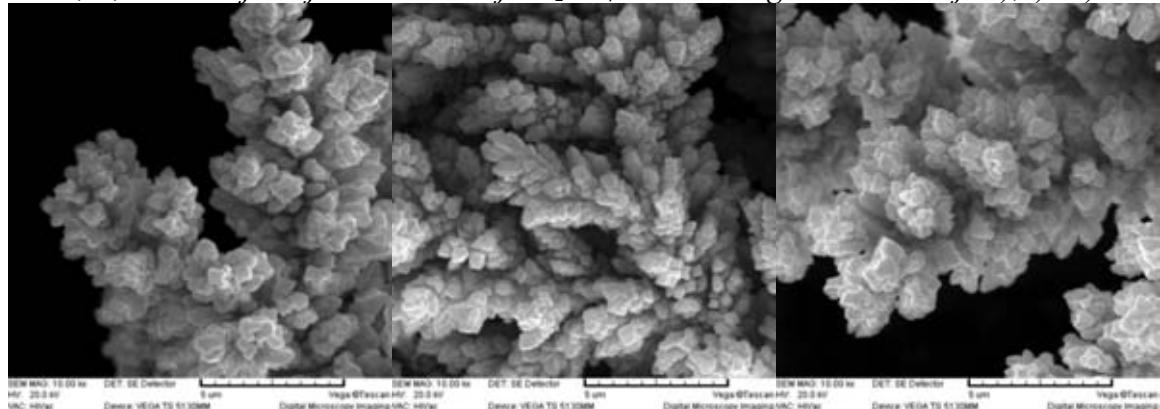
bakarnih jona u elektrolitu promena gustine struje bitno ne utiče na strukturu i morfologiju bakarnog praha. Na slici 4.b. može se videti dentrična struktura bakarnog praha pravilno raspoređena kao zrna kukuruza pri uvećanju od 10 000x. Sa

povećanjem gustine struje dobijaju se sitnija zrna bakarnog praha. Uočljivo je da pri gustini struje od 1500 A/m^2 nemamo tako uređenu strukturu kao pri većim gustinama struje 2000 A/m^2 i 2500 A/m^2 .

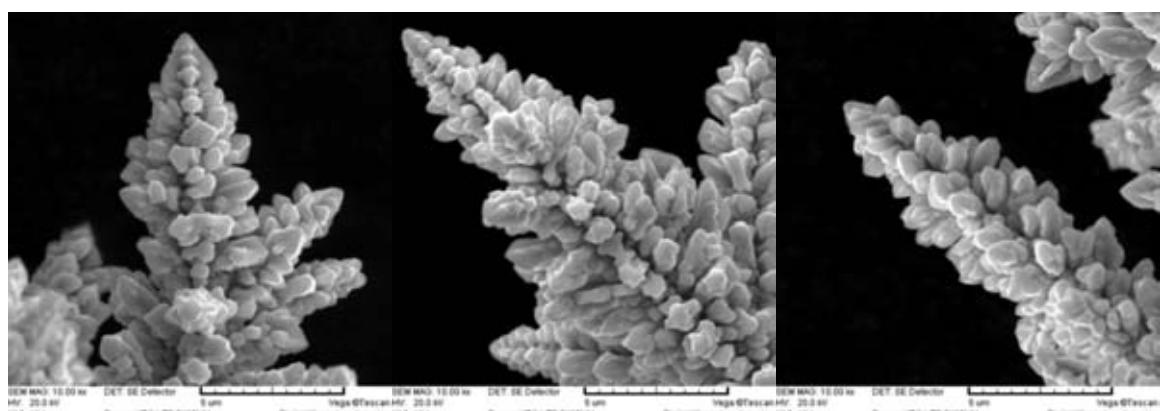


Slika 5. SEM mikrofotografije čestica bakarnog praha dobijene elektrohemski pri razliitim gustinama struje a) $j=1500 \text{ A/m}^2$; b) $j=2000 \text{ A/m}^2$; i c) $j=2500 \text{ A/m}^2$ iz rastvora

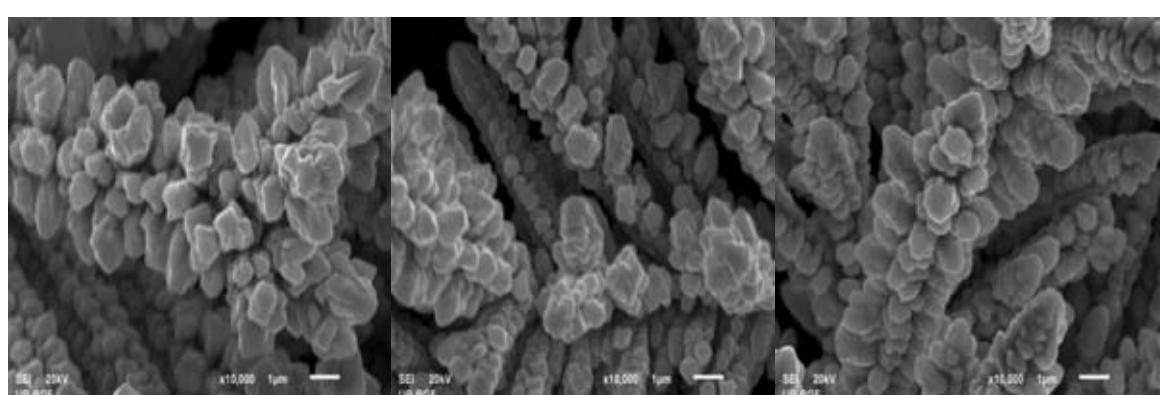
II, V, VIII u kojima je koncentracija H_2SO_4 iznosi $150 \text{ g}/\text{dm}^3$. Uvećanje a), b) i c) 100x



a) $j=1500 \text{ A}/\text{m}^2$; $Cu^{2+}=7 \text{ g}/\text{dm}^3$ b) $j=2000 \text{ A}/\text{m}^2$; $Cu^{2+}=7 \text{ g}/\text{dm}^3$ c) $j=2500 \text{ A}/\text{m}^2$; $Cu^{2+}=7 \text{ g}/\text{dm}^3$



a) $j=1500 \text{ A}/\text{m}^2$; $Cu^{2+}=18 \text{ g}/\text{dm}^3$ b) $j=2000 \text{ A}/\text{m}^2$; $Cu^{2+}=18 \text{ g}/\text{dm}^3$ c) $j=2500 \text{ A}/\text{m}^2$; $Cu^{2+}=18 \text{ g}/\text{dm}^3$



a) $j=1500 \text{ A}/\text{m}^2$; $Cu^{2+}=33 \text{ g}/\text{dm}^3$ b) $j=2000 \text{ A}/\text{m}^2$; $Cu^{2+}=33 \text{ g}/\text{dm}^3$ c) $j=2500 \text{ A}/\text{m}^2$; $Cu^{2+}=33 \text{ g}/\text{dm}^3$

Slika 6. SEM mikrofotografije čestica bakarnog praha dobijene elektrohemski pri različitim gustinama struje a) $j=1500 \text{ A}/\text{m}^2$; b) $j=2000 \text{ A}/\text{m}^2$; i c) $j=2500 \text{ A}/\text{m}^2$ iz rastvora II, V i VIII u kojima je koncentracija H_2SO_4 $150 \text{ g}/\text{dm}^3$. Uvećanje: a), b) i c) 1000x

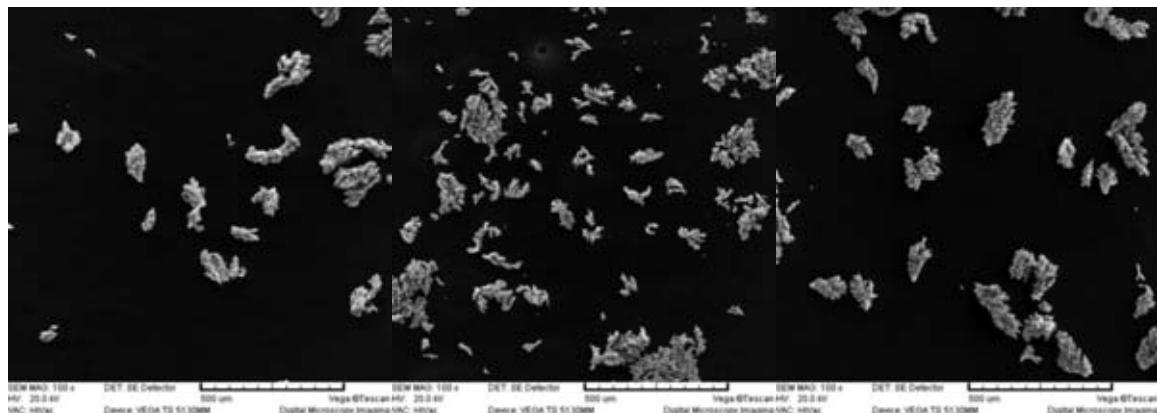
Na slikama 5. i 6. prikazane su SEM mikrofotografije bakarnog praha dobijenog elektrolitički iz elektrolita II, V i VIII u kojima je koncentracija Cu^{2+} jona bila

$7 \text{ g}/\text{dm}^3$, $18 \text{ g}/\text{dm}^3$ i $33 \text{ g}/\text{dm}^3$, a koncentracija H_2SO_4 u sva tri elektrolita $150 \text{ g}/\text{dm}^3$ pri gustinama struje $1500 \text{ A}/\text{m}^2$, $2000 \text{ A}/\text{m}^2$ i $2500 \text{ A}/\text{m}^2$.

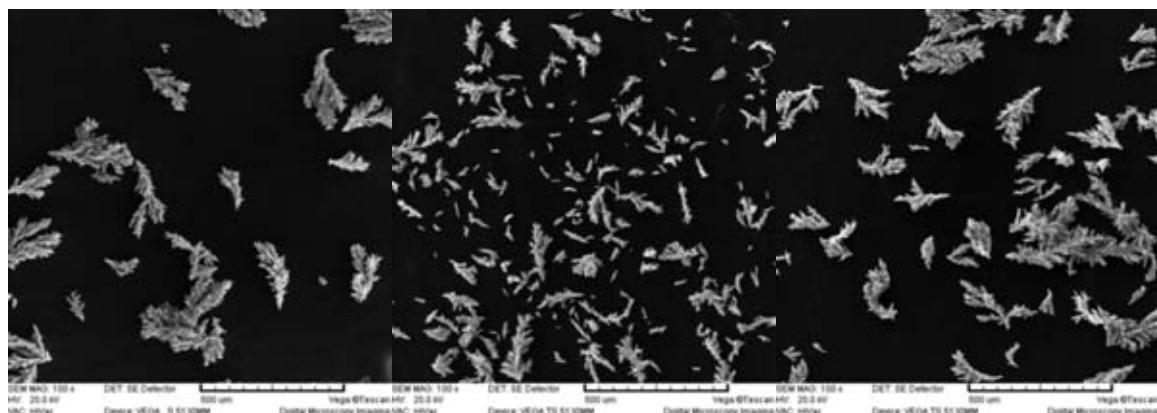
Slike 5 i 6. potvrđuju napred iznetu tvrdnju da se pri datim uslovima taloženja dobija bakarni prah dendritične strukture.

Na slikama 7. i 8. prikazane su SEM mikrofotografije elektrolitički dobijenog

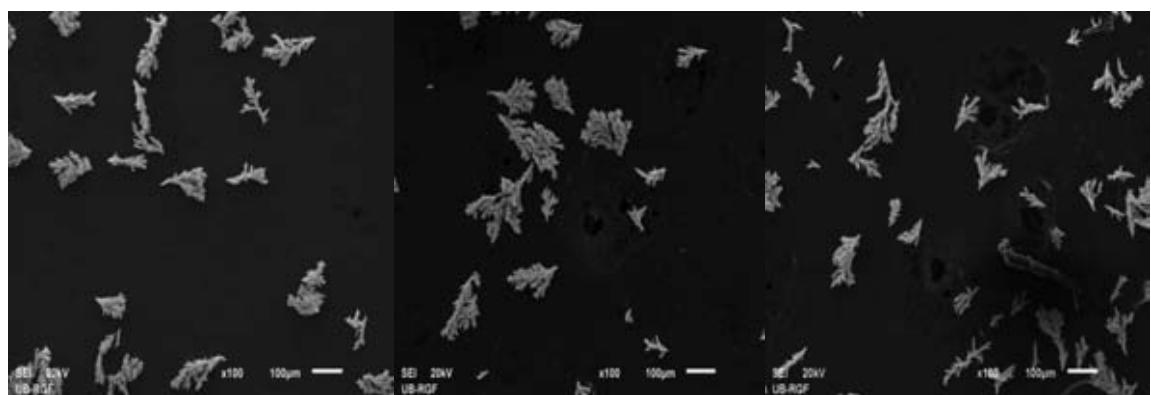
bakarnog praha iz elektrolita III, VI i IX u kojima je koncentracija Cu^{2+} jona takođe bila $7 \text{ g}/\text{dm}^3$, $18 \text{ g}/\text{dm}^3$ i $33 \text{ g}/\text{dm}^3$, a koncentracija H_2SO_4 u sva tri elektrolita $200 \text{ g}/\text{dm}^3$.



a) $j=1500 \text{ A}/\text{m}^2; Cu^{2+}=7 \text{ g}/\text{dm}^3$ b) $j=2000 \text{ A}/\text{m}^2; Cu^{2+}=7 \text{ g}/\text{dm}^3$ c) $j=2500 \text{ A}/\text{m}^2; Cu^{2+}=7 \text{ g}/\text{dm}^3$



a) $j=1500 \text{ A}/\text{m}^2; Cu^{2+}=18 \text{ g}/\text{dm}^3$ b) $j=2000 \text{ A}/\text{m}^2; Cu^{2+}=18 \text{ g}/\text{dm}^3$ c) $j=2500 \text{ A}/\text{m}^2; Cu^{2+}=18 \text{ g}/\text{dm}^3$

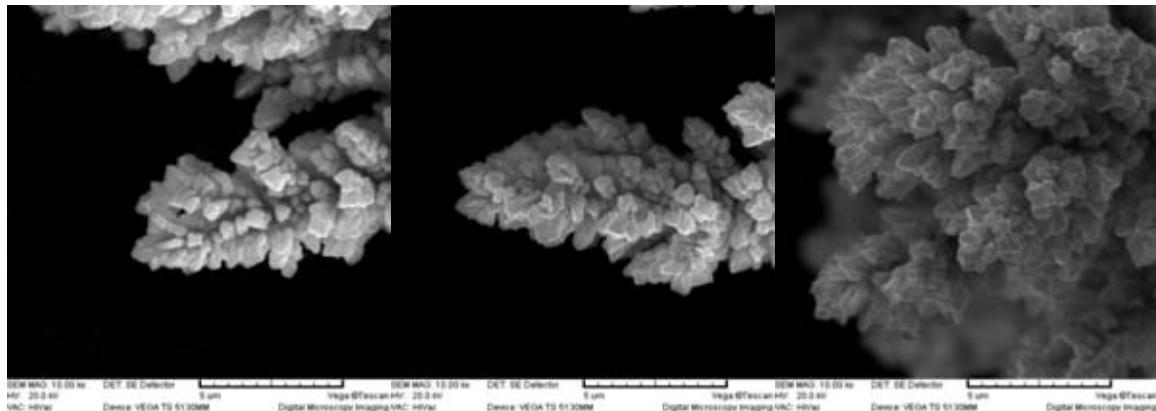


a) $j=1500 \text{ A}/\text{m}^2; Cu^{2+}=33 \text{ g}/\text{dm}^3$ b) $j=2000 \text{ A}/\text{m}^2; Cu^{2+}=33 \text{ g}/\text{dm}^3$ c) $j=2500 \text{ A}/\text{m}^2; Cu^{2+}=33 \text{ g}/\text{dm}^3$

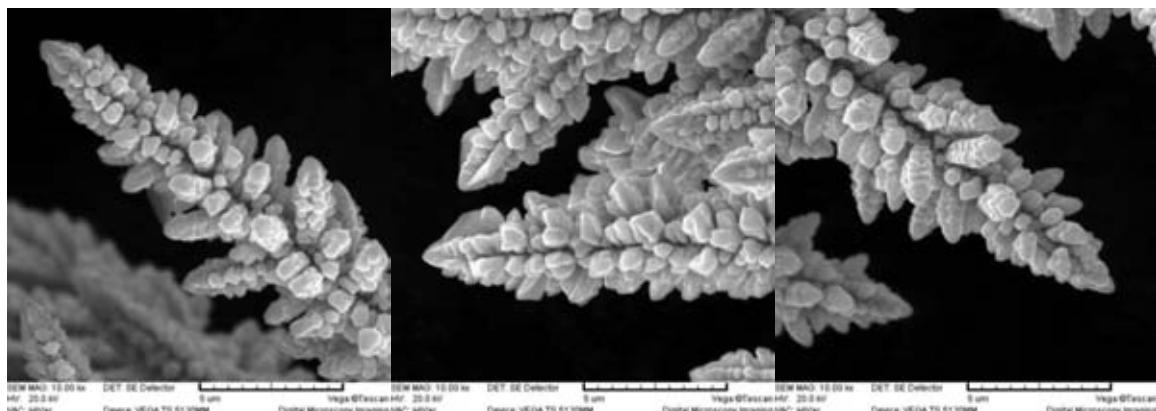
Slika 7. SEM mikrofotografije čestica bakarnog praha dobijene elektrohemski pri različitim gustinama struje a) $j=1500 \text{ A}/\text{m}^2$; b) $j=2000 \text{ A}/\text{m}^2$; i c) $j=2500 \text{ A}/\text{m}^2$ iz rastvora III, VI i IX u kojima je koncentracija H_2SO_4 $200 \text{ g}/\text{dm}^3$. Uvećanje: a), b) i c) 100x

Sa slike 7. se može videti dendritična struktura bakarnog praha. Uočljivo je da su čestice bakarnog praha manje na slici 7.b.($Cu^{2+} = 18 g/dm^3$), gde je bakarni prah

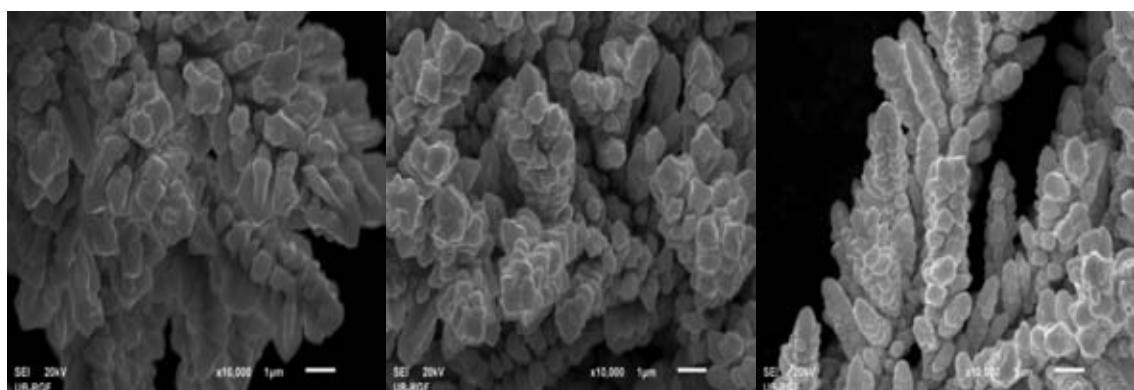
taložen pri gustini struje od $2000 A/m^2$. Povećanjem gustine struje dobijaju se veći aglomerati čestica bakarnog praha.



a) $j=1500 A/m^2; Cu^{2+}=7g/dm^3$ b) $j=2000 A/m^2; Cu^{2+}=7g/dm^3$ c) $j=2500 A/m^2; Cu^{2+}=7g/dm^3$



a) $j=1500 A/m^2; Cu^{2+}=18g/dm^3$ b) $j=2000 A/m^2; Cu^{2+}=18g/dm^3$ c) $j=2500 A/m^2; Cu^{2+}=18g/dm^3$



a) $j=1500 A/m^2; Cu^{2+}=33g/dm^3$ b) $j=2000 A/m^2; Cu^{2+}=33g/dm^3$ c) $j=2500 A/m^2; Cu^{2+}=33g/dm^3$

Slika 8. SEM mikrofotografije čestica bakarnog praha dobijene elektrohemijiski pri različitim gustinama struje a) $j=1500 A/m^2$; b) $j=2000 A/m^2$; i c) $j=2500 A/m^2$ iz rastvora III, VI i IX u kojima je koncentracija H_2SO_4 $200 g/dm^3$. Uvećanje: a), b) i c) $10\,000x$

Sa slike 8. kao i sa slika 4. i 6. može se videti dendritična i veoma slična struktura bakarnog praha pravilno raspoređena kao zrno kukuruza. Može se primetiti da je na slikama (6.c. i 8.c.) veća razgranatost i da su grane sastavljene iz više zrna bakarnog

praha koja su slojevito poređana jedno na drugo sa jasnom kristalnom strukturom. Uočljivo je, da se sa povećanjem gustine struje dobijaju sitnija zrna bakarnog praha (slika 8.c.).

Zaključci

Analizom dobijenih mikrofotografija utvrđeno je da se sa povećanjem gustine stuje morfologija čestica bakarnog praha menja od kompaktnih, masivnih dendrita i masivnih čestica, do razgranatih, 3D dendrita koji imaju strukturu kao zrno kukuruza. Sa povećanjem gustine struje dobijaju se sitnija zrna bakarnog praha

pravilno raspoređena kao zrno kukuruza. Povećanjem koncentracije H_2SO_4 i gustine struje izraženije je grananje od korena čestice ka periferiji. Može se videti da su kristali približno iste veličine i oblika za iste koncentracije i gustine struje i da su složeni jedan na drugi od korena do vrha grane što ukazuje na elektrokatalitičko dejstvo pri promeni gustine struje i koncentracije H_2SO_4 .

Literatura

1. WennerSchatt, Klaus-Peter Wieters, "Powder Metallurgy - Processing and Materials" European Powder Metallurgy Association Technical University Dresden, Germany, 1997.
2. Randall M.German, "Powder Metallurgy Science", Metal Powder Industries Federation, 2nd ed., Princeton, New Jersey, 1994.
3. M.M.Ristić, D.Uskoković, "Struktura i osobine sinterovanih materijala", Elektronski fakultet Univerziteta u Nišu, Niš, 1973, str. 61-73; 123-154.
4. M.M.Ristić, D.Č.Stefanović, L.F.Prjadko, "Principi savremene prognoze osobina materijala", Centar za mulidisciplinarne studije Univerziteta u Beogradu i Institut tehničkih nauka Srpske akademije nauka i umetnosti, Beograd, 1983, str. 12-18.
5. Lj. J. Pavlović, "Uticaj parametara režima elektrolize na morfologiju, raspodelu veličine čestica i nasipnu masu bakarnog praha", Doktorska disertacija, Univerzitet u Beogradu, Tehnološko-metalurški fakultet, Beograd, 2002.
6. A.Calusaru, "Electrodeposition of Metal Powders", Materials Science Monographs, 3, Elsevier, Amsterdam - Oxford - New York, 1979.
7. M.G.Pavlović, K.I.Popov, E.R.Stojilković, Bulletin of Electrochemistry, India, 14 (1998) 6.
8. M.G.Pavlović, "Uticaj strujnog i hidrodinamičkog režima na strukuru i morfologiju metalnih taloga", u knjizi "Primena pulsnih režima u galvanskoj tehnici", (urednici: M.G.Pavlović i A.Dekanski), izd. IHTM - Centarzaelektrohemiju, Beograd, 1992, str.1-47.
9. C.L.Mantell, "Electrochemical Engineering", Fourth Edition, McGraw-Hill Book Company, New York - Toronto - London, 1960, pp. 75-81.
10. K.I.Popov, "Periodično promenljivi režimi u elektrohemiskom teloženju metala" u knjizi "Primena pulsnih režima u galvanskoj tehnici (urednici:M.G.Pavlović i A. Dekanski), izd. IHTM - Centarzaelektrohemiju, Beograd, 1992, str. 49-73.
11. K.I.Popov, M.G.Pavlović, J.N.Jovićević, Hydrometallurgy, 23 (1989) 127.
12. M.G.Pavlović, Š.Kindlova, I. Roušar, Electrochim.Acta, 37 (1992) 23.
13. K.I.Popov, M.G.Pavlović, M.D.Maksimović, J.Appl.Electrochem.,12 (1982) 525.
14. K.I.Popov, M.G.Pavlović, G.Ž.Remović, J.Appl.Electrochem.,21 (1991) 743.
15. K.I.Popov,T.M.Kostić,N.D.Nikolić,E.R.Stojilković,M.G.Pavlović,J.electroanal. Chem., 464 (1999) 245.

FORMIRANJE PROVODNIH PUTEVA KOD LIGNOCELULOZNIH KOMPOZITA PUNJENIH ELEKTROLITIČKIM BAKARNIM PRAHOM

FORMATION OF CONDUCTIVE PATHWAYS IN ELECTROLYTIC COPPER FILLED LIGNOCELLULOSE COMPOSITESA

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Izvod: Ispitivana je električna provodljivost sistema baziranog na lignoceluloznom (LC) biopolimernom matriksu ispunjenog elektrohemijski dobijenim bakarnim prahom. Galvanostatski dobijen bakarni prah sa veoma poroznim, veoma dendritičnim i česticama sa velikom specifičnom površinom je korišćen kao punilac. Zapreminske udeo elektrohemijski dobijenog bakarnog praha je iznosio od 2.0 - 29.8 vol%. Analiza najznačajnijih osobina pripremljenih kompozita je obuhvatala merenja električne provodnosti, impedansnu spektroskopiju (IS) i strukturu analizu. Značajan porast električne provodnosti se javlja kada udeo bakarnog praha dostigne vrednost perkolacionog praga (PP). Pokazano je da PP zavisi od oblika čestica i spatialne distribucije. SEM analiza uzorka je pokazala da čestice sa izraženim granicama zrna igraju veliku ulogu u pojavljuvanju provodnih puteva i na elektroprovodljivost kompozita. Efekat pakovanja i izraženi međučestični kontakti između čestica bakarnog praha sa velikom specifičnom površinom su doveli do pomeranja perkolacionog praga, koji za čestice 45 µm i pritisak od 27 MPa iznosi 7.2% v/v.

Ključne reči: elektrolitički bakarni prah, impedansna spektroskopija, lignoceluloza, kompozit

Abstract: The electrical conductivity of the composite system based on lignocellulose (LC) biopolymer matrix electrodeposited copper powder filler has been studied. Highly porous, highly dendritic galvanostatically produced copper powder was used as filler since these particles have high values of specific area. Volume fraction of the electrodeposited copper powder was varied from 1.9 - 29.4 vol%. Analysis of the most significant properties of prepared composites and its components included impedance spectroscopy (IS) behavior, measurements of electrical conductivity, scanning electron microscopy (SEM) and structural analysis. The significant increase of the electrical conductivity could be observed as the copper powder content reaches the percolation threshold (PT). It was shown that PT depends on both particle shape and type of spatial distribution. IS measurements and SEM analysis have shown that particles having pronounced grain boundaries have great effect on appearance of electric conductive pathways thus on the composite conductivity. The packaging effect and more pronounced interpartical contact with copper powder particles lead to "movement" of PT, which for the particles <45 µm and highest processing pressure of 27 MPa was 7.2% (v/v). IS response of the composites showed existence of electrical conductive layers, each having different resistivity which increases towards interior of the composite.

Keywords: electrolytic copper powder, impedance spectroscopy, lignocellulose, composite.

Introduction

Polymer and fiber reinforced composites play an increasingly important role in commercial, defense, and private sectors. While polymeric systems are well suited for replacing metallic structures with respect to mechanical and processing properties, the electrical properties of polymeric systems are orders of magnitude apart from metals. This transition to polymeric systems occurs concurrently with an increase in utilization of and reliance on digital technologies which are highly sensitive to electromagnetic shielding.

The electrical properties of metal filled polymer systems can be modeled using percolation theory [1-4]. Classical percolation theory considers a connected network of conductive links in a nonconductive matrix across an infinite sample. In a filler composite, this network structure is created by dispersed fillers connecting throughout the polymer. When a sufficient volume of fillers are present to create an electrically conductive path, an abrupt change in conductivity is observed, referred to as the critical percolation threshold. The resistivity of the composite decreases dramatically above the percolation threshold, eventually approaching a stabilized conductivity level at the percolation limit. This limit presents a limiting value for well-dispersed conductive networks. For loadings beyond the percolation limit, a decrease in electrical and mechanical properties is often observed, indicating that the polymer host is no longer capable of facilitating additional increases in filler. Filler polymer composites have been able to achieve conductivities in excess of 5000 S/cm, and have been demonstrated in applications including

electrostatic discharge, electromagnetic shielding, conductive adhesives, caulk and gaskets, paints, and lightning strike protection [5-7]. Previous studies have indicated that the resultant conduction of a filler composite can depend on multiple factors. For example, an early study [8] indicates that the resistivity of filler composites is a function of the type of polymer used as the matrix material. This work extends that early effort through a systematic characterization of fillers across multiple polymer systems, including modeling efforts.

Impedance spectroscopy (IS) is gaining more important role in fundamental and applied electrochemistry and materials science in the last years. In a number of respects it is the method of choice for characterizing the electrical behavior of systems in which the overall system behavior is determined by a number of strongly coupled processes, each proceeding at a different rate [7,9]. Impedance spectroscopy is a relatively new and powerful method of characterizing many of the electrical properties of materials and their interfaces with electronically conducting materials. It can be used for measurements in wide range of materials from solid electrolyte materials (amorphous, polycrystalline and single crystal), solid metallic electrodes, fused salts, aqueous electrolytes and composite materials [9].

The aim of this work was to compare results of electrical conductivity of copper powder filled lignocellulose matrix composites produced under different pressures obtained by different measuring techniques, and to explain the influence of particle shape (i.e. particle morphology) on percolation threshold by impedance spectroscopy.

Experimental

Copper powder was galvanostatically produced with distinct dendritic morphology and large specific area [10-12], with all the same parameters of electrolysis and deposition times as stated in [7].

Celgran® C fraction of the corn cob produced by Maize Research Institute "Zemun Polje" was used as a source of lignocellulose. It was milled and then sieved, with particle sizes below 45 µm. Lignocellulose prepared and obtained in this manner was used as natural polymer matrix.

Investigated composites of lignocellulose matrix filled with copper powder were prepared with filler contents in the range 2.0% (v/v) – 29.8% (v/v), while pure lignocellulose samples were prepared as reference materials. Thoroughly homogenized composite powder mixtures

Results and discussion

As previously mentioned, the conductivity of filled polymers is strongly dependent on the nature of the contact between the conductive filler elements, particle size and shape of the conductive particle filler. This was shown in [7] where highly dendritic copper powder was used, and the percolation threshold was moved to lower filler content. Electrical properties of lignocellulose polymer matrix are altered by addition of conductive copper powder as filler. The electrical conductivity of polymer composites does not increase continuously with increasing electroconductive filler content. Instead it has rapid increase in conductivity when the percolation threshold of the conductive filler content is reached. Therefore, the copper powder was galvanostatically produced since it should have distinct dendritic morphology and large specific area [10-12]. At an interface between two phases in the composite, physical

were pressed into 16 mm diameter pellets under pressures of 10, 20 and 27 MPa.

Impedance spectroscopy (IS) experiments were performed in potentiostatic mode on all prepared composites. Instrumentation involved Bio-Logic® SAS Instrument, model SP-200, guided by EC-Lab® software. Samples were put between two metal plates and they responded to the potential input sinusoidal signal of $\pm 10\text{mV}$ (rms) amplitude. Geometry of the instrument contacts used is such that it minimizes edge effects thus it can be assumed that they do not exist. Experimental IS data were fitted by ZView® software [13].

Sample thickness (necessary for the calculation of conductivity) was determined using micrometer, to an accuracy of 0.01 mm. Several thickness measurements were taken per sample and then averaged.

properties like crystallographic, mechanical, compositional, and, particularly, electrical change precipitously and heterogeneous charge distributions (polarizations) reduce the overall electrical conductivity of a system. The morphology of used copper powder (Figure 1) shows that greater interpartical contact of smaller, highly porous, highly dendritic particles with high values of specific area move percolation threshold towards lower filler content.

It should be mentioned that the resistance of the composites increases due to the increasing contribution of the part of internal surface of polymer matrix as frequency decreases. In the certain frequency range, capacitance and resistance values are similar.

The electrical conductivity of all the particle size composites as a function of filler content for all the samples was measured from impedance characteristics of a composite having the filler of characteristic morphology.

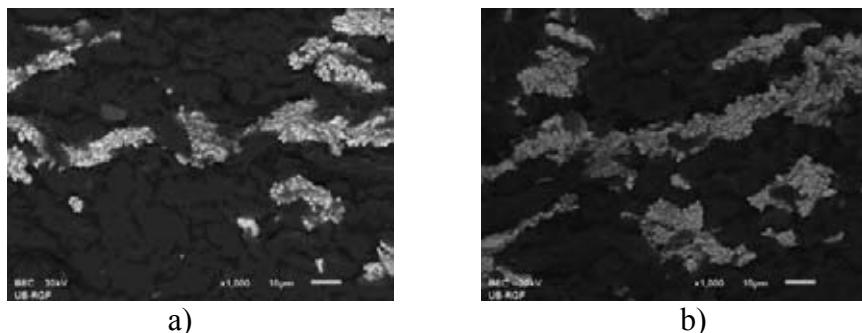


Figure 1. SEM images of the conductive pathways in the composites at percolation threshold. Composites are prepared under a) 10 MPa and b) 27 MPa. Magnification x350

Due to the packaging effect and more pronounced interparticle contact with smaller, highly porous, highly dendritic particles with high values of specific area lead to “movement” of percolation threshold towards lower filler content. The conductivity of the composite is obtained through conductive pathways of the filler that form in the composites. These pathways are formed in 3D in a pure random order which can be observed on Figure 1 [14]. SEM images of the inner structure of the composites are prepared after composite preparation and its braking. There is an influence of the

pressure on electrical conductivity of the composites. For the pressure of 10 MPa the percolation threshold was lowered to 12.5% (v/v), for 20 MPa it was 11.6% (v.v), and for 27 MPa was 7.2% (v/v) which is the difference of 5.8% (v/v) in filler content. At higher pressures less filler is needed to form conductive pathways through a composite.

Flandin et al. [15] state that typical values of 20–40% (v/v) for percolation threshold for spherical filler particles. Hence, electrodeposited copper powder particles represent excellent choice as conductive composite fillers.

Conclusions

Experimental study about the effects of particle morphology of electrodeposited copper powder on the electrical conductivity of lignocellulose composites filled with this powder has been described in this article. It has been shown that particle shape of copper powder with very high surface area and pronounced dendrite branching plays significant role on electrical conductivity of the prepared samples. Electrical conductivity was calculated from the results of impedance spectroscopy measurements and it is in agreement with previously published results [7-9]. Layered electrical conductivity through the samples was found, where the resistance of the inner layers is guiding process of the overall

resistance of the composite. Grain boundary plays significant effect. The response is elongated coupled resistance with constant impedance “tail” towards lower frequencies. It can be pointed out that resistance increases due to the increasing contribution of the part of internal surface of polymer matrix as frequency decreases. The internal space charge that is created at the phase boundaries leads to a significant increase in the concentration of mobile defects, hence giving the circuit response with purely geometric reductions in the conductivity with respect to the single crystal thus showing that grain boundary plays significant effect. This response is elongated coupled resistance with constant impedance “tail” towards lower frequencies. Polycrystallinity, high surface

area, greater number of interparticle contacts and grain boundary effect of the copper powder are key factors influencing percolation threshold in the LC-Cu composites. This research has undeniably

shown that particle morphology of galvanostatically obtained copper powder and lignocellulose matrix plays significant role in electrical conductivity of the composites.

Acknowledgement

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References

1. J. C. Grunlan, A. R. Mehrabi, M. V. Bannon, and J. L. Bahr, *Advanced Materials*, 16, 150, (2004)
2. J.-M. Park, S.-J. Kim, D.-J. Yoon, G. Hansen, and K. L. DeVries, *Composites Science and Technology*, 67, 2121, (2007)
3. J. C. Grunlan, W. W. Gerberich, and L. F. Francis, *J Appl Polym Sci*, 80, (2001)
4. X. Jing, W. Zhao, and L. Lan, *J Mater Sci Lett*, 19, (2000)
5. M.M. Pavlović, V. Čosović, M.G. Pavlović, N. Talijan and V. Bojanić, *Int. J. Electrochem. Sci.*, 6, 3812 (2011)
6. M.M. Pavlović, V. Čosović, M.G. Pavlović, V. Bojanić, N.D. Nikolić and R. Aleksic, *Int. J. Electrochem. Sci.*, 7, 8883 (2012)
7. M.M. Pavlović, M.G. Pavlović, V. Panić, N. Talijan, Lj. Vasiljević, M.V. Tomić, *Int. J. Electrochem. Sci.*, 7, 8894 (2012)
8. G. Hansen, *SAMPE Journal* (2005)
9. E. Barsoukov, J. R. Macdonald, editors, *Impedance Spectroscopy: Theory, Experiment, and Applications*, John Wiley & Sons, Hoboken, New Jersey (2005)
10. K.I. Popov and M.G. Pavlović, in *Modern Aspects of Electrochemistry*, Electrodeposition of metal powders with controlled particle grain size and morphology, B.E. Conway, J.O'M. Bockris and R.E. White, Eds., Vol. 24, Plenum, New York, 299, (1993)
11. M.G. Pavlović, K.I. Popov and E.R. Stojilković, *Bulletin of Electrochemistry*, 14, 211, (1998)
12. M.G. Pavlović, Lj.J. Pavlović, V.M. Maksimović, N.D. Nikolić and K.I. Popov, *Int. J. Electrochem. Sci.*, 5, 1862, (2010)
13. V.V. Panić, R.M. Stevanović, V.M. Jovanović, A.B. Dekanski, *J. Pow. Sour.*, 181, 186, (2008)
14. M.M. Pavlović, M.M. Pavlović, V. Čosović, M. Gligorić, V. Bojanić, *16. YUCORR*, Proceedings, CD, 284-293, (2014), Tara, Serbia.
15. L. Flandin, A. Chang, S. Nazarenko, A. Hiltner and E.J. Baer, *J. Appl. Polymer. Sci.*, 76, 894, (2000)

EFEKAT SLOŽENIH ČVRSTIH ĐUBRIVA NA BAZI RUDE FOSFATA: VEGETACIONI OGLED SA KUKURUZOM

THE EFFECT OF COMPLEX PHOSPHATE ROCK BASED FERTILIZERS ON MAIZE

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Izvod

Ovo istraživanje ispituje efekat novih multifunkcionalnih materijala zasnovanih na sinergističkoj sprezi fosfatne rude, zeolita modifikovanog amonijum jonima i otpadne biomase, na sadržaj hranljivih elemenata i teških metala u zemljištu i korenju kukuruza. Vegetacioni eksperiment sa kukuruzom u realnim uslovima ukazuje da testirana đubriva imaju multifunkcionalne osobine primenljive u održivoj poljoprivredi. Dobijeni rezultati su pokazali da dodavanje zeolita i pepela koštice višnje sirovom fosfatu podstiče njegovu rastvorljivost, istovremeno povećavajući usvajanje hranljivih materija od strane korena kukuruza i zadržavanje toksičnih metala u zemljištu, čime se smanjuje njihova bioraspoloživost.

Abstract

This study investigates the effect of novel multifunctional materials based on the synergistic conjunction of raw phosphate, zeolites modified with ammonium ions and waste biomass, on the content of nutritive elements and heavy metals in soil and maize roots. The field vegetation experiment with maize demonstrates that the tested phosphate rock based fertilizers have multifunctional properties applicable in sustainable agriculture. Obtained results showed that addition zeolite and ash pit cherries to the phosphate rock promotes its solubility, simultaneously enhancing the adoption of nutrients by maize roots and retention of toxic metals in the soil, thus reducing their bioavailability.

Keywords: ash pit cherries, fertilizers, modified zeolite, phosphate rock, soil remediation amendment

Introduction

Direct application of the phosphate rock (PR) in agriculture is poorly prevalent due to its low solubility and its limited in soils with pH below 4.5 [1]. Zeolites, as aluminosilicate porous minerals with high cation-exchange capacity can help control the release of plant nutrients in agricultural systems [2]. When saturated with monovalent nutrient cations, such as NH_4^+ , zeolites have the potential to enhance the PR dissolution [3]. The mechanism proposed is exchange-induced PR dissolution in which plant uptake of NH_4^+ liberates the exchange sites in zeolites

which are then occupied by Ca^{2+} from the PR, lowering the soil solution Ca^{2+} concentration and inducing further dissolution of PR [4]. Also, it has been shown that NH_4^+ -zeolites have a higher capacity than natural zeolite to protect *Hieracium aurantium* and *Rumex acetosella* growing on tailing ponds, by reducing the quantity of heavy metal ions (Pb, Zn, Cu, Fe) these plants would accumulate in their roots and leaves [5]

Waste biomass, such as pitted fruit, due to its mineralogical composition also has the potential to supply plant with main nutrients such as potassium at the same time serving as an acidity regulator and

adsorbent of heavy metals [6].

Furthermore, researchers found that natural apatite from Lisina can be used for in situ phosphate-induced immobilization of heavy metals, Pb and Cd, in polluted soils, and therefore can be used as inexpensive remediation amendments [7].

Material and methods

Zeolite originating from deposit Baia Mare, Romania (K-clinoptilolite) and PR, apatite, from ore deposit "Lisina" Bosilegrad, Serbia (containing 10% P₂O₅) were used in the study. Complete mineral characterization of these materials is presented elsewhere [8, 9]. Modification of zeolites was done with ammonium sulfate (AS) (1 M (NH₄)₂SO₄) by the procedure described by Mihajlovic et al 2013. Agricultural sour cherry stone waste material was obtained from "Vino Župa" Company from Aleksandrovac.

The field experiment was conducted at agricultural holding "Radmilovac", owned by the Faculty of Agriculture – Zemun.

The aim of this study was to investigate the effect of complex phosphate rock based fertilizers on bioavailability of nutrients and heavy metals in soil and maize roots grown in the field.

Hybrid FAO560 planted on leached chernozem soil type.

The field experiment was set up on a plot size of 15m x 60m, which included ten basic plot units of 90 m², with nine rows of corn. Each plot, except the control and treated with different manure. Each variant is composed of different combinations of modified zeolite grain size <100 µm, natural apatite grain size <63 um and ash pit cherries grain size <0.9 mm, as donors of potassium (12.08% K₂O), in two doses. Dose 1 is the input of 25 kg fertilizer and dose 2 is the input of 40 kg fertilizer per unit area (Table 1). Fertilizer efficiency was evaluated by measuring the content of nutritive elements and heavy metal in soil and maize roots.

Table 1. Nutrition treatments

Treatments	Dose
control	without treatment
PR	natural apatite 4kg per unit
AZA 1	20 kg of modified zeolite, 4 kg of natural apatite, (Dose 1)
AZA 2	20 kg of NH ₄ ⁺ -zeolite, 4 kg of natural apatite, (Dose 2)
PEP	20 kg NH ₄ ⁺ -zeolite, 4 kg of natural apatite, 4 kg ash pit cherries, (Dose 1)
PEPK	20 kg NH ₄ ⁺ -zeolite, a natural apatite 4 kg, 4 kg ash pit cherries, (Dose 2)

To get a more complex observation of the ranking of contents of the elements in the soil and maize roots, standard scores (SS) were evaluated using StatSoft Statistica

10.0® software, by integrating the measured values generated from various fertilization treatments.

Results

In order to compare various elements in soil and root samples after different fertilization treatments using multiple measurements, the data in each data set was transformed into SS, dimensionless

quantity derived by subtracting the mean from the raw data divided by the standard deviation (Fig. 1 and 2.). It can be seen from the results that different fertilization treatments strongly influence the final SS result for different elements.

Soil samples treated with zeolite fertilizer mixtures (AZA), exhibited generally lower SS for P, Ca, Na, Cu and K in comparison with other treatments, indicating their enhanced bioavailability. Therefore, the highest content of P in maize roots was noted in zeolite/PR fertilizer mixtures. Peter et all [5], have concluded that NH_4^+ -zeolite reduce the uptake of heavy metal ions in the roots and leaves of *Hieracium aurantium* and *Rumex acetosella*. This is in

agreement with the obtained results for Pb in maize roots when zeolite was added and in contrast to the PEP and PEPK treatments (Fig. 2). The higher content of Pb was noticed in the control samples of maize roots. Thanks to H^+ present in the ash structure, ash pit cherries (Dose 2) contribute to the increasing of the quantity of phosphorus in the maize roots, compared to the control, but not to the same extent as AZA treatments (Fig 2).

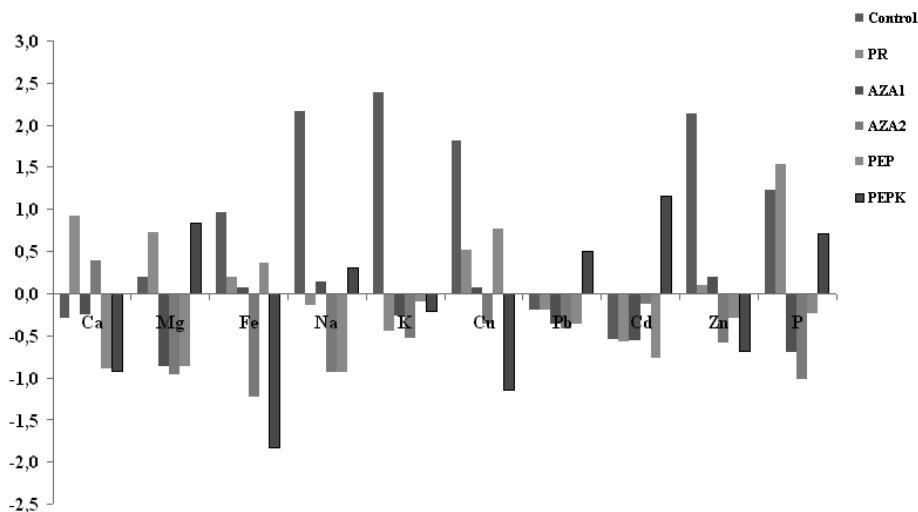


Figure 1. Standard scores of investigated elements in the soil following various fertilization treatments

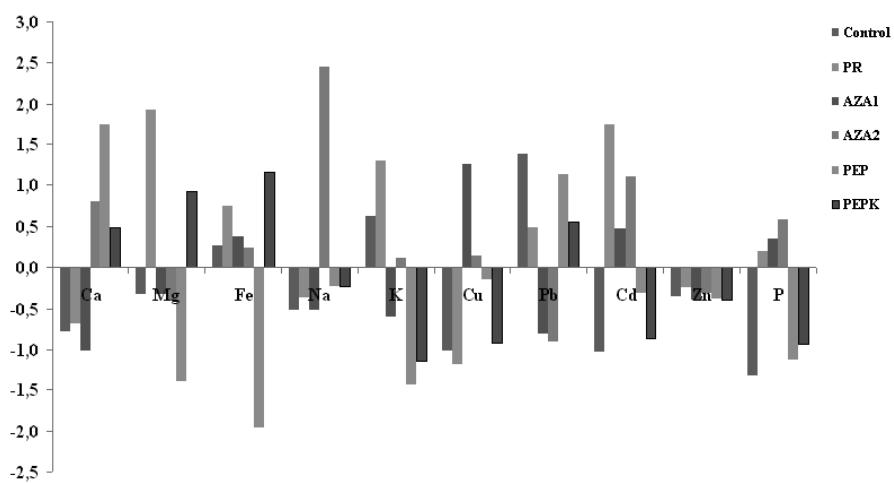


Figure 2. Standard scores of investigated elements in the maize roots following various fertilization treatments

Conclusion

Addition of NH_4^+ -zeolite in the PR promotes its dissolution and facilitates P

bioavailability in soil and thus affects the increase its content in maize roots. Also, the results indicate a chemical immobilization of heavy metals, so that

NH_4^+ -zeolite/RP composite material has a multifunctional effect as an “eco friendly”

fertilizer and as a soil amendment for in situ remediation of heavy metals.

Acknowledgement

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References

- [1] Hinsinger P., Gilkes R.(1997) Dissolution of phosphate rock in the rhizosphere of five plant species grown in an acid P-fixing mineral substrate, Geoderma, 75, 231-249.
- [2] Lai T. and Eberl D. (1986) Controlled and renewable release of phosphorus in soils from mixtures of phosphate rock and NH_4 exchanged clinoptilolite, Zeolites, 6,129-132.
- [3] Allen E., Hossner L., Ming D. (1993) Solubility and cation exchange in phosphate rock and saturated clinoptilolite mixtures Soil Science Society of America Journal, 57,1368-1374.
- [4] Barbarick K.A., Lai T.M., Eberl D.D. (1990) Exchange fertilizer (phosphate rock plus ammonium zeolite) effects on sorghum-sudangrass. Soil Sci. Soc. of America Journal, 54, 911-916.
- [5] Peter A., Mihaly-Cozmuta L., Mihaly-Cozmuta A., Nicula C. (2011) The role of natural zeolite and of zeolite modified with ammonium ions to reduce the uptake of lead, zinc, copper and iron ions in *Hieracium aurantium* and *Rumex acetosella* grown on tailing ponds, Analele Universității din Oradea - Fascicula Biologie, 2, 128-135.
- [6] Stojanović M., Lopičić Z., Milojković J., Lačnjevac Č., Mihajlović M., Petrović M., Kostić A. (2012) Biomass waste material as potential adsorbent for sequestering pollutants, Zaštita materijala, 53 (3), 231-237.
- [7] Raičević S., Kaluđerović T, Zouboulis A. (2005), In situ stabilization of toxic metals in polluted soils using phosphates: theoretical prediction and experimental verification. J. Hazard Mater., 117 (1), 41-53.
- [8] Radulović D.S. (2011) “Uticaj jona apatita i kalcita na njihove površinske osobine”, Doktorska disertacija, Rudarsko-geološki fakultet, Univerzitet u Beogradu
- [9] Marija Mihajlović, Mirjana Stojanović, Zorica Lopičić , Marija Petrović, Jelena Milojković, Časlav Lačnjevac, Dragan Radulović (2013) Raw phosphate composite as a natural fertilizer and soil remediation amendment, Zaštita materijala, (3) 216-223

UTJECAJ KONCENTRACIJE NaCl NA PITING KOROZIJU EKSTRUDIRANE Al–Mg–Si LEGURE AA6060

INFUENCE OF NaCl CONCENTRATION ON PITTING CORROSION OF EXTRUDED Al–Mg–Si ALLOY AA6060

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Izvod

Ekstrudirane Al–Mg–Si legure (serija AA6xxx) najčešće se koriste u konstrukcijske svrhe zahvaljujući prihvatljivim mehaničkim i korozionskim svojstvima. Spontano formirani sloj aluminijeva oksida na površini Al i Al-legura štiti od korozionskih oštećenja u neutralnim medijima, ali u otopinama koje sadrže kloride dolazi do proboga takvog tankog i kompaktnog pasivnog filma. Kao posljedica tog procesa, nastaju na površini lokalna oštećenja i dolazi do pojave jamičaste korozije- pittinga.

U ovom je radu proučavano korozionsko ponašanje komercijalne ekstrudirane Al–Mg–Si legure AA6060 u otopinama NaCl različite koncentracije, metodom anodne potenciodinamičke polarizacije u deaeriranim uvjetima pri sobnoj temperaturi. Pokazalo se da sklonost lokalnoj koroziji raste s koncentracijom kloridnih iona i ovisi o katodnim mikrokonstituentima u ekstrudiranoj Al–Mg–Si leguri.

Ključne riječi: pitting korozija, komercijalna Al–Mg–Si legura, deaerirana NaCl

Abstract

Extruded Al–Mg–Si alloys (AA6xxx series alloys) are the most common aluminum alloys for structural application due to reliable mechanical characteristics and corrosion properties. Spontaneously formed adherent aluminum oxide film on the surface protects Al and Al-alloys from corrosive attack in neutral media, but in chloride containing solutions, such thin and compact passive film is prone to breakdown.

In this study the corrosion behavior of commercial extruded Al–Mg–Si alloy AA6060 was investigated in NaCl solutions of different concentrations using anodic potentiodynamic polarization measurements under deaerated conditions at room temperature. It was shown that sensitivity to chloride attack increase with increasing Cl⁻ concentration and depends on cathodic microconstituents in extruded Al–Mg–Si alloy.

Key words: pitting corrosion, commercial Al–Mg–Si alloy, deaerated NaCl

Introduction

Extruded Al–Mg–Si alloys (AA6xxx series alloys) are widely used for different kinds of aluminium products including profiles for structural applications in the automotive industry, sections for architectural applications and tubes for the

heat transfer segments. The major alloying elements in the heat-treatable 6xxx series are magnesium and silicon. Both elements are required for precipitation strengthening, which is commonly acquired by solutionizing and artificial aging [1]. Their recyclability, high strength-to-weight ratio and resistance to

corrosion make them more and more used as replacement material for expensive Oxide passive layers composed of Al_2O_3 , $\text{Al}(\text{OH})_3$ and $\text{AlO}(\text{OH})$ grow spontaneously on Al and Al-alloys and provide good corrosion resistance in highly aggressive environments. However, different thermomechanical treatments applied to achieve required mechanical properties lead to destruction of the protective film so that Al-alloys are liable to suffer from various forms of corrosion, mainly pitting and intergranular attack, depending on the nature of anion in the neutral solution [3]. It is known that halide ions are aggressive for Al alloys. Physicochemical characteristics of the

AA2xxx and AA7xxx in aerospace industry and military applications [2].

passive layers govern the adsorption of aggressive ions such as Cl^- , their penetration and accumulation in imperfections of the protective film. Therefore, such processes are considered as one of the triggering factors in the nucleation of pitting processes [4].

In order to demonstrate the effect of NaCl concentration on pitting corrosion, the object of this study was to obtain the breakdown potential of passive layer by following the anodic polarization behavior of commercial extruded profiles produced from heat treatable Al-Mg-Si alloy.

Experiment

From the commercial extruded product (hollow quadratic profile), the alloy samples for electrochemical measurements were cut into test plates (80x 50 x 2 mm) in size. Tested Al-Mg-Si alloy is characterized by the following chemical composition: Al-98.72, Mg-0.45, Si-0.49, Fe-0.21, Mn-0.02. Extruded profiles aren commercially available as EN AW6060 and AA6060 [5].

Before each measurement, specimens were mechanically and chemically treated. The surface of sample was mechanically abraded using emery papers (grade 400, 500, 600 and 1000) on test face and rinsed with distilled water. The test panels were subsequently treated by immersion for 1 minute in a solution containing 0.1 mol dm⁻³ NaOH at 40 °C, in order to remove the surface oxide layer and eventually incorporated impurities. Immediately after the rinsing in distilled water, the samples were as quickly as possible placed in the electrochemical cell and then subjected to the experimental procedure.

The corrosive medium was deaerated NaCl solution (with concentration varying between 0.35 and 5 wt. %). Bubbling of high purity nitrogen (5N) through the

electrolyte was performed 30 min before measurements started and subsequently continued (over the solution) during the experiments. All the tests were conducted at ambient temperature (293 ± 2) K and at natural acidity (e.g., pH 5.5 was measured in 3.5 wt. % NaCl solution).

Three-electrode electrochemical cell was used for the electrochemical testing. A circular section of alloy AA6060 (3.14 cm²) was used as a working electrode, while commercial Pt-foil and saturated calomel electrode, SCE were used as counter and reference electrode, respectively.

Electrochemical measurements were carried out using a computer controlled Potentiostat (PARSTAT 2273), managed with appropriate software. After the stabilization of open circuit potential, E_{oep} and subsequent Tafel polarization measurements, the anodic potentiodynamic polarizations curves were recorded (scan rate: 5 mV/sec) in order to detect the pitting potential, where breakdown of passive layer results in pitting corrosion.

Optical microscope OM and SEM/EDS analyses were used to characterize the microstructural constituents in extruded alloy AA6060.

Results and discussion

The representative anodic polarization curves registered for Al-Mg-Si alloy in NaCl solutions of various concentrations

are presented in Figure 1. From these plots, characteristic values of breakdown potentials, E_{pit} are determined as shown schematically.

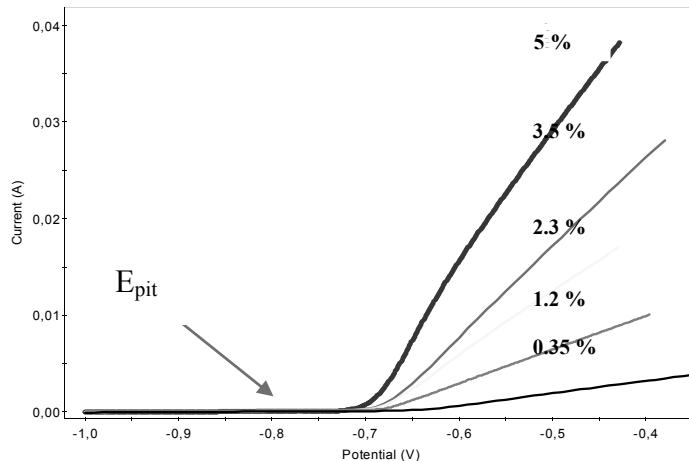


Figure 1. Anodic polarization curves in deaerated NaCl solutions at 293K

The shift of E_{pit} to more negative values clearly indicates the higher pitting susceptibility in solutions with higher Cl^- concentration. Equally, another factor associated with pitting is distribution of intermetallic particles [3, 4]. SEM/EDS analyses performed have shown that in Al-matrix of extruded AA6060 two main intermetallic phases exist, Figure 2. Dark

particles are intermetallic phases composed from Mg and Si (Mg_2Si), while elongated white phases characterized by Fe-content have been identified as iron-base particles, $\text{Al}_x\text{Mg}_y\text{Fe}_z\text{Si}$. Their chemical composition and electrochemical nature can be correlated with difference in potential between the Al-matrix and these particles.

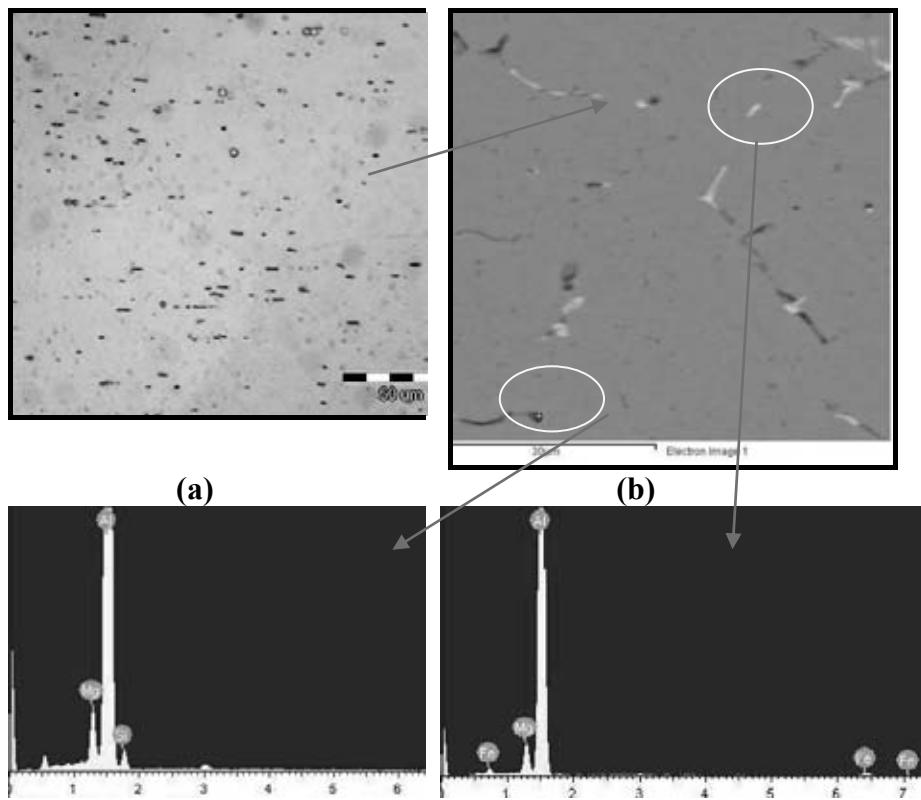


Figure 2. Microscopic images of commercial Al-Mg-Si alloy AA6060: (a) OM- transversal section, etched in Barker reagent, polarized light, tint filter; (b) SEM/EDS micrography of intermetallic phases on the surface

The potential of white phases is higher (more noble) than the one of Al-matrix [6] so that in AA6060 alloy, they act as cathodes and induce local anodic dissolution of surrounding Al- phase, i.e. pitting corrosion process. Dependence of pitting potential on NaCl-concentration is presented in Figure 3 which clearly indicates that E_{pit} values decreased with increasing concentration. In sigmoid shaped curve, two distinct concentration areas can be recognized: at higher concentration (2.3%-5%) E_{pit} shifted

rapidly to more negative potential. It suggests that the pits are formed more easily than they can be repassivated, while in the lower concentration area (0.35%-1.2%) repassivation process is competing with new pits growing. It can be concluded that between 1.2% and 2.3% of NaCl in solution, the critical concentration of choride ions exists where pitting corrosion prevails in comparison to repassivation ability of commercial Al-Mg-Si alloy AA6060.

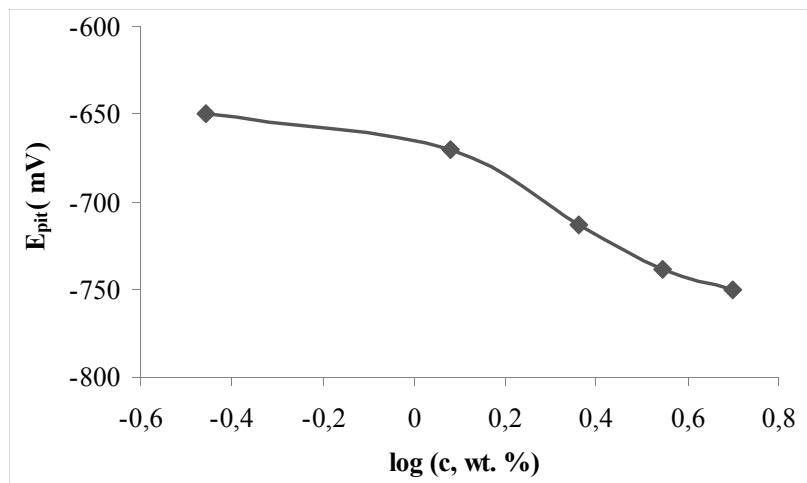


Figure 3. Breakdown potential dependence on NaCl concentration

Conclusion

The electrochemical study of NaCl-concentration effect on pitting corrosion of extruded Al-Mg-Si alloy has shown that local processes of passive film breakdown started at intermetallic particles heterogeneously distributed in the surface of the samples tested.

At the experimental conditions used, E_{pit} dependence on $c(\text{Cl}^-)$ was found to follow the linear relationship in the higher concentration range. In this range, E_{pit} values are lower (less noble), suggesting the detrimental influence on pitting resistance of AA6060.

Acknowledgments

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References

- [1] K. J. Al-Fadhalah, A. I. Almazrouee, A. S. Aloraie, Materials & Design 53 (2014) 550-560.
- [2] B. V. Jegdić, et.al., J. Serb. Chem. Soc. 78 (2013) 997-1011
- [3] H. Allachi, F. Chaouket, K. Draoui, J. Alloys Comp. 491 (2010) 223-229.
- [4] C. Vargel, Corrosion of Aluminium, Elsevier Ltd., Amsterdam, 2004.
- [5] EN 755 - 2 : 2008 Aluminium and aluminium alloys. Extruded rod/bar, tube and profiles.
- [6] K.A. Yasakau, et al., Electrochim.Acta 52(2007) 7651–7659.

**ISPITIVANJE UTICAJA RAZLIČITIH AGRESIVNIH SREDINA NA OTPORNOST
NA HABANJE NISKOLEGIRANOG
CR-NI-MO ČELIČNOG LIVA**

**INVESTIGATION OF THE EFFECT OF VARIOUS AGGRESSIVE
ENVIRONMENTS, THE WEAR RESISTANCE LOW ALLOY
CR-NI-MO STEEL CASTINGS**

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Izvod:

Niskolegirani Cr-Ni-Mo čelični liv se najviše primjenjuje za izradu segmenata hodnog stroja i navlaka rovokopača i utovarivača, noževa buldozera isl. Navlake rovokopača i utovarivača rade u uslovima velikih dinamičkih opterećenja i abrazivnog habanja. Abrazivno habanje je često uvećano prisustvom korozivnih materijala, među kojima možemo ubrojati i vodu. Djelovanje korozije je znatno izraženije mehaničkim odnošenjem materijala. Najčešće, proizvodi korozije imaju vrlo malu otpornost na habanje.

Zemljište, koje sadrži različite hemijske reagense, vlagu i kiseonik, ponaša se kao korozivni elektrolit prema čeličnim odlivcima, koji podliježu elektrohemijskoj koroziji. Prema podacima raznih autora, prosječna brzina korozije niskolegiranih čelika i gvožđa iznosi 0,2-0,4 mm/godišnje, u različitim zemljištima (1,3,4).

Abstract:

Low alloyed Cr-Ni-Mo cast steel is mostly used for making segments undercarriage of the machine and cover the backhoe and loader, bulldozer blades, etc.. Covers the backhoe and loader work under high dynamic loads and abrasive wear. Abrasive wear is often increased by the presence of corrosive materials, among which can be counted, and water. Effect of corrosion is significantly higher mechanical removal of material. Preferably, the corrosion products have very low abrasion resistance.

The land, which includes a variety of chemical reagents, moisture and oxygen, acts as a corrosive electrolyte to the steel castings, which are subject to electrochemical corrosion. According to the data of different authors, the average corrosion rate of low alloy steel and iron is 0.2-0.4 mm / year, in different soils (1,3,4).

Uvod

Niskolegirani Cr-Ni-Mo čelični liv karakteriše visoka čvrstoća i žilavost. Ovaj čelični liv se najviše primjenjuje za izradu segmenata hodnog stroja i navlaka rovokopača i utovarivača, noževa buldozera isl.

Navlake rovokopača i utovarivača rade u uslovima velikih dinamičkih opterećenja i intenzivnog habanja. Iz ovog razloga,

materijal od koga se one izrađuju mora posjedovati visoku otpornost na habanje i dobru udarnu žilavost.

Habanje se u opštem slučaju karakteriše kao promjene dimenzija, oblika, mase i stanja površinskog sloja pod uticajem spoljne sredine. Habanje se može definisati i kao neželjeno uklanjanje materijala sa površine tijela koje se kreće u dodiru sa drugim tijelom. Abrazivno habanje metala je jedna od vrsta habanja koja nastaje

klizanjem, kotrljanjem i udarom nemetalnih materijala o metalnu površinu (7).

Abrazivno habanje je često uvećano prisustvom korozivnih materijala, među kojima možemo ubrojati i vodu, pošto je djelovanje korozije znatno izraženije

Cr-Mo-Ni čelični liv

Cr-Ni-Mo čelični liv najčešće sadrži od 0,3-0,6% C, do 2% Cr, do 2% Ni, a može biti dopunski legiran i sa 0,2-0,4 % Mo. Obično pripada perlitnoj vrsti čeličnog liva. Često se primjenjuje sa odnosom Cr/Ni=2-2,5. Odlivci od ovih vrsta čelika imaju visoke pokazatelje plastičnosti i čvrstoće (6).

Dopunskim legiranjem niskolegiranih hrom-niklovih čelika molibdenom (0,2-0,4%) povećava se granica puzanja. Molibden u ovim čelicima povećava prokaljivost, mehaničke osobine (kod normalnih temperatura), obradljivost odlivaka, a izrazito smanjuje osjetljivost prema krtosti pri otpuštanju (6).

Pošto je u ovom radu ispitivana koroziona otpornost Cr-Ni-Mo niskolegiranog čeličnog liva, opisacemo uticaj osnovnih legirajućih elemenata na proces korozije.

Hrom je najvažniji legirajući element za formiranje pasivnog filma na nerđajućem čeliku. Drugi legirajući elementi mogu da utiču na efikasnost Cr da formira ili održava ovaj film, ali ni jedan od njih ne može, sam, da formira pasivni film. Pasivni film nastaje već pri 10,5% Cr, ali takav film pruža zaštitu od korozije samo u blagim atmosferskim uslovima. Povećanje sadržaja Cr od 17 do 20% Cr, što je tipično

mehaničkim odnošenjem materijala. Najčešće, proizvodi korozije imaju vrlo malu otpornost na habanje.

Cilj ovog rada je bio da se ispita habanje niskolegiranog Cr-Ni-Mo čeličnog liva uslijed korozije.

za austenitne nerđajuće čelike, ili 26 do 29% Cr, što je tipično za feritne nerđajuće čelike, veoma povećava stabilnost pasivnog filma. Međutim, visok sadržaj Cr može nepovoljno da utiče na mehaničke osobine, zavarljivost itd. Zbog toga je često efikasnije povećavati otpornost nerđajućih čelika prema koroziji dodavanjem drugih legirajućih elemenata, sa ili bez povećanja sadržaja Cr (4).

Nikal u dovoljnim količinama stabilizuje austenitnu strukturu, što poboljšava neke mehaničke i proizvodne karakteristike čelika. Nikal je efikasan za održavanje repasivacije, naročito u redukcionim sredinama.

Molibden u kombinaciji sa Cr je vrlo efikasan za stabilizaciju pasivnog filma u prisustvu hlorida, pa povećava otpornost čelika prema obrazovanju pitova i koroziji u zazorima.

Ugljenik je koristan kod martenzitnih čelika jer omogućava njihovu kaljivost i primenljivost odgovarajućih čelika na povišenim temperaturama. U svim drugim slučajevima C je štetan, tj. nepovoljno utiče na otpornost čelika prema koroziji, zbog mogućeg formiranja karbida hroma na granicama zrna i stvaranja zona osiromašenih hromom, gde je stabilnost pasivnog filma jako narušena (5).

Korozija metala

Korozija metala je obrnut proces od dobijanja metala. Predstavlja spontano

razaranje metala pod dejstvom korozione sredine. To je prirodna pojava povratka metala u ravnotežno stanje, pri čemu sistem smanjuje slobodnu energiju

Prema mjestu nastanka korozija može da bude:

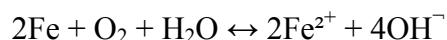
- **atmosferska korozija** - koja obuhvata procese u vlažnom vazduhu, na kiši i insolaciji, aerosolima i hemijskim zagadjivačima vazduha,
- **korozija u tečnosti** - koja obuhvata pojavu razaranja materijala u direktnoj reakciji sa okolnom sredinom: vodom, rastvorima kiselina, baza ili soli,
- **podzemna korozija** - koja djeluje na metale ukopane u zemlju kao što su cjevovodi, cistijerne, noseći stubovi i sl. Kad je u pitanju samo zemlja riječ je o elektrohemijskoj koroziji, ali ako je tle bogato vodom može nastati i mikrobiološka korozija (anaerobne bakterije nalaze pogodne uslove za razvoj, razaraju zaštitni sloj vodonika i izazivaju jaku lokalnu koroziju čeličnih dijelova).

Korozija metalnih dijelova, koji su u dodiru sa zemljom, je složen proces koji ima elektrohemiju prirodu. To je redoks proces pri kojem dolazi do oksidacije atoma metala (donora elektrona) u slobodni katjon, uz istovremenu redukciju nekog oksidansa (depolarizatora – akceptora elektrona)(2).

U kontaktu sa zemljištem, koje sadrži određenu količinu vlage, mineralnih materija i kiseonika i na taj način može da

se ponaša kao jonski električni provodnik (igra ulogu elektrolita u elektrohemijskim reakcijama), navedeni dijelovi na pojedinim mjestima počinju da se rastvaraju, tj.korodiraju.

Zemljište,koje sadrži različite hemijske reagense,vlagu i kiseonik, ponaša se kao korozivni elektrolit prema čeličnim odlivcima, koji podliježu elektrohemijskoj koroziji. U kontaktu sa vlažnim zemljištem, čelični liv se rastvara prema reakcionaloj šemi:



Prikazana reakcionala šema predstavlja ukupnu reakciju korozije u kojoj metal (Fe) prelazi u rastvorene proekte korozije (Fe^{2+}) (1)

Brzina korozije, od koje zavisi dužina eksploatacije odlivaka, zavisi od velikog broja faktora:

- vrste materijala;
- postupka izrade;
- hemijskih osobina zemljišta;
- strukture i granulometrijskog sastava zemljišta;
- PH vrijednosti zemljišta;
- vlage zemljišta;
- električne provodljivosti zemljišta;
- koncentracije minerala u zemljištu;
- spoljnje temperature isl.

Svaki od navedenih faktora ima svoj udio u brzini i karakteru korozije čeličnog liva u zemljištu. Isti se usložnjava ako se u razmatranje uzme uticaj zajedničkog djelovanja više činilaca (2).

U raznim vrstama zemljišta, brzina korozije raznih vrsta čeličnog liva i gvožđa

se jako razlikuje. Prema podacima raznih autora, prosječna brzina korozije niskolegiranih čelika i gvožđa iznosi 0,2-0,4 mm/godišnje (1,3,4). Podaci se odnose na nezaštićene predmete, od gvožđa i čelika, u odsustvu lutajućih struja i diferencijalne aeracije.

U nekim slučajevima korozija se odvija malom brzinom, iako sa termodinamičke tačke gledišta brzina rastvaranja metala treba da bude znatno veća. Takvo stanje visoke otpornosti prema koroziji naziva se pasivnost. Otpornost prema koroziji nerđajućih čelika se zasniva na njihovoj osobini da se spontano prekrivaju pasivnim filmom u prisustvu kiseonika. Pasivnost se održava u određenim sredinama, što zavisi od vrste čelika, njegovog sastava i strukture.

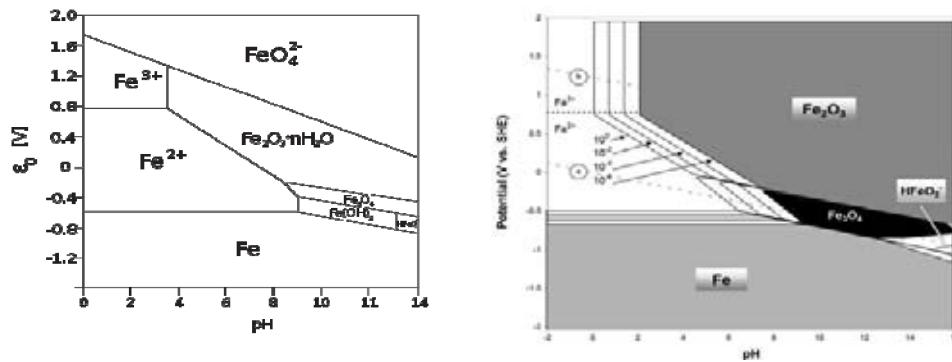
Sastav korozione sredine znatno utiče na tok korozije. Promjenu uticaja sredine može izazvati i veoma mala promjena koncentracije njenih komponenata.

Ako se film ošteti mehanički ili hemijski (posebno u prisustvu Cl^- jona), može doći do njegovog ponovnog formiranja (repasivacija) ili do odvijanja korozionih procesa.

Kada su uslovi pogodni za održavanje pasivnosti brzina korozije čelika je veoma niska. Korozija se može spriječiti ukoliko su u rastvoru prisutni anjoni (na primer

Tu se razlikuju tri oblasti:

- koroziona,
- imuna na koroziju i
- pasivizirana.



SLIKA 1 Purbeov dijagram – domeni korozionih svojstava

Dijagram pokazuje da korozija gvožđa i čelika uglavnom nastaje u kiselim sredinama.

Ako se prirodni elektrodnji potencijal pogodno modifikuje pomoću spoljašnjeg

NO_3^- , SO_4^{2-} itd.), koji otežavaju adsorpciju Cl^- jona, ili ih istiskuju sa površine metala. Pomenuti anjoni konkurišu jonima Cl^- za adsorpciju na pasivnoj površini metala(4). Korozija se može spriječiti ukoliko su u rastvoru prisutni anjoni koji otežavaju adsorpciju Cl^- jona, ili ih istiskuju sa površine metala. Dodavanje drugih anjona u rastvor koji sadrži hloride (na primer NO_3^- , SO_4^{2-} itd.).

Ti anjoni konkurišu jonima Cl^- za adsorpciju na mjestima na pasivnoj površini, ne izazivajući razaranje pasivnog filma niti obrazovanje pitova.

Korozioni procesi zavise ne samo od vrste metala već i od sredine u kojoj se taj metal nalazi. Uticaj korozionog medijuma (kiseli, neutralni, alkalni voden rastvor), prikazuje se Purbeksovim (Pourbaix) dijagramom E-pH.

električnog izvora, moguće je prevesti gvozdjeni uzorak u oblast označenu kao "imunitet". Promjena od korozionih uslova do imuniteta nije tako ostra, ali je usvojeno da ona nastaje pri $E = -0.62 \text{ V}$.

Eksperimentalni dio

Za potrebe ispitivanja polaznog materijala, uzete su probe od tri navlake proizvođača

iz uvoza: Caterpillar, Hendrix i Liebherr (slika 2).



SLIKA 2 Uvozne navlake

Hemijski sastav uvoznih navlaka je dat je u tabeli 1.

Tabela 1

Proiz.	Hemijski sastav (%)											
	C	Si	Mn	P	S	Cr	Ni	Mo	Al	Cu	V	B
CAT	0.32	0.28	0.81	0.019	0.017	0.57	0.65	0.19	0.051	0.18	-	0.0023
HEND	0.30	0.96	0.71	0.012	0.020	1.87	0.75	0.48	0.031	0.09	0.02	-
LIEB.	0.28	0.32	1.36	0.014	0.023	0.32	0.19	0.03	0.029	0.13	0.01	-

U okviru eksperimentalnog dijela obrađen je niskolegirani Cr-Ni-Mo čelični liv, osmišljen i testiran u Institutu za crnu metalurgiju (interne oznake NK3M), a primijenjen kao čelični liv za izradu habajućih dijelova rudarskih i građevinskih mašina.

Od ovog čeličnog liva urađene su dvije probne šarže na otvorenoj indukcionoj

peći, kapaciteta 120 kg i jedna šarža na indukcionoj peći ITMK 2000, kapaciteta 1000kg.

Od svake šarže uzet je po jedan odlivak (slučajan izbor), od kojeg su izrađene probe za mehanička, hemijska i koroziona ispitivanja.



SLIKA 3 Probni odlivci izrađeni od NK3M čeličnog liva (isporučeni firmi APEX)

Hemijski sastav izrađenih šaži dat je u tabeli 2.

Tabela 2

Br.šarže	Hemijski sastav (%)									
	C	Si	Mn	P	S	Cu	Cr	Ni	Mo	Al
M588	0,21	1,00	0,74	0,018	0,015	0,14	2,01	0,90	0,45	0,010
M593	0,22	0,94	0,74	0,020	0,010	0,22	2,02	0,92	0,43	0,011
V737	0,22	1,00	0,75	0,016	0,018	0,23	2,05	0,91	0,46	0,012

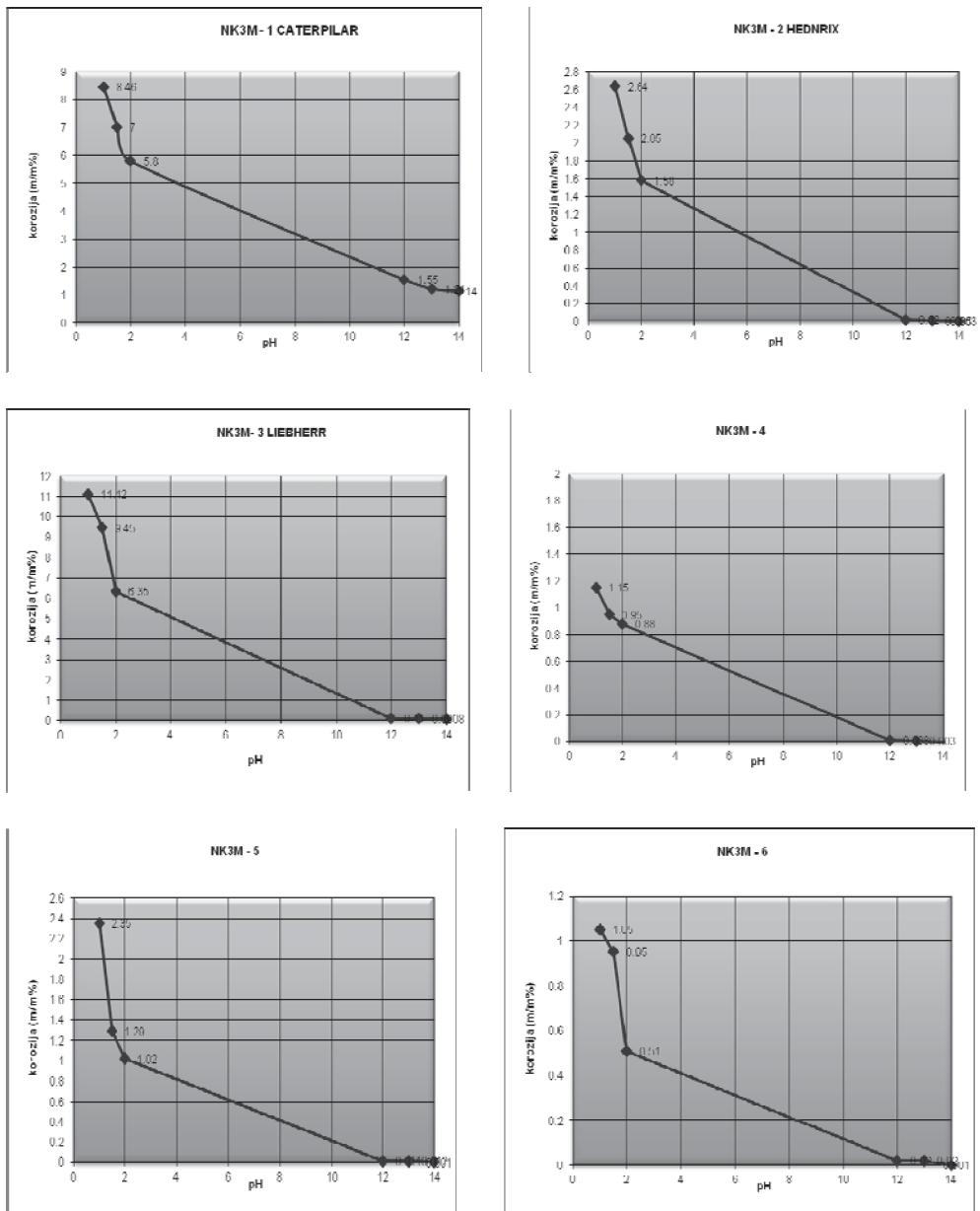


SLIKA 4 Izgled uzoraka za ispitivanje otpornosti na koroziju

Prema standardu ASTM G 48 - 2000 koji obuhvata postupke za određivanje otpornosti prema koroziji vršena su ispitivanja potapanjem uzorka u 1%, 3%, 6% rastvore kiseline, baze i soli u ciklusima od po 16h držanja uzorka u rastvoru, 4h sušenja na vazduhu i 4h

usušnici na 105 °C. Uzorci su tretirani u vodi na isti način.

Gubitak mase uzorka (izražen u masenim procentima – m/m%) urađenih od uvoznih materijala i NK3M čeličnog liva, nastao kao posledica korozije, prikazan je na slijedećim dijagramima.



SLIKA 5 Gubitak mase uzoraka urađenih od uvoznih materijala i NK3M čeličnog liva, nastao kao posledica korozije

Posmatrajući dijagrame možemo suditi o otpornosti na koroziju uvoznih i naših navlaka. Vidimo da, od uvoznih dijelova, najmanju otpornost na koroziju imaju oni rađeni u firmi Liebherr. Nešto veću otpornost na

koroziju imaju Caterpillar navlake, a najveću Hendrixove.

Navlake zuba, rađene u Livnici Instituta za crnu metalurgiju imaju sličnu ili veću otpornost na koroziju od navlaka nabavljenih iz uvoza.

Sa porastom sadržaja Cr,Ni,Mo u čeličnom livu, smanjuje se gubitak usled korozije (4). Ova činjenica i objašnjava za 25% veću izdržljivost

institutovih navlaka u odnosu na Hendrixove, u uslovima eksploracije (8).

Zaključak

1. Uzorci su prilično korodirali u kiseloj sredini:
 - gubitak metala korozijom kod uzoraka urađenih od uvoznih navlaka je najveći kod Liebherra, a najmanji kod Hendrixa (zbog većeg sadržaja Cr,Ni,Mo)
 - gubitak metala korozijom kod uzoraka urađenih u Livnici Instituta manji je od gubitka metala uzoraka od uvoznih navlaka.
 - gubitak metala korozijom kod uzoraka urađenih u Livnici Instituta je međusobno dosta ujednačen.
2. Uzorci u baznoj sredini pasiviziraju.
3. Uzorci u vodi su neznatno korodirali. Najveći gubitak mase imali su uzorci izrađeni od Liebherrovih navlaka.

Literatura

- 1) S.Mladenović: "Korozija materijala", TMF, Beograd 1990.g.
- 2) M.Antonijević,M.Pavlović,Č.Lačnjevac,S.Mladenović: " Korozija i zaštita čelika", SITZAMS, Beograd 1998.g.
- 3) M.Milenković,S.Mladenović,I.Vučković: " Korozija i zaštita", Tehnička knjiga, Beograd,1980.g.
- 4) Biljana Bobić, Bore Jegdić: „Piting korozija nerđajućih čelika”, 2005
- 5) Metals Handbook Ninth Edition,Volume 3,p 576 American Society for Metals
- 6) Blagoje Kočovski: " Ugljenični i legirani čelični liv" , Bor 1996.g.
- 7) F.Maratray: "L'amélioration de la recherche de nouveaux matériaux résistants à l'abrasion", Quatrième Colloque International de l'Abrasion –Grenoble, 9,10,11 mai 1979.g.
- 8) APEX Fördertechnik GmbH: " Bucket tooth points produced in Institut", Geilenkirchen 2013.g.

**POBOLJŠANJE OSOBINA NISKOLEGIRANOG CR-NI-MO ČELIČNOG LIVA
NAMIJENJENOG ZA IZRADU REZERVNIH DIJELOVA GRAĐEVINSKIH I
RUDARSKIH MAŠINA**

**IMPROVING THE PROPERTIES OF LOW-ALLOY CR-NI-MO STEEL CASTINGS
INTENDED FOR THE MANUFACTURE OF SPARE PARTS OF CONSTRUCTION
AND MINING MACHINERY**

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Institut za crnu metalurgiju AD Nikšić

Izvod:

Navlake rovokopača i utovarivača rade u uslovima velikih dinamičkih opterećenja i intenzivnog habanja. Iz ovog razloga, materijal od koga se one izrađuju mora posjedovati visoku otpornost na habanje i dobru udarnu žilavost. Osnovni uzrok, koji izaziva dotrajalost ovih dijelova i kao posledicu toga potpunu zamjenu istih – je proces habanja. Habanje je prisutno svuda gdje se oprema ili njene komponente, kreću ili se pak, preko nje ili pomoću nje prerađivani materijal kreće. Isto tako, zbog izuzetno teških uslova rada i dinamičkih opterećenja čest je i lom ovih dijelova.

Kod izbora materijala, odabrani kvalitet mora postići zahtijevani nivo tvrdoće, čvrstoće, prokaljivosti i udarne žilavosti.

Abstract:

Covers the backhoe and loader work under high dynamic loads and intensive wear. For this reason, the material from which they are made must have high wear resistance and good impact strength. The main reason that causes the deterioration of these parts, and as a consequence a complete replacement of the same - the process of wear. Wear is present wherever the equipment or its components, move or turn over it or using it processed material moving. Also, due to the extremely difficult working conditions and dynamic loads and frequent breakage of these parts. When choosing materials, selected quality has achieved the required level of hardness, strength, fracture toughness and hardenability.

Uvod

Opšte je poznato da određeni broj dijelova rudarskih i građevinskih mašina radi u uslovima dinamičkih opterećenja i habanja, te da ovi dijelovi najčešće predstavljaju potrošni materijal. Godišnji izdaci, koje savremena industrija mora izdvojiti za zamjenu dotrajalih dijelova ili pojedinih elemenata, nijesu uopšte mali, pa je za ljude koji rade u ovim granama industrije, krupan zadatak obaranje ovih troškova. Takav primjer su i navlake

utovarivača, rovokopača isl, koje se masovno koriste u rudarstvu i građevinarstvu.

Osnovni uzrok, koji izaziva dotrajalost opreme i kao posledicu toga potpunu zamjenu iste – je proces habanja. Habanje je prisutno svuda gdje se oprema ili njene komponente, kreću ili se pak, preko nje ili pomoću nje prerađivani materijal kreće (3). Isto tako, zbog izuzetno teških uslova rada i dinamičkih opterećenja čest je slučaj i lom ovih dijelova.

Ovo su samo neki od razloga za pristupanje projektovanju čeličnog liva čije bi se upotrebe vrijednosti dokazale i

iskoristile preko odlivaka namijenjenih za rad u rudarstvu i građevinarstvu.

Ispitivanje uvoznih materijala

U cilju najbržeg dolaženja do odgovarajućeg materijala za izradu navlaka rovokopača, pristupilo se karakterizaciji

strukture i osobina uvoznih navlaka koji se mogu naći na ovim prostorima. Rađena su ispitivanja tri navlake od proizvođača: Caterpillar, Hendrix i Liebherr. Hemski sastav je dat je u tabeli 1.

Tabela 1

Proiz.	Hemski sastav (%)											
	C	Si	Mn	P	S	Cr	Ni	Mo	Al	Cu	V	B
CAT	0.32	0.28	0.81	0.019	0.017	0.57	0.65	0.19	0.051	0.18	-	0.0023
HEND.	0.30	0.96	0.71	0.012	0.020	1.87	0.75	0.48	0.031	0.09	0.02	-
LIEBH	0.28	0.32	1.36	0.014	0.023	0.32	0.19	0.03	0.029	0.13	0.01	-

Iz tabele 1 se vidi da je navlaka Caterpillar urađena od niskolegiranog čelika, mikrolegiranog borom, pri čemu je primjetan uticaj austenitoobrazujućih elemenata (Ni, Mn).

Hendrix navlaka je urađena od niskolegiranog Cr-Ni-Mo čeličnog liva, sa odnosom Cr/Ni=2,5, kojim se, uz dopunsko legiranje sa molibdenom,

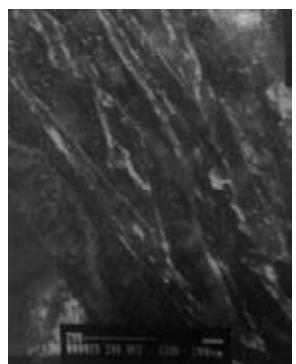
postižu visoke vrijednosti čvrstoće i pokazatelja plastičnosti.

Liebherr je svoju navlaku uradio od niskolegiranog manganskog čelika sa povišenim mehaničkim osobinama, a koji je namijenjen za dijelove koji su podvrgnuti udarnim, promjenljivim opterećenjima i habanju uslijed trenja. Tvrdoća i žilavost date su u tabeli 2.

Tabela 2

Proizvođač	Tvrdoća, HRc	Žilavost, J
CATERPILLAR	41	68
HENDRIX	43	65
LIEBHERR	41	75

Metalografska analiza Navlaka CATERPILLAR



a)



b)

SLIKA 1 Mikrostruktura Caterpillar navlake
a) TEM – tamno polje; b) TEM – svijetlo polje

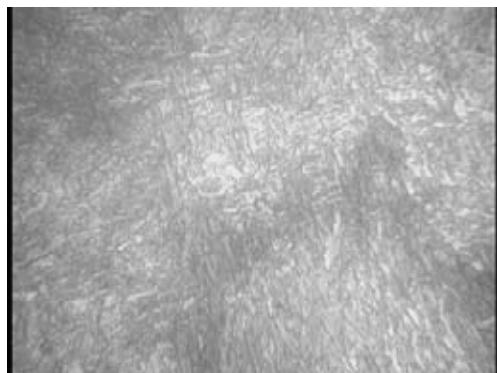
Strukturna analiza je izvršena na transmisionom i optičkom mikroskopu. Čelik, od kojeg je izrađena ova navlaka, posjeduje mikrostrukturu paketnog ili dislokacionog martenzita u kome su fino dispergovani karbidi tipa M₃C. Metodom

tamnog polja ustanovljeno je prisustvo kontinuiranog filma zaostalog austenita (sl.1a) između martenzitnih lamela. Optičkim mikroskopom je utvrđeno da je ova navlaka urađena kovanjem(4).

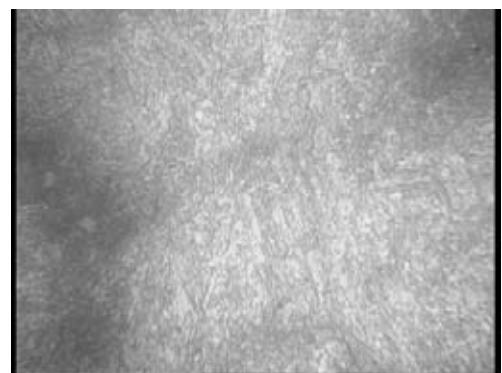
Navlaka HENDRIX

Mikrostruktura ove navlake sastoji se, uglavnom, od otpuštenog martenzita sa

nešto zaostalog austenita. Takođe je uočeno prisustvo mikrosegregacija (sl.2a).



a)
x 530



b)
x530

SLIKA 2 Mikrostruktura navlaka Hendrix i Liebherr.

Navlaka LIEBHERR

Mikrostruktura ove navlake je veoma slična mikrostrukturi navlake Hendrix (sl.2b). Martenzitna struktura je dobijena oštrim hlađenjem, a primjetna je i manja

količina zaostalog austenita.. Optičkim mikroskopom je utvrđeno da je i ova navlaka urađena kovanjem.

Izbor čeličnog liva

Navlake rovokopača i utovarivača rade u uslovima velikih dinamičkih opterećenja i intenzivnog habanja. Iz ovog razloga, materijal od koga se one izrađuju mora posjedovati visoku otpornost na habanje i dobru udarnu žilavost.

Kod izbora materijala, odabrani kvalitet mora postići zahtijevani nivo tvrdoće, čvrstoće, prokaljivosti i udarne žilavosti. Kako je njegovo ukupno ponašanje, u radnom uslovima, određeno

mikrostrukturom, to je i neophodno projektovanje iste.

Primjena čelika mikroleđiranog borom, za izradu navlaka livenjem u ICM-u, je teško izvodljiva s obzirom na teškoće mikroleđiranja.

Isto tako, izrada navlaka kovanjem u Institutu nije moguća.

Sa druge strane 1997.g., u ICM-u je projektovan i osvojen čelični liv interne oznake NK-2. Projektovanje je obavljeno na istim principima kao i kod čelika uvozne Caterpillar navlake, stim što se za

povećanje prokaljivosti, umjesto bora koristio hrom(4).

Kod NK-2 čeličnog liva postignuta je struktura slična strukturi Caterpillar navlaka, ali je udarna žilavost bila niža (34-36 J). Iz ovog razloga često su se dešavali lomovi navlaka, pogotovo kod rovokopača. Takođe je i termička obrada bila komplikovana i zahtjevna.

Iz gore navedenih razloga u Institutu se prišlo osmišljavanju novog kvaliteta

čeličnog liva veće udarne žilavosti i solidne otpornosti na habanje trenjem.

U ovom radu je obrađen niskolegirani Cr-Ni-Mo čelični liv, osmišljen i testiran u Institutu za crnu metalurgiju (interne oznake NK3M), a primijenjen kao čelični liv za izradu habajućih dijelova rudarskih i građevinskih mašina. Predloženi hemijski sastav, dat je u tabeli 3.

Tabela 3

	C	Si	Mn	P	S	Cr	Ni	Mo	Cu
min	0.20	0.80	0.65	-	-	1.80	0.90	0.35	-
max	0.25	1.00	0.75	0.030	0.030	2.00	1.00	0.45	0.30



SLIKE 3 i 4 Probni odlivci izrađeni od NK3M čeličnog liva (isporučeni firmi APEX)

Niskolegirani Cr-Ni-Mo čelični liv

Niskolegirane čelike ove grupe karakteriše visoka čvrstoća i žilavost. Prvobitno su bili namijenjeni za potrebe vojne tehnike, ali je njihova primjena kasnije proširena u civilne svrhe. Sastav ovih čelika značajno varira od proizvođača do proizvođača. Ovaj čelični liv se najviše primjenjuje za izradu segmenata hodnog stroja i navlaka rovokopača i utovarivača, noževa buldozera isl. Obično se isporučuju u intervalu tvrdoće 43 – 48 HRc i minimalne udarne žilavosti 20 – 27 J (3).

Ovaj čelični liv najčešće sadrži od 0,3-0,6% C, do 2% Cr, do 2% Ni, a mogu biti dopunski legirani i sa 0,2-0,4 % Mo. Obično pripadaju perlitoj vrsti čelika. Često se primjenjuju ca odnosom Cr/Ni=2-2,5.

Odlivci od ovih vrsta čelika imaju visoke pokazatelje plastičnosti i čvrstoće(2).

Dopunskim legiranjem niskolegiranih hrom-niklovinih čelika molibdenom (0,2-0,4%) povećava se granica puzanja. Molibden u ovim čelicima povećava prokaljivost, mehaničke osobine (kod normalnih temperatura), obradljivost odlivaka, a izrazito smanjuje osjetljivost prema krtosti pri otpuštanju(2).

Teži se dobijanju što čistijih vrsta čeličnog liva, jer sadržaj elemenata (P,S) i gasova jako negativno utiče na žilavost.

Povećanje sadržaja ugljenika znači i povećanje tvrdoće, a samim tim i otpornosti na habanje. Međutim, sa povećanjem sadržaja ugljenika smanjuje se žilavost, pa je u praksi kompromis neizbjegjan (1).

Sadržaj silicijuma se mora kretati oko 1%, radi održavanja dobre livkosti. Kod većih sadržaja Si, tako se snižava žilavost.

Sa porastom sadržaja mangana, povećava se količina karbida u strukturi, a time se povećava i otpornost na habanje. Međutim, treba voditi računa da ukupni sadržaj mangana i hroma ne pređe 3% (uz sadržaj ugljenika max 0,25%) - zbog izrazitog pada žilavosti(3).

Termička obrada ovih vrsta čeličnog liva je jednostavnija od termičke obrade

čeličnog liva NK-2. Sastoje se od normalizacionog žarenja odlivaka, a nakon toga se pristupa kaljenju u ulju. Sadržaj Mo, ukoliko je bliže gornjoj granici, daje bolju prokaljivost pa je martenzitnu strukturu moguće dobiti i kaljenjem u struji vazduha (1). Nakon kaljenja, obavezno je i niskotemperaturno žarenje radi uklanjanja unutrašnjih naprezanja.Od uspješno izvedene termičke obrade jako zavisi kvalitet odlivaka (otpornost na habanje, žilavost).

Eksperimentalni dio

Hemijska ispitivanja

Za potrebe ovog rada urađene su dvije probne šarže na otvorenoj indukcionoj

peći, kapaciteta 120 kg i jedna šarža na indukcionoj peći ITMK 2000, kapaciteta 1000kg – za konkretnog kupca. Hemijski sastav izrađenih šaži dat je u tabeli 4.

Tabela 4

Br.šarže	Hemijski sastav (%)									
	C	Si	Mn	P	S	Cu	Cr	Ni	Mo	Al
M588	0,21	1,00	0,74	0,018	0,015	0,14	2,01	0,90	0,45	0,010
M593	0,22	0,94	0,74	0,020	0,010	0,22	2,02	0,92	0,43	0,011
V737	0,22	1,00	0,75	0,016	0,018	0,23	2,05	0,91	0,46	0,012

Odlivci koji su upotrijebljeni u svrhu ovog rada, koriste se kao radna tijela na utovarivačima i rovokopačima firme

APEX iz Geilenkirchena (Njemačka). Od ove firme smo dobili i potvrdu o kvalitetu naših odlivaka (5).



SLIKA 5 Navlake isporučene firmi APEX

Mehanička ispitivanja

Od svake šarže uzet je po jedan odlivak (slučajan izbor), od kojeg su uzete probe za

mehanička ispitivanja. Rezultati ispitivanja prikazani su u tabelama 5 i 6.

Tabela 5

Šarža	Fm, KN		A, %		Rm, MPa	
	I proba	II proba	I proba	II proba	I proba	II proba
M588	37.6	44	15	15	748	875
M593	41.5	41	17.5	17.5	826	816
V737	42.5	41.4	15	15	846	824

Tabela 6

Šarža	Tvrdoća, HRc			Žilavost, J		
	I proba	II proba	Srednja vrijednost	I proba	II proba	Srednja vrijednost
M588	41	40	40.5	68	71	69.5
M593	42	43	42.5	67	58	62.5
V737	42	41	41.5	55	61	58

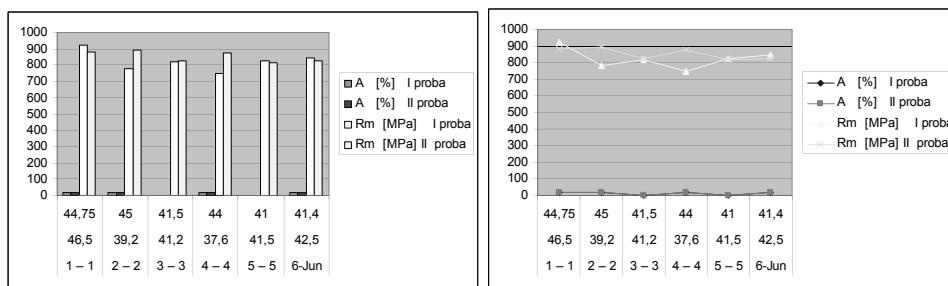
Za ispitivanje zatezanjem korišćene standardne epruvete:

$d_0 = 8 \text{ mm}$, $l_0 = 40 \text{ mm}$

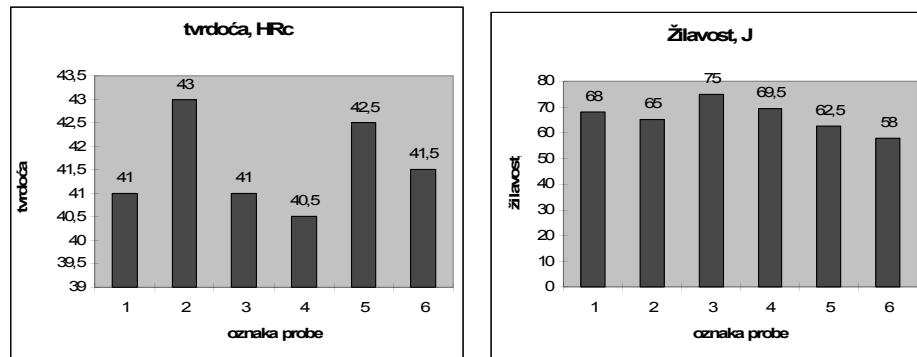
Za ispitivanje žilavosti korišćene su probe dimenzija $10 \times 10 \times 55 \text{ mm}$, sa „v“ zarezom. Poređenje zateznih karakteristika uvoznih i naših navlaka dato je u tabeli 7 i na slici 6.

Tabela 7

Navlaka	Fm [KN]		A [%]		Rm [MPa]	
	I proba	II proba	I proba	II proba	I proba	II proba
1-1	46,5	44,75	15	15	925	880
2-2	39,2	45	19	19	780	895
3-3	41,2	41,5	19,5	19,5	820	826
4-4	37,6	44	15	15	748	875
5-5	41,5	41	17,5	17,5	826	816
6-6	42,5	41,4	15	15	846	824



SLIKA 6 Grafički prikaz poređenja zateznih karakteristika uvoznih i navlaka rađenih u Livnici ICM-a.
Oznake navlaka: 1-1 (Caterpillar), 2-2 (Hendrix), 3-3 (Liebherr),
4-4 (šarža M588), 5-5 (šarža M593), 6-6 (šarža V737).



*SLIKA 7 Grafički prikaz poređenja tvrdoće i žilavosti uvoznih i navlaka rađenih u Livnici ICM-a.
Oznake navlaka: 1 (Caterpillar), 2 (Hendrix), 3 (Liebherr),
4 (šarža M588), 5 (šarža M593), 6 (šarža V737).*

Metalografska analiza

Poslije standardne metalografske pripreme uzorci su najprije pregledani u nenagriženom stanju, a potom nagriženi u 2% - om nitalu. Pregledom uzorka na svjetlosnom mikroskopu NEOPHOT 21, pri povećanju od 530x, izvršena je metalografska analiza.

Navlaka 1 (šarža M588)

Mikrostruktura se sastoji uglavnom od otpuštenog martenzita sa nešto zaostalog

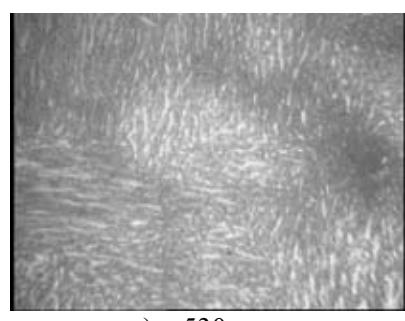
austenita. Takođe je uočeno prisustvo mikrosegregacija, sl.4a.

Navlaka 2 (šarža M593)

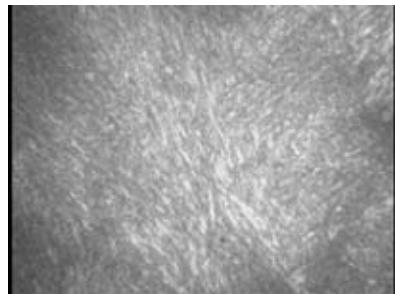
Mikrostruktura ove navlake je veoma slična mikrostrukturi navlake 1, sl.4b.

Navlaka 3 (šarža M737)

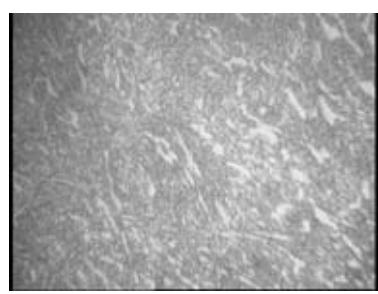
Kao i kod prethodne dvije navlaka mikrostruktura navlake 3 je martenzitna, sa nešto zaostalog austenita i prisutnim mikrosegregacijama sl.4c.



a) x530



b) x530



c) x530

SLIKA 8 Mikrostruktura uzorka navlaka šarži M588,M593 i V737 (žareno stanje)

Metalografska analiza i mehanička ispitivanja uzorka urađena su u Institutu za crnu metalurgiju u Nikšiću.

Ispitivanje odlivaka u uslovima eksploatacije izvršeno je na utovarivačima

i rovokopačima firme APEX iz Geilenkirchena (Njemačka), i na rovokopačima firme YUBRIV iz Kotora.



SLIKA 9 Zub i navlake rađeni za YUBRIV Kotor (rovokopač HITACHI)

Zaključak

- 1) Rezultati ispitivanja mikrostrukture govore o velikoj sličnosti uvoznih i navlaka rađenih u Livnici ICM-a. Ovo govori o dobro planiranom pristupu projektovanja čeličnog liva, koji će zadovoljiti stroge uslove eksploatacije. I navlake rađene u Institutovoj Livnici i one uvozne, nakon termičke obrade, u strukturi imaju martenzit sa nešto zaostalog austenita koji im daje povećanu žilavost(1). Takođe je kod svih ispitivanih navlaka uočeno prisustvo mikrosegregacija.
- 2) Uporedna ispitivanja mehaničkih osobina uvoznih navlaka i navlaka rađenih u Livnici ICM-a, govore o približnom kvalitetu. Zatezne karakteristike proba izrađenih od naših i uvoznih navlaka su dosta ujednačene (tabela 7; slika 6), iako su neke od uvoznih navlaka urađene kovanjem.
- 3) Mjeranjem tvrdoće navlaka mogu se konstatovati gotovo identične vrijednosti i kod uvoznih i institutovih odlivaka (tab.2 i 6, slika).
- 4) Vrijednost žilavosti je za nijansu niža, kod odlivaka rađenih u Livnici ICM-a, od uvoznih (tab.2 i 6, slika 7). Ovo se dijelom može objasniti i samim načinom izrade navlaka. Dvije od tri ispitivane uvozne navlake urađene su postupkom kovanja čelika, a samo je jedna urađena livenjem. Navlake urađene u ICM-u imaju za nijansu izraženije mikrosegregacije i grublju mikrostrukturu.
- 5) Izvještaj od strane firme Apex iz Geilenkirchena, govori o 25% većoj izdržljivosti naših odlivaka u odnosu na ranije isporučivane odlivke koje je radila firma HENDRIX iz SAD. Pogotovo je važna informacija da uopšte nije bilo lomova navlaka, što je i povećalo ukupni vijek eksploatacije isporučenih odlivaka (5).
- 6) Firma YUBRIV iz Kotora još nije dostavila svoj izvještaj o ponašanju odlivaka. Isti su ugrađeni prije šest mjeseci i još su u eksploataciji. Zasada su rezultati izdržljivosti i habanja navlaka zadovoljavajući.

Literatura

- 1) Metals Handbook Ninth Edition, Volume 3,p 576 American Society for Metals
- 2) Blagoje Kočovski: "Ugljenični i legirani čelični liv", Bor 1996.g.
- 3) F.Maratray: "L'amélioration de la recherche de nouveaux matériaux résistant à l'abrasion", Quatrième Colloque International de l'Abrasion – Grenoble, 9,10,11 mai 1979.g.
- 4) Š. Tomašević, D. Tadić, D. Manojlović, Z. Matijašević: "Osvajanje proizvodnje odlivaka za građevinske i rudarske mašine", Nikšić 1997.g.
- 5) APEX Fördertechnik GmbH: "Bucket tooth points produced in Institut", Geilenkirchen 2013.g.

THERMAL DEGRADATION STUDY OF POLYLACTIC ACID / TITANIUM DIOXIDE NANOCOMPOSITES BY DIELECTRIC THERMAL ANALYSIS

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Sustainable systems comprising biodegradable polymers and inorganic nanoscaled particles attract a big attention due to the improved mechanical and barrier properties which are very important for the material used as a food packaging, but also for the possibility to be degraded after their disposal. Therefore, an attempt was made to use dielectric thermal analysis (DETA) in the identification of structural changes of polylactic acid/titanium dioxide (PLA/TiO₂) nanocomposites as a result of their thermal degradation (aging). So, PLA/TiO₂ nanocomposites consisting of 5 wt% nanofillers, modified and unmodified, were prepared using a melt mixing Brabender plastograph at 180 °C. Hydrolytic degradation test are usually done at 37 °C in phosphate buffer solution, hence test samples of a known diameter, weight and thickness were introduced in a vacuum oven at 37 °C, and were allowed to be aged at different time. Parameters identifying changes in the dielectric behavior of polymers in the electric field, and thus the changes in the polymer structure, are the dielectric constant (ϵ'), phase lag ($\text{tg}\delta$), and dielectric losses (ϵ'').

Key words: DETA, nanocomposites, food packaging, thermal aging

Introduction

One of the main functions of the packaging material is to protect the product, e.g. food from the contaminants and to preserve its' taste and nutritional value. Polymer materials are very attractive in food packaging because they offer preservation of physical and chemical integrity of the product. On the other hand, the quantity of the used packaging material in the food industry is very big, so a small reduction of the volume and/or weight of the material would contribute to the decrease of cost and improvement of the solid waste problem. The environmental concern might be smaller by the replacement of the fossil oil-based materials with the eco-friendly naturally originated, sustainable materials. Sustainable packaging are considered to be beneficial, safe, and healthy for individuals and communities throughout its life cycle; designed to optimize materials and energy; sourced, manufactured, transported and recycled

using renewable energy, it maximizes the use of renewable or recycled source materials [1]. The traditional non-biodegradable plastic polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), etc. have tendency to be replaced by biodegradable and biocompatible materials, among which polylactic acid offers superior properties. The techniques usually applied in lowering the brittleness and increasing the toughness of PLA are blending with low molecular weight polymers, such as polyethylene glycol (PEG), polypropylene glycol or polyhydroxy butyrate [2], or preparation of nanocomposites with the introduction of nanoscaled fillers, in the form of nanoparticles, nanorods and/or nanotubes, and nanosheets in polymer matrix [3]. The presence of nanofillers, in which at least one dimension is between 1 and 100 nm, involved in a polymer matrix, create big interfaces with the matrix improving the features of the nanocomposite, e.g. flexibility, gas barrier properties,

temperature/moisture stability, etc., in respect to their microscaled complement. Thus, it was shown that Ag and TiO₂ nanoparticles help in the control of the growth of pathogenic microorganisms on the food surfaces, so they increase the application of their nanocomposites as antimicrobial materials. Except the strong antimicrobial their photocatalitic properties as well make TiO₂ particles very attractive filler in polymer nanocomposites [3].

In this study, an attempt was made to identify the opportunity of application of dielectric thermal analysis (DETA) in determination of structural changes of thermally aged PLA/TiO₂ nanocomposites. It is known [4] that the dependence of dielectric properties of our interest, dielectric permittivity (ϵ'), dielectric loss (ϵ''), and phase lag ($\text{tg } \delta$), on materials

configuration, allow the application of DETA in the analysis of the structure of polymer materials after thermal degradation. Conventional techniques of hydrolytic degradation involve treatment of samples at 37 °C in a phosphate buffer. So, the thermal degradation of our PLA/TiO₂ nanocomposite samples was performed in vacuum oven at 37 °C, with different time duration. Therefore PLA/TiO₂ nanocomposites using the concentration of 5 wt% TiO₂ were prepared by the melt mixing, and the films of thickness of about 150 μm were obtained by compression molding. The influence of the surface modification of TiO₂ particles on the structural changes during aging was also studied.

Experimental

Surface modification of TiO₂ nanoparticles, as well as nanocomposite films preparation was performed as previously described [5].

Dielectric properties were measured on Polymer Laboratories Dielectric Thermal Analyzer (PL-DETA) equipped with parallel plate capacitance cell using *ac* current. Thermal scans were performed from the room temperature to 180 °C at heating rate of 2 °C min⁻¹. Capacitance, C_p

(pF), for the parallel equivalent electrical circuit, and phase lag, $\text{tg } \delta$ as D ($\text{tg } \delta = \text{tg } (90^\circ - D)$), were the measured parameters at 1 kHz and 200 mV *ac* signal.

Dielectric permittivity, ϵ' , and dielectric loss, ϵ'' , for the known thickness (L , cm) of the treated samples, and electrode area (A = 7.07 cm²), were calculated by the equations: $\epsilon' = (11.3 \times L \times C_p)/A$ and $\epsilon'' = \epsilon' \cdot \text{tg } \delta$.

Results obtained by DETA were confirmed by DSC and FTIR analyses [5].

Results and Discussion

$\epsilon' - T$ and $\text{tg } \delta - T$ dependences in Figs. 1-3 illustrates slight changes in the structure of plain PLA and PLA/TiO₂ nanocomposites during aging. Heating rate of 2 °C min⁻¹ ensures appearance of a wide peak from ~64° to ~ 96 °C typical for relaxation processes influenced by glass transition temperature (T_g) in the temperature range ~62° ÷ ~66 °C ($\text{tg } \delta - T$ curves), and a cold crystallization process from ~70° to

~96 °C ($\epsilon' - T$ curves). Glass transition temperature appears as a shoulder on the $\text{tg } \delta - T$ curves in the temperature range from 64°-68 °C for the PLA before aging. It seems that thermal aging at 37 °C at shorter times enables additional restructuring and reorganization of PLA chains, which slightly shifts T_g and cold crystallization peak to higher temperatures. Also, ϵ' takes lower values, indicating existence of a more organized structure. Longer aging times enable an increased

mobility of polymer chains, expressed by decreasing the T_g s and shifting of ε' to a

higher values in respect to the samples aged shortly.

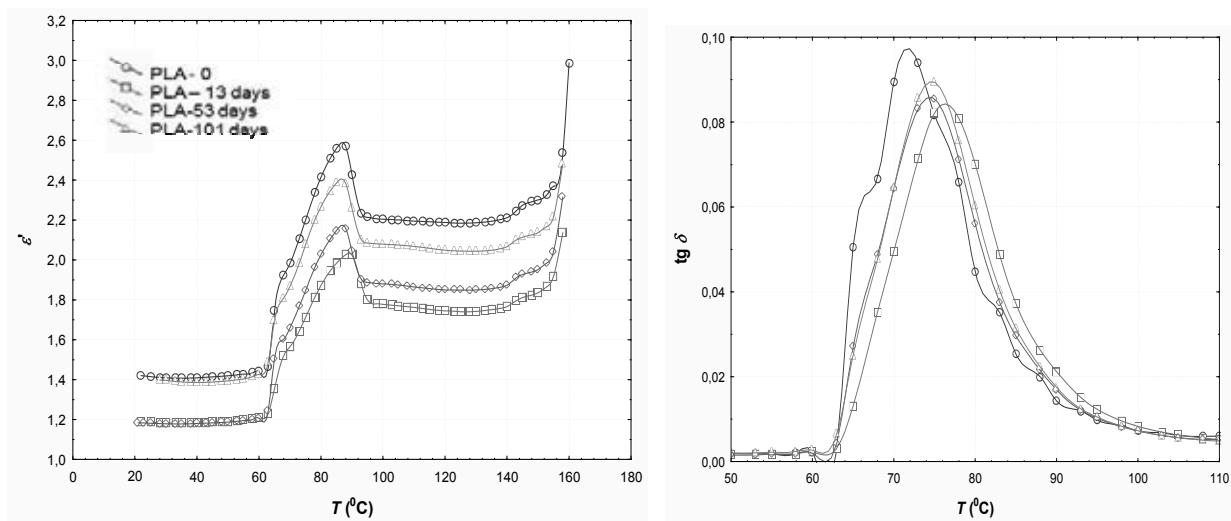


Fig 1. ε' - T and $\text{tg } \delta$ - T dependences of “neat” PLA aged at 37 °C, at different times; heating rate 2 °C/min

It seems that the amorphous material from the beginning develops its crystallizability during the thermal treatment. At the beginning of aging the lower values of dielectric permittivity for nanocomposite

containing both unmodified and modified TiO₂ particles in respect to the untreated samples, Figs. 2 and 3, indicate a restricted movement and a higher chain orientation.

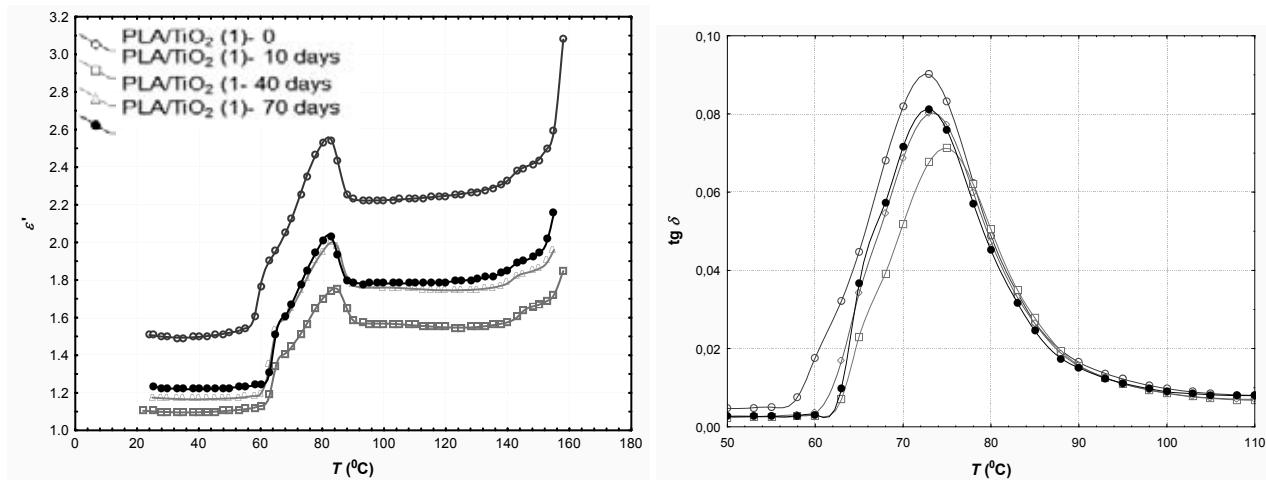


Fig 2. ε' - T and $\text{tg } \delta$ - T dependences of PLA nanocomposites containing unmodified TiO₂ (5 wt%), aged at 37 °C, at different times; heating rate 2 °C/min

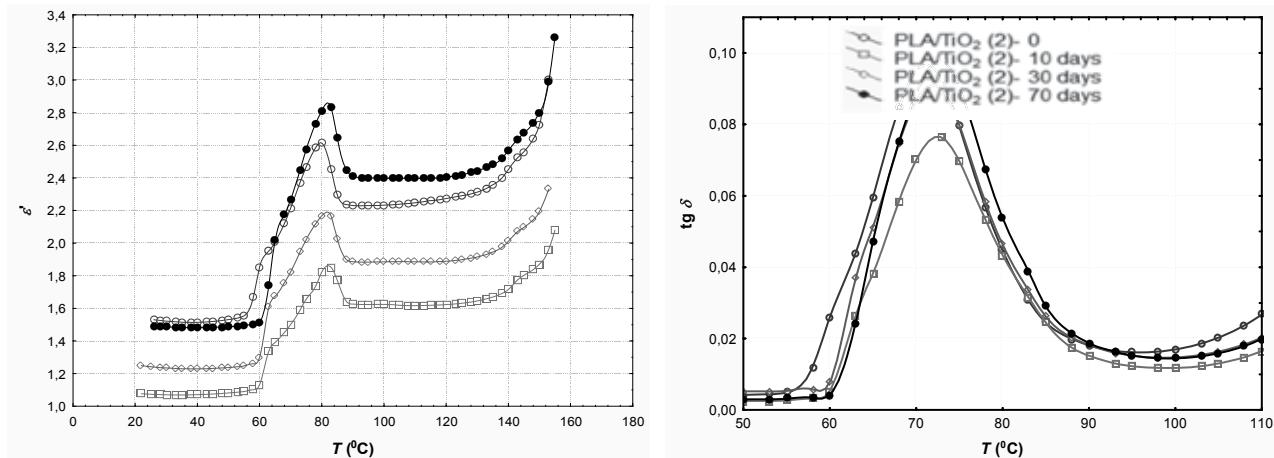


Fig 3. ε' - T and $\text{tg } \delta$ - T dependences of PLA nanocomposites containing modified TiO_2 (5 wt%), aged at 37 °C, at different times; heating rate 2 °C/min

A slight shift of a cold crystallization peak, and the glass transition temperatures, Figs. 2 and 3, to the higher temperatures also confirms the aforementioned observations. A difference in the dielectric behavior of nanocomposite containing unmodified and modified TiO_2 is obvious at upper aging times. Namely, in the case of the nanocomposite with modified TiO_2 particles, both, ε' and $\text{tg } \delta$ values are shifted toward higher values, which is typical for species which movement is easier. But, at the same time, the cold crystallization peak, and T_g , Figs. 2 and 3,

shifts toward higher temperatures that is characteristic for a ordered structures. Most probably the modified TiO_2 facilitate the degradation process of the polymer, and at the same time enables easier restructuring of macromolecules. It is well known that the crystallization process is easier in the polymers with lower molecular weights, i.e., shorter macromolecules. The remarks given for the samples studied by DETA analysis were confirmed by DSC and FTIR analyses.

Conclusions

Dielectric constant and dielectric losses which reflex the behavior of the polymer in the electric field, depend on the chemical composition and structure of the polymer, the temperature, the frequency

and the voltage of the applied a.c. electrical field. The relationship between dielectric properties and structure of the polymers gives the opportunity dynamic electrical thermal analysis (DETA) to be used as a study technique for polymer structure and structure changes.

References

1. Garlotta, D. A Literature Review of Poly(Lactic Acid), *Journal of Polymers and the Environment* 2001, 9, 63-84.
2. Ahmed, J. Varshney, S.K. Auras, R. Hwang, S.W. Thermal and Rheological Properties of L-Polylactide/Polyethylene Glycol/Silicate Nanocomposites Films, *Journal of Food Science* 2010, 75, N97-N108.
3. Nakayama, N. Hayashi, T. Preparation and Characterization of Poly(L-Lactic Acid) / TiO₂ nanoparticle nanocomposite films with high transparency and Efficient Photodegradability, *Polymer Degradation and Stability*. 2007, 92, 1255-1264.
4. Porjazoska, A. Grchev, T. Cvetkovska, M. Karal-Yilmaz, O. Baysal, B.M. Thermal Aging of Poly(D,L-Lactide-co-Glycolide) films followed by Impedance Spectroscopy and Dielectric Thermal Analyses, *Bulletin of the Chemists and Technologists of Macedonia* 2002, 21, 199-206.
5. Kujundziski, A.P. Chamovska, D. Marra A. Duraccio D. Silvestre C. In: *Proceedings of International Conference 15 YUCCOR*, 17-20 September, 2013, Tara, Serbia, 252-260.

RELATIONSHIP BETWEEN PACKAGING TECHNOLOGY AND/OR FOOD PROCESSING AND PACKAGING MATERIAL

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The new techniques used in the food production, which evolved as a constant effort for save and high quality food, are reflected in new trends in packaging materials. Food processing at high pressures or high energized ionizations, and application of ozone, but also for some procedures of disinfection and sterilization, require treatment of an already packed food. Consequently, the persistence of food quality mainly depends on the quality of packaging material. In general, the proper selection of the material and packaging technology for a given application in food industry contribute to the extension of a product shelf-life or provides the evidence for the condition of the foodstuff in contact. Therefore the novel techniques introduced in packaging industry are considered to be valuable in delivery of the quality and safe food to the consumers. Taking into consideration the rigorous Legislations in this area, we can easily understand increasing number of studies focused on development of new packaging expertise. In this work an attempt was made to emphasize the importance of a certain packaging techniques.

Application of microwaves

The frequency range of microwaves is between 300 and 30 000 MHz. The main role in the food heating by microwaves takes the dipole nature of water. Water dipoles cannot be oriented at such a high frequency, so the microwave energy transforms to heat. So, the heating efficiency besides on performances of the microwave devices, and some of the materials' properties (dimensions, specific heat, heat conductivity), mostly depends on the dielectric properties of the material [1].

It is considered that the application of microwaves for sterilization,

pasteurization, or food processing is a convenient method for preparation of high quality food. The packaging used should be compatible and convenient for these methods of processing. Considering the activity toward microwaves, mainly, three types of materials could be considered: passive, active, and reflecting. Materials passive to microwaves, such ceramics, glass, paper and plastics, are convenient for food processing in microwave oven. These materials do not absorb heat directly, or absorb it in a much smaller extent in respect to the heat taken by the food [2].

Table 1. Materials for containers of food treated by microwaves

Material*	Food / Application
PP/EVOH/PP	Sauces, ready meals, creams
PP/PVDC/PP	Sauces, ready meals, creams
CPET/APET	Sauces, ready meals, creams
(HT)PS/EVOH/PP	Sauces, dressings
PP/PP with filler/EVOH/PP with filler/PP	Ready meals
PS/PVDC/PS	Creams, pasteurized cheese
PS/PPO/EVOH/PP	Sauces, ready meals, creams

*PP – Polypropylene; EVOH – Ethylene Vinyl Alcohol; PVDC - Polyvinylidene chloride;
CPET - Crystalline Polyethylene Terephthalate; APET - Amorphous Polyethylene Terephthalate;
PS – Polystyrene; (HT)PS – Hi-temperature Polystyrene; PPO – polypropylene oxide.

In practice, the packaging is multilayer structure, so that the benefits of each of the layers could be used in fulfilling the specific requirements. The list of typical

materials for preparation of food containers and flexible packaging used for food treatment in microwave oven are given in Tables 1 and 2, respectively [3].

Table 2. Flexible packaging used for microwaves treatment

OPA/SiOx/PE	Metalized PET/PE
OPA/PVDC/PE	PET/PVDC/PE
OPA/PVDC/PE	PET/SiOx/PP
OPP/SiOx/OPP	OPA/CPP
PET/OPA/CPP	PET/amorphous PA/CPP

PA – Polyamide; OPA – Oriented Polyamide; SiOx – Silicon Oxide; PE – Polyethylene;
PVDC - Polyvinylidene Chloride; CPP – Crystalline Polypropylene;
OPP – Oriented Polypropylene; PET – Polyethylene Terephthalate.

The uniform distribution of heat throughout is considered to be the biggest problem in the preparation of the multicomponent food. This issue can be solved by the materials active toward microwaves, called “susceptors” and / or “receptors”. They are usually made of inorganic metal oxides or nitrides in the form of coatings (thickness from 3 to 400 Å). Laminate films made of metalized polyester and paperboard film were generally used, but silicon oxide, silicon nitride and aluminum oxide should be also considered. Susceptors are designed in such a way that they absorb the microwave energy, which in the form of heat is

transferred by contact or radiation to the food [4].

Microwaves are form of a unionized radiation holding energy which is not sufficient to break a chemical bond. But, as a result of high temperatures there is a big concern for the possibility of degradation, as well as migration of degradation products and additives from the packaging materials to the food. According to some studies [4] the total quantity of generated PET oligomers from PET materials shaped as roasting bags, or susceptors’ coatings fits in the range of 0.02 and 2.73 ppm. But, that quantity is 10 times smaller when the food is prepared in PET dishes using

conventional oven. Except on the food type, the quantity of migrants depends on the contact of packaging with food, the temperature, and the time of treatment [5]. It was found [6] that during food preparation PVDC/PVC films release 51% acetyl tributyl-citrate and 58% bis(2-ethylhexyl) adipate. Also, many gasses, such aldehydes, ketones, alcohols, carboxylic acids, are released during food preparation in a microwave oven. Even, some references [7] indicate a number of over 34 compounds, this number

continuously grow as the percentage of paper in the packaging material is increased. Very rigorous Regulations assisting the control of migration of harmful substances from the packaging material to the foodstuff have been established. However, the specific rules for the contact between microwave food and packaging doesn't exist, just some suggestions of the way of cooking have been usually given. Therefore, setting appropriate Regulations in this area is very important issue.

Application of ionization radiation

Two types of cold sterilization and pasteurization of food are used: γ -rays derived from ^{60}Co and beams of accelerated electrons. Accelerated electrons produce smaller number of vaporous products than γ -rays, so their application for food sterilization is preferred. Radiation by γ -rays is also very efficient method in reduction of microbes' populations, but their commercial application is restricted as a result of public questions related to the safety of irradiated food. But, the International Food Agency and the International Agency for Atomic Energy issued an agreement of a food radiation in the dosage of 10 kGy. More than 40 countries use this treatment to around 60 products, such as fresh or frozen poultry, vegetables, fruits, and grains. Food and pharmaceutics are already packed when irradiated. That means that the packaging is also irradiated, so it is necessary to know does the packaging experience some changes during exposure. Consequently, the glass irradiation cause disrupt of a structure, and thus the lost of the color and generation of oxygen would decrease the food shelf-life [3,4]. Some physical and chemical properties of polymer materials could be changed as a result of their irradiation. In accordance to the polymers' nature and the conditions of the radiation, two types of processes might

occur, degradation or development of networks. The creation of networks decreases the elongation, crystallinity and solubility of polymers, but increases their strength, and it is characteristic for PE, PP and PS. On the other hand, degradation deteriorates mechanical properties, and in vacuum atmosphere, it can assist the release of H_2 , CH_4 , and HCl from chlorinated polymers. When oxygen present, the degradation products are peroxides, alcohols and different low-molecular compounds containing oxygen. The dependence of the crystallinity of LDPE, HDPE, PP, PET, PVC and PVDC on the intensity of the irradiation in the range 0 - 8 kGy was not noticed. Also, for the dosages between 10 and 50 kGy the changes in the molecular structure in LDPE and OPP was not observed. Above 100 kGy the number of double bonds was increased and the release of CO_2 was detected. The concern of the irradiation of polymers results from the release of monomers or free radicals which might form additional changes in the polymer structure (degradation, branching, network), to activate the monomers (polymerization, and other chemical reactions), to be captured in the crystalline zones, to assist aging, etc.

In general, the possible changes induced by irradiation of polymers depend on: the chemical structure of polymers, the

additives, the history of polymer processing, the atmosphere in which the irradiation is performed, the dosage, and sometimes the irradiation speed. The issue

arose in the cases of multilevel packaging (laminates or co-extrudates), but it is considered that still there is a lack of information in that area [3,6].

UV and ozone treatment

The gaseous and liquid ozone, which is a strong oxidants / disinfectant, has been used not just for food treatment, but also for packaging sterilization and sterilization of production plants. Ozone mainly reacts with the polymers' surface, thus creating oxygen containing functional groups, and the degradation of polymer chains, as well. UV radiation has been also very efficient in the packaging sterilization, especially in the range from 250 to 280 nm. UV and ozone treatment increase the surface tension and the polymer hydrophilic character. PP is transparent for UV rays, so the ozone treatment is more convenient, whereas UV treatment is more appropriate when PET packaging is used. Different oxidation mechanisms in polymers could be distinguished during UV and ozone

irradiation. So, PP is more resistant to the treatment with both, UV and ozone, while PET is significantly oxidized. PS is more sensitive to ozone as a result of existence of benzene ring. Mainly, ozone doesn't penetrate in the crystalline regions, thus the oxidation occurs on the surface of crystalline domains.

It was also found that the ozone irradiation facilitates the migration of additive and monomers from the polymer films towards food. So, as a result of oxidation processes in LDPE packaging, where the commonly used antioxidants are butylated hydroxyanisol and butylated hydroxytoluen, the formation of phthalic esters, alkanes, alkenes, ketones, and peroxides was observed [3,4]. It was also noticed [4] that these substances could change the taste of the food.

Application of high pressure

Food protection by high pressure (up to 1000 MPa) is one of the modern techniques for food processing, when usually the flexible packaging material is used. Nevertheless, it is considered that there isn't sufficient information for the influence of high pressures to the features of polymer materials in contact with foodstuff. It was found [4] that high pressure treatment of around 400 MPa of packed food during 5-20 minutes contribute to slightly small quality deterioration. When the behavior of different laminate films: PET/SiOx/PUadh/LDPE, PET/Al₂O₃/PUadh/LDPE, PET/PVDC/Nylon/ HDPE/PP, PE/Nylon/PE, PET/EVA, PP, etc., were compared at pressures between 600 and 800 MPa, only metalized PET foil showed

increase in permeability of oxygen, CO₂ and water vapor. At the same time the significant variations in the polymer structure was not recognized, contrary, it was registered a decrease of the absorption of aromatic substances in the films. Most probably an additional restructuring of the polymer under high pressure occurred. However, longer high pressure exposure might lead to substantial increase of migration of low-molecular components from and to the food [4]. That means that the additional studies in this area are necessary.

The techniques stated here are the generally applied in food industry when non-ionization or ionization radiation is required. The other novel processes used in the food treatment, e.g., by chlorine dioxide, mainly for sterilization, and ultrasound in drying and extraction

processes, need additional studies, since there is a lack of information about their

impact on the quality of both, food and packaging.

References

1. Hoogenboom R, Wilms TFA, Erdmenger T, Schubert US (2009) Microwave-Assisted Chemistry: a Closer Look at Heating Efficiency. *Aust J Chem*, **62**, 236-243.
2. Holdsworth D, Simpson R, Thermal Processing of Packaged Foods, 2nd Ed., Ed. Barbosa-Canovas GV, Springer, 2007.
3. Cvetkovska M, Porjazoska Kujundziski A (2008) Polymers and Polymer materials as a packaging material, Food packaging, University “Ss. Cyril and Methodius” Faculty of Technology and Metallurgy, Skopje.
4. Ozen BF, Floros JD (2001) Effects of emerging food processing techniques on the packaging materials, *Trends in Food Science & Technology*, **12**, 60–67.
5. Sheftel VO, Indirect food additives and polymers: migration and toxicity, CRS Press LLC, Boca Raton, 2000.
6. Zygoura PD, Goulas AE., Riganakos KA., Kontominas MG (2007) Migration of di-(2-ethylhexyl)adipate and acetyltributyl citrate plasticizers from food-grade PVC film into isoctane: Effect of gamma radiation, *J. Food Eng.*, **78**, 870-877.
7. Marsh K, Bugusu B (2007) Food Packaging—Roles, Materials, and Environmental Issues, *J. Food Sci.*, **72**, R39-R55.

KOROZIJA ZAŠTITNIH CEVI CORROSION PROTECTIVE TUBE

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IZVOD:

Da bi se pravilno i u potpunosti sagledali složeni mehanizmi korozije zaštitnih zavarenih cevi u naftnim bušotinama, potrebno je uzeti u obzir sve činioce koji utiču na delovanje korozije. Najčešći mehanizmi korozije cevi u bušotinama su uzrokovani sadržajem ugljen - dioksida, vodonik - sulfida i hlorida u proizvodnom fluidu. Ugljen - dioksid i vodonik - sulfid u uslovima delovanja visokog pritiska i povišenih temperatura uz prisustvo vode, stvaraju veoma korozivnu sredinu karakterističnu za naftne i gasne bušotine. Proizvođači opreme za bušotine daju stručne komentare, pre svega u obliku studija. Postoji veliki broj radova iz ove oblasti, što pokazuje koliko je problem korozije u bušotinama složen. Ovo naročito dolazi do izražaja u dubokim bušotinama, gde se zahteva visoka čvrstoća materijala i otpornost na koroziju, što se ostvaruje upotrebom kvalitetnijih materijala za zacevljenje bušotine.

ABSTRACT:

In order to properly and fully comprehend the complex mechanisms of corrosion protection of welded pipes in oil wells, it is necessary to take into account all the factors affecting the operation of corrosion. The most common mechanisms of corrosion of pipes in the wells caused by the content of carbon - dioxide, hydrogen - sulphide and chloride in the production fluid. Carbon - dioxide and hydrogen - sulphide in terms of action of high pressure and high temperatures in the presence of water, creating a corrosive environment characteristic of oil and gas wells. Production equipment for wells provide expert comments, primarily in the form of studies. There are a large number of works in this field, which shows how the problem of corrosion in boreholes complex. This is particularly evident in the deep wells, where high material strength and corrosion resistance, which is achieved by using higher-quality materials for the tubing bore.

Uvod

U buštinama se susreću veoma složeni uslovi koji utiču na pojavu korozije, kao što su: visoki pritisci i temperature, prisutnost agresivnih fluida (CO_2 i H_2S) i vode sa hloridima. Proizvedeni fluidi, koji sadrže CO_2 i H_2S pod visokim pritiskom i na visokoj temperaturi uz prisutnost vode sa malom vrednošću pH, omogućavaju

pojavu veoma agresivne korozije kojoj mogu odoleti samo neki materijali. Koroziju zaštitnih cevi uglavnom izaziva delovanje: Ugljen-dioksida (CO_2); Sumpor-vodonika (H_2S); Hlorida; Slojne vode i kondenzata ugljovodonika; Temperature (uticaj na stepen korozivnog dejstva)[1].

Uticaj ugljen-dioksida na pojavu i razvoj korozije

Najvažnijim kriterijumima za pojavu korozije usled prisustva CO_2 smatraju se

parcijalni pritisak CO_2 i pH-vrednost vode. CO_2 je posebno razoran kod velikih brzina u sistemu i visokih pritisaka, gde kombinacija korozije i erozije dovodi do stvaranja opšte i pitting korozije [2].

Elektrohemijska korozija pri kojoj se gvožđe-sulfid taloži na površini metala u obliku crnog taloga predstavlja opštu koroziju, dok elektrohemijska korozija koja nastaje na vrlo malom delu površine materijala predstavlja pitting koroziju, koja je opasna zbog velike dubine prodiranja.

Ugljen-dioksid u prisustvu vode svojim rastvaranjem stvara ugljeničnu kiselinu, koja smanjuje pH - vrednost vode i izaziva nastajanje korozije [3]. Glavni faktori rastvaranja CO₂ u vodi su temperatura i parcijalni pritisak, ukoliko iznosi više od 0,2 MPa.

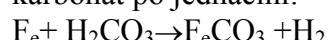
Tabela 1. Zavisnost korozivnog rastvora CO₂ od parcijalnog pritiska

PARCIJALNI PRITISAK	KOROZIVNOST
0,5 bar	Nije korozivan
0,5-2 bar	Moguće korozivan
2 bar	Korozivan

Ugljendioksid se rastvara u vodi i formira ugljenu kiselinu prema reakciji:

CO₂+H₂O→H₂CO₃ - ugljenična kiselina
Rastvorljivost CO₂ u vodi je direktno proporcionalna pritisku, a obrnuto proporcionalna temperaturi.

Ugljena kiselina sa gvožđem stvara fero-karbonat po jednačini:



Najčešća pojava korozionog oštećenja usled delovanja CO₂ na metal je u obliku

tačkaste korozije, koja se povećava sa brzinom protoka po čitavoj površini metala. U naftnim bušotinama CO₂ prouzrokuje koroziju kad sadržaj vode u proizvodnji postane dovoljno visok da prouzrokuje promenu kvašljivosti, tj. kad metal postaje vodo-kvašljiv. Taj uslov je teško predvideti jer su konstatovani podaci od minimalne vrednosti zavodnjavanja ležišta (1-5%), do srednjih (20-30%) i maksimalnih (60-90%).

Uticaj vodonik-sulfida na pojavu i razvoj korozije

Uticaj vodonik-sulfida (H₂S) na pojavu korozije raste (materijal apsorbuje višak

vodonika) sa smanjenjem pH vrednosti, naročito ispod vrednosti pH-4. Korozija prouzrokovana sadržajem H₂S naziva se još i „kisela“ (sour corrosion).

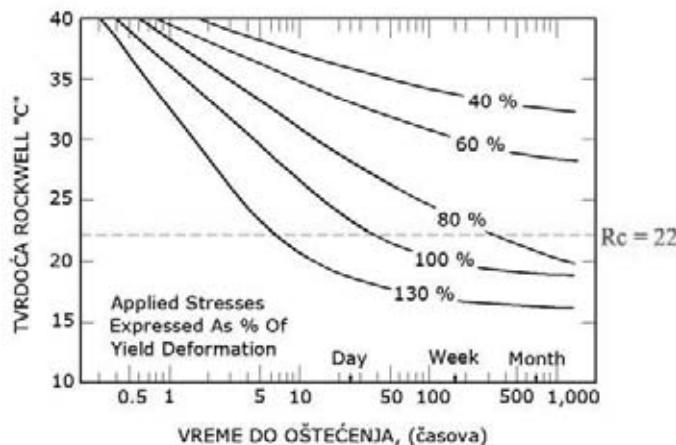
Vodonik-sulfid može prouzrokovati više tipova korozije;

- Korozija opšteg tipa-nastaje u prisustvu vode, zbog razlike u potencijalu između gvožđa i gvožđe sulfida. Ova korozija je naročito jaka iznad 93 °C;
- Pitting korozija-nastaje stvaranjem sulfida gvožđa koji se u zavisnosti od pritiska i pH vrednosti mogu pojaviti u obliku minerala troilita (FeS), pirita (FeS₂), pirotita (Fe₇S₈) i kanzita (Fe₉S₈);
- Naponska korozija (SCC-stress corossion cracking), nastaje stvaranjem sulfida gvožđa na granicama zrna ili duž inicijalnih prslina nastalih zamorom materijala. Grupacija NACE definiše dve vrste korozije, tj. „SCC“ i kombinaciju uticaja H₂S i atomskog vodonika „hidrogen embrittlement“ pod nazivom „SSC-sulfide stress cracking“[4]. Prema NACE standardu MR-01-075, SSC korozija se javlja u svim sistemima gde je parcijalni pritisak H₂S veći od 0,0035 bar;

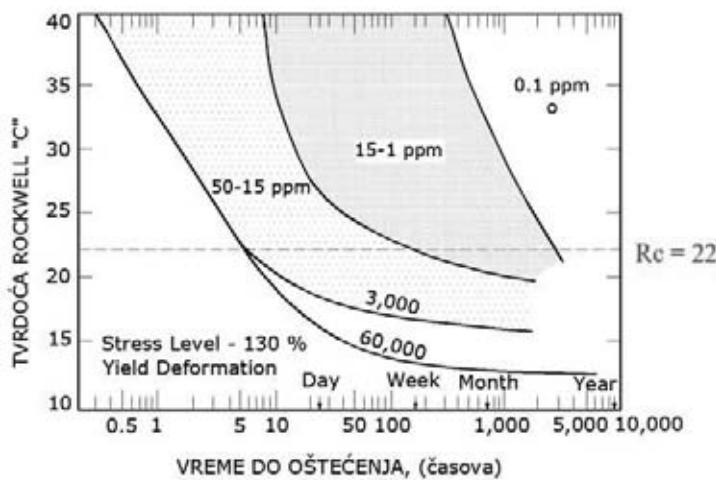
- Razaranje materijala vodonikom (Hydrogen Embrittlement)-nastaje apsorpcijom atomskog CO₂ u strukturu metalne rešetke, izazivajući pri tome krtost ili lomnost.
- Vodonikovoj koroziji ne podležu ugljenični i niskolegirani čelici, osim ako im tvrdoća prelazi 22 HRC.
- Niske vrednosti pH vode u slojnom fluidu predstavljaju idealne uslove za stvaranje H₂S.

Tabela 2. Korozivnost H₂S u odnosu na veličinu parcijalnog pritiska

PARCIJALNI PRITISAK, (bar)	KOROZIVNOST H ₂ S
0,01	Korozivan
0,01-0,001	Moguće korozivan
0,001	Nije korozivan



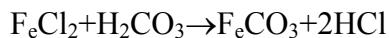
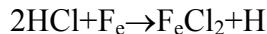
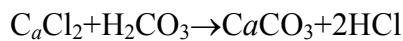
Slika 1. Uticaj naprezanja na vreme loma materijala-oštećenja, usled H₂S korozije za različite tvrdoće ("Rockwell").



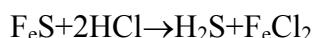
Slika 2. Uticaj koncentracije H₂S na vreme loma materijala za različite tvrdoće ("Rockwell").

Uticaj hlorida na pojavu i razvoj korozije

Hloridi, naročito u topлом stanju, izazivaju jaku koroziju koja može dovesti i do loma



Mora se uzeti u obzir i moguća reakcija hlorovodonične kiseline sa troilitom



U laboratorijskim uslovima je dokazano da mala koncentracija hlorida uzrokuje pitting koroziju [5]. Takođe je utvrđeno da temperatura iznad 65°C podstiče reakciju. Kao drastičan primer delovanja korozije

(chloride stress corrosion). Ovaj tip korozije najčešće nastaje u prisustvu kisele sredine i H₂S. Uz nisku pH vrednost koja je nastala rastvaranjem CO₂ u vodi nastaju sledeće reakcije:

izazvane hloridima spominje se slučaj polja „Thomasville“ u SAD, gde dolazi do smanjenja debljine zida cevi za 7 - 8 mm/god.

Uticaj slojne vode i kondenzata ugljovodonika na pojavu i razvoj korozije

Prisutnost agresivnih gasova, njihov parcijalni pritisak, temperatura i brzina protoka, nisu jedini parametri relevantni za prognozu korozije. Ovim parametrima treba pridodati vodu u protoku. Voda u protoku se javlja kao kondenzat vodenih para slojne vode, koja je u ležištu u faznoj ravnoteži sa gasom. CO₂ otapanjem u vodi može znatno uticati na pH vrednost vode i pojavu naponske korozije tipa SSC.

Slojna voda sa većim sadržajem natrijumovog i kalcijumovog hlorida deluje na pH vrednosti tako što veći sadržaj navedenih soli smanjuje uticaj CO₂ na pH vrednost. Pojava bikarbonata (HCO₃) u slojnoj vodi ima gotovo odlučujući uticaj na povećanje pH vrednosti. Slojna voda u obliku kondenzata ili u izvornom obliku predstavlja faktor koji je bitan za koroziju. Zbog čega je istraživanje uticaja slojne vode na koroziju od velikog značaja. Zavisnost pH vrednosti slojne vode i stepena H₂S korozivnosti data je u tabeli 3.

Tabela 3. Zavisnost pH vrednosti slojne vode i stepena H₂S korozivnosti

pH SLOJNE VODE	H ₂ S KOROZIJA
do 6,0	Područje H ₂ S korozije
6,0-9,5	Lomovi usled H ₂ S korozije retko se dešavaju
Iznad 9,5	Ne dolazi do lomova usled H ₂ S

Uticaj temperature na pojavu i razvoj korozije

Temperatura je značajan činilac u procesima korozije, jer već na 65 °C, podstiče koroziju u uslovima delovanja hlorida. Sa druge strane, temperatura iznad 80 °C utiče na smanjenje opasnosti od pojave naponske korozije „SCC“ (u literaturi nije zabeležen slučaj loma nastalih usled naponske korozije u temperaturnom intervalu između 65 °C i 80 °C).

Objašnjenje za tu pojavu u literaturi je sledeće: pokretljivost vodonika na temperaturi 20 °C je velika, ona se udvostručuje na 100 °C, a na 200 °C je

četiri puta veća. Ubrzanje difuzije dovodi do veće koncentracije vodonika u metalu, ali i njegovog lakšeg izlaska iz metala. Literaturni podaci pokazuju da iznad 150 °C nije zabeležen slučaj loma usled ulaska atoma vodonika u metal (H.E.). Međutim, iznad 220 °C atomi vodonika reaguju sa karbidima gvožđa i stvaraju metan. Delovanje vodonika dovodi do dekarbonizacije čelika, što dovodi do gubitka čvrstoće; stvaranja prslina, zbog pritiska stvorenog molekulima metana na granicama zrna.

Povišena temperatura negativno utiče na čvrstoću materijala, pa se na temperaturi od 200 °C čvrstoća smanjuje i za 25%.

Literatura

- [1] Ž. Šarkočević: „Otpornost prema oštećenju i lomu zaštitnih zavarenih cevi u naftnim bušotinama“, Doktorska disertacija, Univerzitet u Beogradu, 2010
- [2] Garber J. et al. A model for predicting corrosion rates in oil wells containing carbon dioxide, *presented at the SPE/EPA/DOE Exploration and Production Environmental Conference held in San Antonio, Texas, 2001*; Paper 66651.
- [3] Sridhar N, Dunn DS, Anderko AM, Lencka MM, Schutt HU. Effects of water and gas compositions on the internal corrosion of gas pipelines-modeling and experimental studies, *Corrosion*, 2003; 57: 221-35.
- [4] Russell HJ. Stress - corrosion cracking, Materials Performance & Evaluation, ASM, 1992.
- [5] Heitz E, Henkhaus R, Rahmel A. Corrosion science, an experimental approach, Ellis Horwood Limited, Chichester, England, 1992.

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Bijeli kristalni prah.Zbog svojih svojstava **masovno se koristi u proizvodnji kompozitnih raketnih goriva**, a takođe i u pirotehnici.

KALIJUM PERHLORAT KClO_4

Bijeli kristalni prah.Zbog svojih svojstava koristi se eksploziva, posebno u proizvodnji privrednih eksploziva, kao i u pirotehnici.

KALIJUM HLORAT KClO_3

Bijeli kristalni prah.Veoma jak oksidans, koji nalazi široku primjenu u pirotehnici.

KALIJUM NITRAT KNO_3

Bijeli kristalni prah.Veoma široka primjena u mnogim oblastima, posebno u pirotehnici i proizvodnji mineralnih đubriva.

BARIJUM NITRAT $\text{Ba}(\text{NO}_3)_2$

Bijeli kristalni prah.Nalazi primjenu u pirotehnici, naročito za bojenje plamena.

BARIJUM HROMAT BaCrO_4

Žuti kristalni prah.Široka primjena u mnogim granama, naročito u pirotehnici.

BARIJUM PEROKSID BaO_2

Sivobijeli kristalni prah.Zbog izraženih oksidacionih svojstava koristi se u pirotehnici, ali i za dobijanje kiseonika.

OLOVOFEROCIJANID $\text{Pb}_2[\text{Fe}(\text{CN})_6]$

Svjetložuti kristalni prah.Osnovna primjena je pirotehnika.

OLOVO HROMAT PbCrO_4

Žuti do žutocrveni kristali.Upotrebljava se u pirotehnici, ali i u proizvodnji mineralnih boja.

STRONCIJUM NITRAT $\text{Sr}_2(\text{NO}_3)_2$

Bijeli kristalni prah.Upotrebljava se u pirotehnici, ali i u mnogim drugim granama industrije.

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MONITORING ° ANALIZE ° UZORKOVANJE ° ELABORACIJA REZULTATA

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Centar za ekotoksikološka ispitivanja Podgorica DOO (CETI) je osnovala Vlada Crne Gore za vršenje poslova ispitivanja svih segmenata životne sredine: vazduha, vode, mora, zemljišta, flore i faune, klimatskih promjena, jonizujućeg i nejonizujućeg zračenja, buke i vibracije, izrade posebnih toksikoloških studija, analiza i programa za potrebe državnih organa, naučnoistraživačkih ustanova, privrede i građana, kao i poslova kontrole zdravstvene ispravnosti životnih namirnica i predmeta opšte upotrebe.

CETI vrši:

- ekotoksikološka i ispitivanja kvaliteta (fizičko-hemijska ispitivanja i ispitivanje sadržaja radionuklida) svih segmenata životne sredine (vode, vazduha, zemljišta, sedimenta, mora...);
- kategorizaciju otpada;
- ispitivanje otpadnih gasova - emisija;
- ispitivanje radona;
- snimanje „nultog“ stanja potrebnog za izrade studija lokacija i elaborata o procjeni uticaja na životnu sredinu;
- izradu toksikoloških studija, analiza i programa za potrebe državnih organa, naučnoistraživačkih ustanova, privrednih društava i drugih subjekata;
- dozimetrijska mjerjenja, osiguranje i kontrola kvaliteta (QA/QC);
- kontrolu i izdavanje sertifikata za promet roba (hrane i predmeta opšte upotrebe) u uvozu, izvozu i proizvodnji;
- ispitivanje radne sredine (komfor-mikroklimatski uslovi, hemijske i fizičke štetnosti);
- ispitivanje buke i vibracije u radnoj i životnoj sredini;
- pripremu i izradu akta o procjeni profesionalnih rizika zaposlenih sa predlogom mjera za njihovo otklanjanje.

CETI se trudi da neprestano unapređuje kvalitet svojih usluga kako bi obezbijedio ispunjenje zahtjeva i očekivanja korisnika, održava na vrhunskom nivou sistem etaloniranja za svu opremu koju koristi za kontrolisanje i ispitivanje, sprovodi sistem međulaboratorijskih ispitivanja i kontrolnih i funkcionalnih proba u cilju provjere i obezbjeđenja tačnosti i preciznosti laboratorijskih rezultata i kompetentnosti rada Laboratorije i stalno podiže nivo obrazovanja i povećava motivaciju i zadovoljstvo zaposlenih.

CETI je institucija koja pored visoke stručnosti posjeduje i višegodišnje iskustvo u djelatnosti ekotoksikoloških ispitivanja svih segmenata životne sredine. Od osnivanja je postigao da svoju djelatnost proširi po obimu, vrsti ispitivanja, broju analiza što je rezultiralo i širenjem liste klijenata tj. korisnika usluga. Danas može da ponudi široki spektar analiza koje se rade po savremenim, svjetski priznatim metodama i sa najkvalitetnijom i najpouzdanimanjem laboratorijskom opremom.

Osnovni cilj djelovanja CETI je kreiranje i realizacija uspješne strategije zasnovane na konkurenčkim prednostima sopstvene organizacije i uvažavanju potreba i interesa klijenata s ciljem širenja liste klijenata i jačanja i osvajanja povjerenja korisnika usluga na domaćem i tržištu regiona. Ostvarenje ovih zadataka podrazumijeva prije svega veliku angažovanost

zaposlenih, odgovarajuću instrumentalnu opremu, finansijska sredstva i vrijeme. Temelj uspjeha ujedno i prednost CETI jeste angažman svih zaposlenih, spremnost na nove izazove, a sve sa ciljem ostvarivanja zajedničke vizije – da CETI bude institucija prepoznata, u regionu i šire po stručnosti, pouzdanosti analiza, uvijek raspoloživa na tržištu uz konkurentne cijene.

Naši klijenti cijene implementaciju standardnih metoda analiza EN, MEST ISO, ISO, DIN, pridržavanje najviših profesionalnih standarda i dobre laboratorijske prakse, primjenu poznatih i priznatih metoda ispitivanja, obezbjeđenje tačnosti i preciznosti laboratorijskih rezultata i kompetentnosti rada Laboratorije, visoke sposobnosti i mogućnosti CETI, kratko vrijeme realizacije posla, konkurentne cijene, potpuno osiguranje kvaliteta rezultata i kontrolu sistema kvaliteta.

LABORATORIJSKE TEHNIKE

- *gasna hromatografija – masenomasena spektrometrija (GC-MSMS)*
- *gasna hromatografija - masena spektrometrija (GC-MS)*
- *gasna hromatografija (GC – ECD, FID, NPD, TCD, PID,FPD)*
- *tečna hromatografija visokih performansi (HPLC - UV, RF, DAD, RID)*
- *tečna hromatografija sa masenim spektrometrom LC- MS*
- *induktivno spregnuta plazma - optička emisijska spektrometrija (ICP-OES)*
- *atomska apsorpciona spektrofotometrija (AAS)-plamena i sa grafitnom kivetom*
- *spektrofotometrija i spektroskopija (UV, VIS, FTIR)*
- *Analizator žive*
- *TOC analizator*
- *analizatori emisija izduvnih gasova*
- *analizator gasova po VDI za mjerjenje emisije iz velikih ložišta preko 3 MW*
- *γ - spektrometri sa 40% i 38% efikasnosti*
- *α - spektrometar*
- *scintilacioni brojač, scintilaciona sonda*
- *α , β - counter*
- *Oprema za kontrolu Rentgen aparata*
- *Oprema za mjerjenje radona i njegovih potomaka*
- *Oprema za mjerjenje buke i vibracija, mikroklima, temperature, vlažnosti i brzine strujanja vazduha (anemometar)*
- *Automatske monitorske stanice za praćenje kvaliteta vazduha*
- *Automatske stanice za kvalitet riječne i morske vode*
- *Uzorkivači vazduha za određivanje PM 10 i PM 2,5*
- *Uzorkivač vazduha za dioksine*
- *Uzorkivači za vode, sediment, zemljište i opasne materije*

Tokom 15 godina uspješnog poslovanja najznačajniji klijenti CETI su: Elektroprivreda Crne Gore, Kombinat aluminijuma, Termoelektrana Pljevlja, Luka Bar, Brodogradilište Bijela, Kliničko bolnički centar, Agencija za zaštitu životne sredine, Novi Volvox, Cerovo, 16 Februar, Porto Montenegro, Tradeunique, Okov, Nivel i dr.



- *O preduzeću*

Preduzeće „MEDIX“ d.o.o. Podgorica osnovano je u oktobru 1998. godine. Zapošljava 4 radnika koji su u stalnom radnom odnosu, a u honorarnom odnosu ima 15-tak radnika.

- *Djelatnost*

Osnovna djelatnost preduzeća je izrada Elaborata procjene uticaja na životnu sredinu, Strateških procjena uticaja, Studija izvodljivosti i Projekata iz oblasti životne sredine.

U svom dugogodišnjem radu ovo preduzeće je uradilo preko 500 Elaborata procjene uticaja, kao i značajan broj Strateških procjena uticaja i Studija izvodljivosti.

Preduzeće okuplja veliki broj stručnjaka iz različitih oblasti koji za pojedine poslove čine multidisciplinarni tim. Svi angažovani stručnjaci imaju veliko iskustvo u izvršavanju poslova iz oblasti životne sredine, tako da je ovo preduzeće jedno od vodećih u pružanju usluga koje se odnose na sferu njegove djelatnosti.

Osim saradnje sa domaćim institucijama i preduzećima, jedan dio aktivnosti preduzeća je vezan i za saradnju sa inostranim partnerima koji se bave problemima životne sredine.

- *O sposobljenost*

Preduzeće „Medix“ je u svakom pogledu osposobljeno za obavljanje svoje djelatnosti.



COMPANY PROFILE

TARA AEROSPACE AND DEFENCE PRODUCTS A.D.

PYROTECHNICAL PROPULSION CARTRIDGES AND ROCKET ENGINES

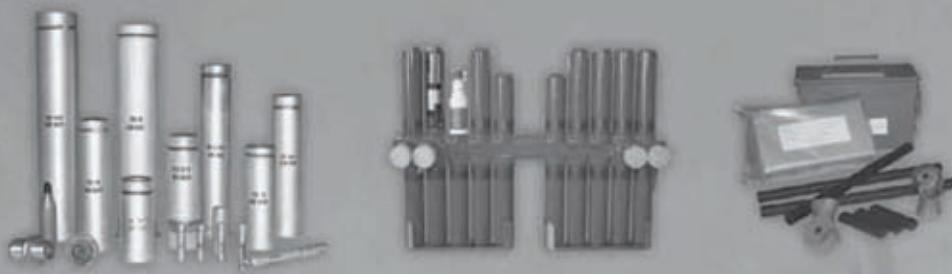
The development and manufacturing of Pyrotechnical Activation and Propulsion Cartridges for Pilot Ejection Seats of Western and former Soviet design is the core expertise of Tara Aerospace and Defence Products A.D.

Certified by Martin Baker and accredited by many Air Forces and Aviation Repair and Maintenance Factories around the world, Tara Aerospace and Defence Products A.D. are acknowledged as the leading independent manufacturer of Pyrotechnical Aviation Cartridges. Being equipped with modern environment testing facilities and by conducting 100% performance and conformity tests, Tara is ensuring OEM specifications and the highest quality of its products.



Pyrotechnical Activation Charges and Rocket Engines are used in the following products:

- Pyrotechnical Activation Charges and Rocket Engines for all Russian design Ejection Seats type KM-1, KM-1M, K36L and K36DM, used in various Aircraft types, MIG21, MIG23, SU25, SU27, MIG29, L39
- Pyrotechnical Activation Charges and Rocket Engines for Martin Baker Ejection Seats Mk-9, Mk-10 and Mk-11 as well as Folland Mk-1 used in Aircraft types, Tornado, F4 Phantom, F5 Tiger, F16 and others as well as Galeb and Super Galeb
- Pyrotechnical Blasting Caps for firing initiation type PPL, PPL-T, PP-9 and for Aircraft Machine Guns type Yak-B and Gsh-23 gun as well as TK-M71 for the D30 Howitzer
- Counter measure Infrared and Anti-Radar Chaff Flares type PPI-26, PPR-26 and PPI-50 and PPR-50
- Signal Flares 38/40mm and Personal Rescue Flare Kits for Pilots and other users
- Anti Riot Ammunition 37/38 and 38/40mm



RESEARCH AND DEVELOPMENT OF PYROTECHNICAL CHARGES

The extensive laboratories and experienced team of Engineers of Tara Aerospace are providing a wide range of possibilities for research and development of almost any type of pyrotechnical charges and rocket engines according to customer requirements and specifications.

FUSE PRODUCTION

Initially established in cooperation with the main Mortar Shell Manufacturer of former Yugoslavia, the company Krusik Valjevo, Tara Aerospace and Defence Products were the main suppliers of Mortar Shell fuses and other Artillery Ammunition and Rocket Fuses that were in production by the Yugoslavian Defence Industries. Also, Tara is manufacturing several types of Fuses for Mines and Fuses for Aviation Bombs.

- Mortar Shell Fuses Calibers 60mm, 80mm, 81mm, 82mm and 120mm
- Hand Grenade Fuses for Hand Grenades type M-75 and ARGES
- Fuses for various types of Mines



DEMILITARIZATION OF OBSOLETE MUNITIONS

Tara Aerospace and Defense Products A.D. is offering the knowledge and safe infrastructure to disassemble all types of Munitions and Rocket engines. Because of the expertise and experience in working with Fuses, Pyrotechnics and Explosives, Tara has recently been selected by the Ministry of Defense of Montenegro under the MONDEM Project as a partner for the professional disassembly and ecologic disposal of various types of obsolete Large Caliber Ammunitions. Further projects and expansion of the demilitarization projects are in preparation.



AVIATION AND AIRCRAFT SERVICES

In cooperation with other Aviation Servicing Companies, Tara Group is offering specific expertise in support of aviation and aircraft maintenance services and components supply. Maintenance, Overhaul and Upgrade of Russian pattern aviation platforms such as:

- MIG-21, MIG-23 MIG-29, SU-25, SU-27, MI-8, MI-17, MI-24, MI-26

Maintenance, Overhaul and Upgrade of Western pattern helicopters and aircrafts such as:

- Bell and Bell Augusta 204, 205, 206, 412
- Rotor Blades from Composite materials for most types of Helicopters
- Overhaul and Supply of Aviation Rockets 57mm S5 and 80mm S8

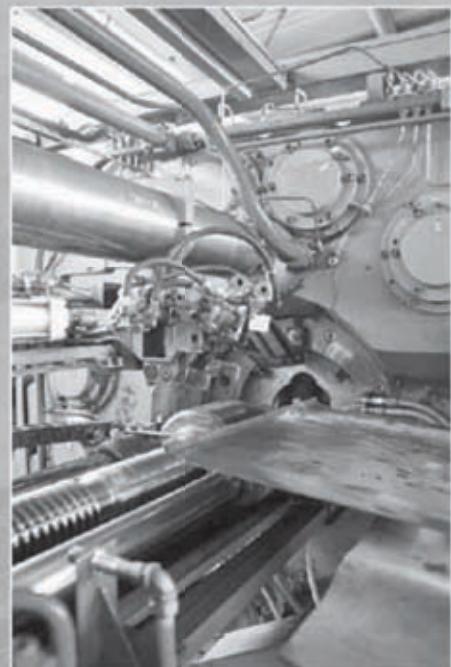
TARA PERFECTION D.O.O.

FIREARM TECHNOLOGY - QUALITY STANDARDS, PRECISION AND DURABILITY

TARA Perfection D.O.O. became a member of the TARA GROUP, situated in the “Wild Beauty” of Montenegro in 2009 and leads the Small Arms Division of the Concern. Although all processes within the GROUP are strongly related, each section concentrates in special fields to guarantee maximum efficiency and autonomy.

Together with Tara Precision Works and Tara Aerospace, the factory can offer complete solutions to modern Law Enforcement and Military customers around the world. The Services of the Group include the production and sale of new products entirely produced in Montenegro, as well as system-upgrades for individual customers and the selection and procurement of related material for our partners.

The development and production of the TM-9 standard size service pistol and the TM-4 assault rifle with a polymer lower receiver and a short-stroke piston system are only the first step towards the introduction of a complete and consistent weapon family, comprising all relevant sizes and calibers in the small-arms world. All future developments and product launches shall follow the vision and company philosophy of employing latest technologies and best materials only to provide new technical solutions to professional users.



TM-9 PISTOL

The TM-9 semi-automatic service pistol combines the latest developments and features of cutting edge firearm technology not only with regards to quality standards, precision and durability but also considering the strictest safety requirements. The extremely hard and anticorrosive slide can be disconnected from the Polymer Lower Receiver without the need to pull the trigger. This can be considered an additional passive safety – just like the pistol's ability to allow consecutive striker actions (real double action) without the need to rack the slide.



State-of-the-art characteristics like anti-corrosive surface protection, high capacity double stag magazines and picatinny rails to mount tactical lights are the answer to the requirements of modern forces. In addition the TM-9 features an ambidextrous magazine release button and a special lanyard connection point to cover all possible scenarios. The DARE-Trigger system allows for a fast and simple training of new users and for a smooth transition for those who come from old conventional systems, in order to reach maximum safety and effectiveness with minimum effort and costs.

TM-4 ASSAULT RIFLE

The TM-4 Assault Rifle represents the ultimate evolution of the battle proven M16 Rifle design for the 21st Century. Without compromise, Tara Perfection has eliminated the weaknesses of the open gas system by designing a highly reliable and adjustable short stroke piston system, a revolutionary steel reinforced high strength polymer lower receiver with fully ambidextrous magazine release and fire selector lever. The cold hammer forged and NITREX coated barrel guarantees the highest accuracy in all weather conditions and is ideal for tropical climates due to its total corrosion protection. This unique process increases the barrel life and reliability of the rifle.



The high number of compatible parts with existing M16A1, M16A2 and M4 Carbines allow Tara Perfection to offer existing users of the M16 Rifle Systems different types of refurbishments and upgrades to improve their current rifles to the unique TM-4 Standard.

The TM-4 Assault Rifle is the ideal choice for Military and Law Enforcement units that require an up-to-date weapon which provides the highest reliability, accuracy and great user facilities.



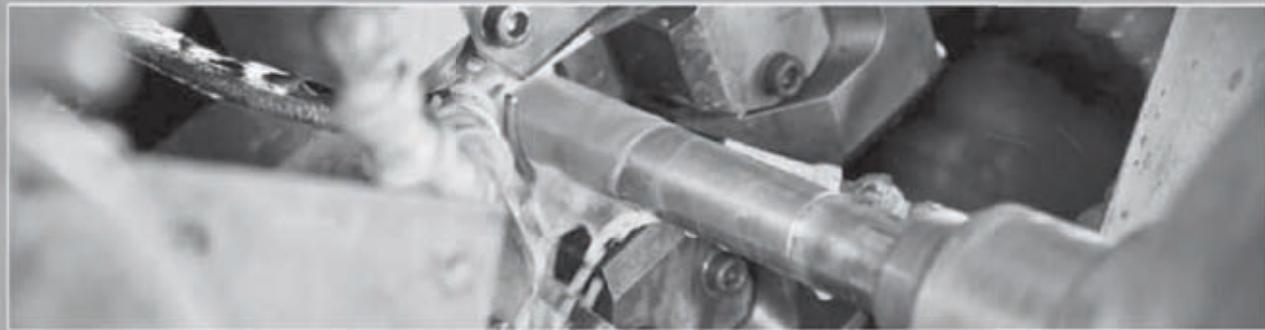
TARA PRECISION WORKS A.D.

PRODUCTION FACILITY

Tara Precision Works is a fully equipped production facility specializing in the execution of all processes required for developing, testing and manufacturing of up-to-date components of all types for the requirements of the Aviation, Aerospace, Defence and Automotive Industry.

The company has highly qualified personnel and production potential for:

- Machining, turning, milling, drilling and grinding
- Hammer forging of barrels for small caliber weapons
- mechanical treatment by deformation
- heat treatment
- surface coating and protection
- testing of products in the chemical laboratory
- testing of products in the test station
- 3d measurements in the metrology laboratory
- Assembly of specialized products.



COLD HAMMER BARREL FORGING

Tara Precision Works A.D. is equipped with a complete production line for Cold Hammer Barrel Forging made by GFM Austria. The process of cold hammer forging produces the best quality barrels featuring highest precision and lifetime. Tara Precision Works offers barrel blanks in most common Calibers to its customers as well as in various steel configurations. Tara Precision Works can offer machining and heat treatment of the barrels to individual customer requirements.

- Maximum hammering diameter of Barrel Blank up to 40mm
- Maximum Length after hammering is 580mm
- Barrel Steels available in Military Standards and Stainless Steel
- Caliber Range for all common Rifle, Handgun and Automatic Weapons

WEAPON SUPPORT AND MAINTENANCE SERVICES

Tara Precision works is offering a wide range of manufacturing capacities for manufacturing of specialized accessories and equipment for all types of armament. Based on customer requirements and focused on ultimate serviceability and quality, Tara is providing services in Design Studies, Rapid Prototyping, Testing Prototypes and Serial Production of almost any type of mechanical components.

- Rotating Vehicle Mounts for Light and Heavy Machine Guns such as PKM, MAG-58, M60, M2HB, NSV, DSHK
- Tripods for Heavy Machine Guns DSHK and NSV
- Optical Sight Mounts for Medium and Heavy Machine Guns and Mechanical Mortar Goniometers.



SURFACE TREATMENT, REFURBISHING AND REMANUFACTURING

Tara Precision Works is equipped with full line of surface treatment equipment for cleaning, preparation, coating and galvanization of ferrous and non ferrous steels. Phosphating (iron and steel), Chrome-plating (aluminum and Al alloys), Chrome-plating (copper and brass), Anodic oxidizing (aluminum and Al alloys), Cadmium-plating, Zinc-plating, Silver-plating, Tin-coating, Nickel-plating, Copper cyaniding, Hard chrome-plating, Shellac-varnishing, Burnishing.

Tara Precision Works is providing services for complete repair, refurbishment and remanufacturing for all types of Light and Medium Armament. Scope of work includes:

- Disassembly
- Cleaning, Sand Blasting, Surface polishing etc.
- Measuring and control of individual parts
- Surface coating
- Assembly and lubricating
- Function testing and certification
- Packing and storage services



TEST STATIONS

The Test Station is equipped with the most modern test equipment for environmental tests of various armaments and defence equipment and other products at all development stages:

- Chemical tests laboratory is authorized to issue test certificates (attests) certifying quality of surface protection based on tests conducted in salt and humidity test chambers
- Four-channel oscilloscope - NICOLET
- Vibrator with a random vibrations setting and control device – RANDOM
- Pressure and thrust test bench
- Conditioning chamber
- Jolting test equipment (verifying transport safety according to Russian and US standards)
- Transport Safety Testing station to NATO and Russian Standards
- Quality Control Standards (ISO 9001, ISO 1474)

TARA GROUP

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FOUNDATION & PEAK OF PRODUCTION

Founded in 1984 and build up until 1986 the Factory was established under the name "4th Novembar" by the Ministry of Defense of Former Yugoslavia. The mission of 4th Novembar was manufacturing and developing of mechanical fuses for Mortar Shells and Artillery Rockets in cooperation with the Krusik factory in Valjevo, Serbia as well as manufacturing all types of Pyrotechnical Propulsion Cartridges, Pyrotechnical Activation Charges and Rocket Engines for Ejection Seats for Soviet Military Aircrafts and Helicopters as well as Pyrocartridges and Rockets Engines for the British Martin Baker Ejection seats.

During the peak of the production in the late 1980's and early 1990's the company was manufacturing up to 500'000 mortar fuses per year and the number of employees was over 500. 4th Novembar was the largest fuse and pyrotechnics manufacturer of the former Yugoslav Republic and cooperating strongly with all the other Military Factories.

PRIVATIZATION AND NEW TECHNOLOGIES

The hard years of the embargo times during the Balkan Conflicts as well as the lack of International co-operations has caused the bankruptcy of the company in the beginning of 2001. During the years 2002 to 2007 the company was held alive with subsidies from the Montenegro Government, who in due course came to the decision that only a privatization could bring the company back to life and would ensure the re-structuring of the company and allow fresh capital and new technologies to flow into the company.

On July 31st, 2007 the Swiss registered company BT International Ltd. won the tender for privatization and took over the operational management of the factories on December 20th, 2007. In the process of privatization, the company has been renamed and divided into two companies, Tara Precision Works A.D. which is the heart of the company with all the metal processing and treatment plant and, Tara Aerospace and Defence Products A.D. which is covering the military part of the factory and is responsible for assembly and marketing of the final products. New production lines and machinery have been installed, together with a team of highly qualified engineers to operate them.





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