

Oznaka poročila: ARRS-RPROJ-ZP-2012/29

ZAKLJUČNO POROČILO O REZULTATIH RAZISKOVALNEGA PROJEKTA

A. PODATKI O RAZISKOVALNEM PROJEKTU

1. Osnovni podatki o raziskovalnem projektu

Šifra projekta	Z2-2298
Naslov projekta	Karakterizacija tribokorozijskih procesov
Vodja projekta	22315 Tadeja Kosec
Tip projekta	Zt Podoktorski projekt - temeljni
Obseg raziskovalnih ur	3400
Cenovni razred	B
Trajanje projekta	05.2009 - 04.2011
Nosilna raziskovalna organizacija	1502 Zavod za gradbeništvo Slovenije
Raziskovalne organizacije - soizvajalke	
Raziskovalno področje po šifrantu ARRS	2 TEHNIKA 2.04 Materiali 2.04.02 Kovinski materiali
Družbeno-ekonomski cilj	13.02 Tehnološke vede - RiR financiran iz drugih virov (ne iz SUF)

2. Raziskovalno področje po šifrantu FOS¹

Šifra	2.05
- Veda	2 Tehniške in tehnološke vede
- Področje	2.05 Materiali

B. REZULTATI IN DOSEŽKI RAZISKOVALNEGA PROJEKTA

3. Povzetek projekta²

SLO

Pri relativnem gibanju kontaktnih površin je tribološki kontakt zelo zapleten proces, saj vključuje simultani proces trenja, deformacije in obrabe. Meja med mehanizmi na makro in mikro nivoju je težko določljiva, saj so med seboj prepleteni in povezani. V kolikor je pri omenjenih procesih prisoten

elektrolit (npr. oksidirano mazivo, kondenz, tkivo, slina) se mehanski procesi obrabe kombinirajo s korozijskimi. V splošnem omenjena kombinacija ni vsota temveč sinergija obeh vrst procesov, zato so vplivi posameznih parametrov pri skupnih tribokorozijskih procesih izrazito nelinearni in nestacionarni. Določene zakonitosti pri uporabi posameznih materialov v izbranih okoljih in določenih obremenitvah so sicer poznane, vendar je povezovanje znanj s področja tribologije in korozije materialov še vedno relativno neraziskano področje. Glavna vzroka za to sta težavnost simuliranja realnih pogojev in nestacionarnost procesov. To pomeni, da je uporabnost konvencionalnih elektrokemijskih tehnik (potenciodinamska polarizacija, elektrokemijska impedančna spektroskopija), ki so sicer primerne za napoved splošne korozijske obstojnosti, pri triboloških procesih delno omejena. Zato je ovrednotenje elektrokemijskega vpliva pri sinergijski kombinaciji z mehanskimi procesi problematično, posledično pa je nezanesljivo tudi modeliranje teh procesov.

Glavni cilj raziskovalnega projekta je karakterizacija osnovnih tribokorozijskih procesov, oziroma študij medsebojnega vplivanja mehanskih in elektrokemijskih procesov. V ta namen smo nadgradili tranzientne elektrokemijske tehnike (elektrokemijski šum, metoda merjenja delnih tokov z mikroelektrodami), ki smo jih razvili pri študiju drugih lokalnih oblik korozije (napetostno-korozijsko pokanje, špranjska korozija). Z omenjenimi metodami lahko spremljamo časovni razvoj in porazdelitev korozijskih tokov med različnimi stopnjami procesa obrabe. Pri izvedbi eksperimentov in analizi mehanskih procesov smo sodelovali s Centrom za tribologijo in tehnično diagnostiko, Institutom za materiale in tehnologijo ter institutom Jožef Stefan. Raziskave smo izvajali na izbranih materialih, katerih trajnost je problematična: pri pogonskih agregatih in procesni industriji (orodna jekla, siva litina) ter v biomedicini (nerjavna jekla, titanove zlitine). V okviru projekta smo določili osnovne parametre in njihov vpliv na tribokorozijske procese izbranih materialov pri tipičnih pogojih okolja (mehanska obremenitev, elektrolit). Rezultat projekta je tako nabor primernih tehnik, ki lahko služijo kot orodje za napoved tribokorozijskih lastnosti določenih materialov pri realnih problemih: npr. uporaba biogoriv, evalvacija učinkovitosti inhibitorjev, trajnost različnih vrst implantantov.

ANG

Tribological processes, which occur during the relative motion of contact surfaces, present a complex combination of friction, deformation and wear. It is difficult to differentiate between these processes on a micro and macro scale since they are interconnected. Mechanical processes can induce corrosion in the presence of a corrosive environment, i.e. an electrolyte such as oxidative lubricants, condensation, tissues, and saliva. Mechanical and corrosion processes cannot be simply combined as their sum, but as their synergy, which makes the effects of non-linear and non-stationary tribo-corrosion processes difficult to distinguish. The interdependence of mechanical and electrochemical mechanisms has recently received increased attention due to the fact that this is a relatively unknown scientific field. The main reason for this is the complexity of the simulation of the real conditions and the non-stationary processes. Conventional electrochemical techniques (such as potentiodynamic polarization and electrochemical impedance spectroscopy) are a good tool for predicting corrosion processes, but are not very useful in the prediction of tribocorrosion. The evaluation of electrochemical mechanisms in synergy with mechanical processes can be difficult, including the modelling of the processes. The main goal of the

research project is the characterization of the basic tribocorrosion processes, and the study of the corresponding mechanical and electrochemical effects. An upgrade of the transient techniques (electrochemical noise, the measurement of partial currents with microelectrodes) was performed. These techniques have been developed in our laboratory in connection with the study of some local corrosion phenomena (stress corrosion cracking and crevice corrosion). The time effect and corrosion currents were monitored during different stages of wear. Some experiments were performed, and mechanical processes analysed, in collaboration with the Centre for Tribology and Technical Diagnostics, Institute for metals and Technologies and Institute Jožef Stefan.

The research was carried out on different materials that show problematic durability, such as engine fuel generators, as well as in process technology (steels, grey castings) and biomedicine (stainless steels, titanium alloys). Theoretical modelling together with experiments under well-controlled electrochemical and mechanical conditions provides an insight into the interactions of the different parameters (mechanical forces, electrolytes) which govern the behaviour of tribocorrosion systems. Some of the results was interpreted in collaboration with partners from other countries. Thus, the result of the proposed project is the selection of techniques as tools for the prediction of the tribocorrosion behaviour of certain materials in real systems, e.g. the use of biodiesel, the evaluation of corrosion inhibitors, and the durability of different types of implants.

4. Poročilo o realizaciji predloženega programa dela na raziskovalnem projektu³

V okviru postdoktorskega projekta z naslovom »Karakterizacija tribokorozijskih procesov« sem nadaljevala delo na vseh predlaganih delovnih področjih v projektu. Med izvajanjem podoktorskega projekta sem skladno s predlaganimi aktivnostmi znotraj 1., 2., 3. in 4. sklopa uspešno sledila ciljem projekta: meritve sem izvajala na tribokorozijskem elektrokemijskem sistemu za meritve tribokorozijskih procesov, vpeljevala in preskušala sem konvencionalne in nove metode in načine za tribokorozijsko preskušanje ter karakterizirala tako mehanske kot korozijske lastnosti obrabljenih površin. Poseben poudarek raziskovalnega projekta je bil na četrtem predlaganem sklopu Uporaba razvite metodologije za študij izbranih sistemov.

Iz prvega delovnega sklopa Izdelava tribokorozijske naprave sem uporabila vse potrebne parametre za nadaljnjo študijo vpliva tribološke obrabe na elektrokemijski odziv materiala v izbranem korozijskem okolju.

Prav tako sem novo pridobljena znanja iz drugega dela delovnega sklopa z naslovom »Razvoj metodologije za karakterizacijo tribokorozijskih procesov« uporabila za študij tribokorozijskih vplivov na izbranih primerih.

Poleg tribokorozijskih/tribo-elektrokemijskih preiskav izbranih materialov v korozijskem okolju sem izvajala tudi referenčne meritve tudi na materialih v enakem izbranem korozijskem okolju samo z elektrokemijskim vplivom. Poznavanje elektrokemijskega vpliva ter elektrokemijskih lastnosti na materialu, ki se pod tribološko obrabo obnaša drugače, namreč omogoča primerjavo lastnosti ter njun medsebojni vpliv. Med procesom obrabe sem v korozivnem elektrolitu na kovinskih materialih študirala elektrokemijski odziv z uporabo tako konvencionalnih elektrokemijskih tehnik in elektrokemijski šum kot novo predlagano tehniko za spremljanje tribokorozijskih procesov.

Določevala sem naravo procesov med obrabo; merjen signal je vsota dogajanj na stacionarnem delu delovne elektrode kot tudi odziva na obrabljenem delu. Dobljene rezultate sem primerjala s podobnimi sistemi, ki so že predstavljeni v različnih objavah.

Z obravnavanimi elektrokemijskimi tehnikami ter izborom primernih tehnik za optimalno tribokorozijsko napoved vedenja materialov v izbranih sistemih sem uspešno proučila različne načine za prepoznavanje tribokorozijskih procesov.

Aktivnosti znotraj tretjega delovnega sklopa »Karakterizacija površine, morfološke in mehanske lastnosti« sem izvajala preko vseh faz projekta in raziskav v trajanju projekta v letih 2009–2011. Na tribokorozijskih in referenčnih vzorcih sem pred in po obrabi karakterizirala in določila njihove lastnosti: pregledala sem korozijsko stanje površine, njene morfološke in mehanske lastnosti. Merila sem trdoto in hrapavost pred in po obrabi. S profilometrom sem določila profil obrabne sledi in iz nje preračunala hitrost obrabe. Prav tako sem površino delovne elektrode-kovinskega materiala vizuelno pregledala pod optičnim mikroskopom ter konfokalnim mikroskopom. Primerjala sem oblike profilov, pridobljenih z dvema različnima tehnikami in sicer klasičnim profilometrom (kontaktni način) ter določanjem profila s konfokalnim mikroskopom (nekontaktni način). Študirala sem prednosti in slabosti posameznih tehnik, določila hitrost obrabe in za vsako metodo ocenila velikost napake pri določanju hitrosti obrabe.

S pomočjo elektronskega mikroskopa sem pri večjih povečavah določila obliko korozijskih produktov, mesta, kjer so se korozijski produkti odlagali in z analizo EDS določila njihovo sestavo. Podrobneje smo z elektronskim mikroskopom lahko določili širino obrabne sledi, vključke, ki nastanejo v obrabni sledi, opazovali smo deponiranje obrabljene plasti (Third Body Effect).

Prav tako smo merili trdoto na izbranih materialih zunaj in v obrabni sledi ter na vključkih v obrabni sledi. Študirali smo vpliv sile obrabe na obrabno pot, obliko ter hitrost obrabe. Na Ramanskem mikroskopu pa sem (laser 632,8 nm) uspešno detektirala različne oblike oksidov na obrabni sledi, ob sledi ter na različno oddaljenih območjih ob sledi. Tudi Ramanska spektroskopija je novost pri karakterizaciji različnih korozijskih produktov po tribokorozijskem preskušanju.

V drugem letu podoktorskega projekta je bil poudarek na raziskovalnih aktivnostih znotraj delovnega sklopa »Uporaba razvite metodologije za študij izbranih primerov«.

Za študijo smo izbrali tri različne, tehnološko in biomedicinsko pomembne materiale, in sicer: nerjavno jeklo tipa AISI 316 L, Stelitno zlitino Stellite 6-CoCrNiW zlitino ter nikelj-titanovo zlitino, ki se uporablja v biomedicinske namene- NiTi zlitino. Tako nerjavno jeklo kot stelitne zlitine spadajo v pasivirajoče materiale. Posebej stelliti so bili razviti kot materiali z izrazito majhno obrabo. Nerjavno jeklo AISI 316 L in Stellite 6 zlitino sem študirala v 0,5 M raztopini H_2SO_4 , medtem ko je bil za korozijski medij NiTinol zlitine izbrana umetna slina, ki posnema naravno slino. Tribokorozijski sistemi in aktivnosti so bile naslednje:

- elektrokemijsko testiranje jekla 316 L in Stellite 6 zlitine in dentalnih žic ter NiTinol folije
- elektrokemijska impedančna spektroskopija jekla 316 L in Stellite 6 zlitine ter dentalnih žic in NiTi folije v simulirani raztopini slin (simulirana raztopina

sline)

- mikrostruktura izbranih kovinskih materialov -vzdolžno in prečno
- tribološki eksperimenti za ugotavljanje koeficienta trenja in sile trenja
- triboelektrokemijski eksperimenti pri različnih obremenitvah (1 N, 2 N, 5 N in 10 N), hitrostih obrabe, poteh obrabe.
- konfokalna mikroskopija, iz katere sem pridobili podatek o hitrosti obrabe (suho-tribološki kontakt, mokro-tribokemijska obraba). Iz teh podatkov smo ocenjevali vrsto in hitrost obrabe s profilometrom (kontaktni način) ter primerjala obe tehniki.

Z aktivnostmi v omenjenem sklopu sem dosegla cilje kot so poznavanje tehnološko zanimivih materialov, določitev specifičnih korozijskih razmer za tribokorozijsko preskušanje ter reševanje industrijskih izzivov med samim tehnološkim procesom pridobivanja končnega produkta. Tako sem z primernim pristopom in izborom pravih elektrokemijskih tehnik optimirala metode za tribokorozijsko preskušanje, ki bo z novimi znanji pripomoglo k uspešnejšem dizajniranju lastnosti materialov, ki so podvrženi tako koroziji kot obrabi.

V objavo smo poslali izvirni znanstveni članek o vplivih mikrostrukture tehnološko izredno pomembnega materiala-zlitine na osnovi niklja in titana-Nitinola. Obravnavane so bile tako tribološke, elektrokemijske in tribokorozijske lastnosti preiskovane zlitine v pravi in simulirani raztopini sline. Poudariti je pomembno tudi sodelovanje z Medicinsko fakulteto UL-odsek za dentalno medicino. Z njimi prav tako pripravljamo strokovni članek o vzrokih porušitve na NiTiNol dentalnih žicah.

V sodelovanju z Institutom Jožef Stefan-Odsekom za tanke plasti smo prijavi projekt o študiji in mehanizmi korozijskega obnašanja biokompatibilnih prevlek na kovinskih materialih. Študija vključuje tribokorozijsko preskušanje in vrednotenje. V okviru sodelovanja smo opravili del preiskav na DLC (Diamond Like carbon coating) prevlekah na različnih kovinskih podlagah v Hankovi raztopini. Prav tako smo preskušali možnost detekcije vključkov in napak na prevlekah (kjer se začne in pospešuje korozija) na mikro X-žarkovni tomografiji.

Podoktorski projekt je tako finančno omogočil odpiranje novega področja raziskav, kjer se prepletajo različne vede, tako kemija, strojništvo kot fizika. Z novim znanjem in rezultati projekta smo se uspešno predstavili tudi industrijskim partnerjem. Tako smo v letu 2011 po zaključku projekta že načrtovali nov skupni manjši aplikativni projekt, ki ga bo v četrtinskem deležu sofinancirala Hidria-Rotomatika. Skupaj z njimi ter Institutom za materiale in tehnologije smo prijavi aplikativni raziskovalni projekt »Tribokorozija: raziskave mehanizmov, materialov in prenosa v prakso«.

Na področju tribokorozijskih raziskav obrabe dentalnih žic smo uspešno sodelovali z Medicinsko fakulteto. Na področju medicinskih ved smo tako prijavi aplikativni raziskovalni projekt z naslovom »Učinkovitost ortodontske obravnave z nesnemnimi ortodontskimi aparati pri različnih površinskih spremembah njihovih kovinskih delov«.

5.Ocena stopnje realizacije programa dela na raziskovalnem in zastavljenih raziskovalnih ciljev⁴

Predlagani cilji v okviru postdoktorskega projekta »Karakterizacija tribokorozijskih procesov« so bili štiri, in sicer: Izdelava tribokorozijske naprave, Razvoj metodologije za karakterizacijo tribokorozijskih procesov,

Karakterizacija površine, morfoloških in mehanskih lastnosti ter Uporaba razvite metodologije za študij izbranih procesov.

V obsegu prvega sklopa so bile realizirane vse potrebne aktivnosti za začetek uporabe tribokorozijskega sistema kot osnovnega orodja za karakterizacijo tribokorozijskega sistema. Tribokorozijski sistem je dobro razvit in je uporabljen za različne tribološke in tribokorozijske študije.

V okviru zastavljenih ciljev znotraj drugega sklopa je bilo opravljeno večji del nalog. Različne elektrokemijske metode in meritve sem v drugem letu podoktorskega projekta izvajala na drugih različnih izbranih kovinskih materialih. Izvedli smo tudi vrsto preiskav na sklopljenih elektrodnih mrežah CMEA (*angl.* Coupled Multi Array Electrodes). Na sistemu CMEA iz nerjavnega jekla smo v kloridni raztopini optimizirali preiskave za detekcijo tokovnih in napetostnih odzivov ter optimizirali naprave za detekcijo, da smo pridobili ustrezno čistost signala. Ugotovili smo, da lahko uspešno spremljamo depasivacijo in ponovno repasivacijo izbranih kovinskih materialov. Preiskave na mreži elektrod so zelo pomembne, saj podobnih preiskav v svetu še ni. V letu 2012 bomo poskušali objaviti rezultate preskušanj v reviji s faktorjem vpliva- Wear ali Tribology International.

V tretjem sklopu sem uporabila številne metode za karakterizacijo in pregled lastnosti materialov pred in po obrabi v korozijskem sistemu. V okviru poteka projekta sem uporabljala različne metode za spektroskopsko analizo kovinskih površin, kot je SEM/EDS analiza, kontaktna profilometrija za oceno obrabe ter Ramanska spektroskopija. Dodatno sem vpeljala pregled obrabljene površine s konfokalnim mikroskopom in ugotovila, da nam nudi številne dodatne informacije, ki so na tribokorozijskem področju novost.

Poudarek aktivnosti temeljnega podoktorskega projekta je bil na sklopu «Uporaba razvite metodologije za študij izbranih sistemov». V okviru tega sklopa so bile pridobljene pomembne tribokorozijske študije. Pridobljeno znanje in ugotovitve realnih tribokorozijskih primerov smo predstavili v izvirnih znanstvenih prispevkih.

Znanstveni in strokovni prispevki projekta Karakterizacija tribokorozijskega preskušanja so bili predstavljeni na dveh mednarodnih konferencah in enem mednarodnem simpoziju, ter članek z naslovom The tribocorrosion behaviour of NiTi alloy v reviji s faktorjem vpliva (Wear-priponka1). Rezultati in osnove tribokorozijskega preskušanja bodo objavljeni tudi kot strokovni članek v reviji Vakuumist (priponka2). Opravljeno je bilo tudi diplomsko delo z naslovom Vpliv mikrostrukture na korozijo nikljevih zlitin pod mehansko obremenitvijo.

6. Utemeljitev morebitnih sprememb programa raziskovalnega projekta oziroma sprememb, povečanja ali zmanjšanja sestave projektne skupine⁵

Ni sprememb v izvajanju programa projekta.

7. Najpomembnejši znanstveni rezultati projektne skupine⁶

	Znanstveni dosežek		
1.	COBISS ID	XX	Vir: vpis v poročilo
	Naslov	SLO	The tribocorrosion behaviour of NiTi alloy
		ANG	Tribokorozijske lastnosti Niti zlitin
			Nikelj titanove zlitine so znane po dobri korozijski odpornosti. Posebej

Opis	SLO	zaradi lastnosti oblikovnega spomina se uporabljajo tudi v biomedicinske namene. Kljub temu pa je v nekaterih primerih prisotna luknjičasta in špranjska korozija. NiTi žice so se v uporabi v dentalni praksi pokazale kot problematične, saj mnogokrat prihaja do pretrgov zaradi različnih vrst obrabnih procesov. Predvidevamo, da kljub dobrim elektrokemijskim in hkrati korozijskim lastnostim zlitin na osnovi titana mikrostruktura vpliva na kemijske kot tudi na mehanske lastnosti. Preiskave smo izvedli na dveh mikrostrukturno različnih vzorcih in sicer na dentalni žici ter na pločevini iz zlitine NiTi, v dobavljenem in sveže brušenem stanju. Elektrokemijske preiskave so bile merjene v raztopini umetne sline, dodatne preiskave materialov so bile opravljene na tribokorozimetru. Mikrostrukturne lastnosti so bile pregledane v prečnem ter vzdolžnem preseku pločevine ter dentalne žice. Obrabne raze so bile analizirane s SEM/EDS analizo, profilometrom ter merilcem trdote. Rezultati elektrokemijskih raziskav so pokazali, da vzorci pločevine in žice zlitine NiTi brez oksidne plasti kažejo podobne korozijske lastnosti. Večje razlike v korozijski odpornosti so bile vidne na vzorcih z oksidno plastjo. Tribokorozijske preiskave so pokazale, da je celotna obraba zlitine NiTi večja, če sta kombinirani korozijska in mehanska obraba. Večje obremenitve vodijo do večjih sprememb na pasivni površini in večje obrabe materiala. Ugotovili smo, da so pri večji obremenitvi v obrabno razo vključeni večji obrabni delci in da trdota materiala po obrabi poveča.	
	ANG	Nickel titanium alloys are known for their good corrosion resistance. NiTi alloy is due to its shape memory properties particularly used in biomedical application. Their corrosion properties are satisfactory (sufficient), but in some circumstances they suffer from pitting and crevice corrosion. Since dental NiTi archwires experience severe failures in applications it is assumed that their performance is affected also by microstructure. Beside corrosion the wear resistance of this alloy is of critical concern in many applications. In the present work, two types of NiTi alloy samples were investigated, NiTi plate and NiTi dental wire with and without surface oxide. The electrochemical investigation was conducted in artificial saliva and was proved by the use of tribocorrosimeter. Microstructural characteristics were studied in cross section and longitudinal direction. The wear scare was investigated by the use of SEM/EDS analysis and profilometer. The hardness of the wear scar was followed as well. The results of electrochemical investigation showed that the dental alloy and NiTi plate without surface oxide exhibit very similar corrosion properties. The variation in corrosion performance in artificial saliva was bigger at specimens covered with surface oxide films. Tribocorrosion studies showed that the total wear of the NiTi alloy is greater when corrosion is combined by the wear. The bigger wear loads lead to greater changes in passive film and wear scar. Greater loads resulted in bigger inclusions in the wear. Also, the hardness in the wear scar is increased after applying the load. It can be concluded that microstructure of the investigated NiTi sample has effect on electrochemical and tribocorrosion properties of the samples as well.	
	Objavljeno v	Wear	
Tipologija	1.01 Izvirni znanstveni članek		
2.	COBISS ID	1808231	Vir: vpis v poročilo
Opis	Naslov	SLO	Vpliv mikrostrukture na tribokorozijske lastnosti dentalnih zlitin
		ANG	The effect of microstructure on tribocorrosion properties of dental alloys
		SLO	Različni mikrostrukturni vzorci NiTi zlitine imajo različne elektrokemijske in triboelektrokemijske lastnosti. Dentalne NiTi žice z oksidno plastjo imajo najslabše lastnosti. Tribokorozijske preiskave so pokazale, da se način obrabe močno spreminja glede na obrabno silo.. Korozijski potencial se med drgnjenjem zniža. Obrabna raza pri tribološkemv raztopini vsebuje manj vključkov, kot pri suhi tribološki obrabi, hkrati je obraba v kraztopini slin-korozijski medij-večja.

	ANG	Different NiTi samples with different morphological properties have also different electrochemical properties. Dental NiTi wires with oxide film exhibits worse electrochemical behaviour. Tribochemical experiments have shown that the wear regime varies at different applied loads. Corrosion potential is decreased the most at the higher applied force. Wear track after triboelectrochemical wear has lower number of inclusions whereas the wear rate is higher then after dry tribological wear.
Objavljeno v		Developing solutions for the global challenge : book of abstracts : EUROCORR 2011, The European Corrosion Congress, 4-8 September 2011, Stockholm, Sweden, (European federation of corrosion, event no. 325). [S. l.: s. n.], 2011, str. 654. [COBISS.SI-ID 1808231]
Tipologija	1.08	Objavljeni znanstveni prispevek na konferenci

8. Najpomembnejši družbeno-ekonomsko relevantni rezultati projektne skupine²

	Družbenoekonomsko relevantni dosežki		
1.	COBISS ID	35703301	Vir: COBISS.SI
	Naslov	SLO	Vpliv mikrostrukture na korozijo nikljevih zlitin pod mehansko obremenitvijo
		ANG	The effect of microstructure on tribocorrosion properties of nickel alloys
	Opis	SLO	Z novo pridoblejnim znanjem na področju tribokorozije smo omogočili prenos znanja iz raziskovalne institucije do univerze in s tem omogočili širitev znanja na področju tribokorozije. Izredno kvalitetno diplomsko delo bo omogočilo razširitev programa korozije in elektrokemije na dodiplomskem in podiplomskem študiju.
		ANG	With the newly achieved knowledge on the tribocorrosion field, the knowledge transfer was enabled from research institution onto University level. High quality diploma work will enable to widen the program of corrosion and electrochemistry at for university students as well as post graduate students.
	Šifra	D.10 Pedagoško delo	
	Objavljeno v	[P. Močnik]; 2011; 56 f.; Avtorji / Authors: Močnik Petra	
	Tipologija	2.11 Diplomsko delo	
2.	COBISS ID	1581671	Vir: COBISS.SI
	Naslov	SLO	Projektna naloga: ocena poškodb na ceveh
		ANG	Project task: Evaluation of damages on pipelines
	Opis	SLO	V projektni nalogi smo pregledali, analizirali in opisali korozijske poškodbe, ki so bile ugotovljene v NEK (jederska elektrarna Krško) na ceveh uparjalnika. Izvedene so bile kompleksne metalografske in mikroskopske preiskave dostavljenih vzorcev. Izvedene so bile tudi elektrokemijske preiskave na izbranih materialih. V rezultatih raziskave smo natančno podal vplive in dejavnike za nastanek korozijskih poškodb ter način nastanka in potek korozijskih poškodb. Na osnovi elektrokemijskih meritev pa so podane ocene za občutljivost preiskovanih materialov v izbranem korozijskem okolju.
		ANG	In the project corrosion damages observed on pressuriser in NEK (Nuclear Power Plant Krško) were inspected, analyzed and evaluated. Complex metallographic and microscopic studies were realized on received specimens. Additionally, electrochemical research on selected materials was performed. In the results the influences and parameters for inspected corrosion damages and the ways of intimation and growth are described.

		On the basis of electrochemical measurements performed on selected materials the susceptibility of those materials to corrosion in selected environment was estimated.
	Šifra	D.01 Vodenje/koordiniranje (mednarodnih in domačih) projektov
	Objavljeno v	Zavod za gradbeništvo Slovenije; 2009; 64 str.; Avtorji / Authors: Kosec Tadeja, Legat Andraž, Kovač Jaka, Kuhar Viljem, Gartner Nina, Švara Erika, Smirić Sanja
	Tipologija	2.13 Elaborat, predštudija, študija
3.	COBISS ID	1834599 Vir: COBISS.SI
	Naslov	<i>SLO</i> Trajnost materialov vodovodnih sistemov v stavbah
		<i>ANG</i> Durability of materials i drinking water systems in buildings
	Opis	<i>SLO</i> Izkušnje korozijskih inspekcij so narekivale potrebo po ozaveščanju javnosti o prepotrebem sodelovanju strokovnjakov in znanstvenikov iz ožjega korozijskega področja in uporabnikov: zdravstveno varstvo in ministrstvo za zdravje. Opisano področje so napeljuje za distribucijo pitne vode. Zaradi pomanjkanja znanja je pogosto poroblem uporabe pravih materialov, postopkov dezinfekcije za ohranjanje neoporečnosti pitne vode. Ozaveščamo in povezujemo različne institucije, ki bi omogočile zagotavljanje zdravja in dvig kvalitete življenja.
		<i>ANG</i> Corrosion inspection experiences have led to the need to inform public for the need to use know-how and knowledge in the applied field:drinking water system. The lack of corrosion knowledge in the field highly affects people's health and quality of living. Materialcs used in drinking water system are usually not appropriate according to disinfection procedures. The awareness of the collaboration of scientific laboratories, Government and health system is emphasized.
	Šifra	F.18 Posredovanje novih znanj neposrednim uporabnikom (seminarji, forumi, konference)
	Objavljeno v	Tehnis; Gradbenik; 2011; Letn. 15, št. 11; str. 52-54; Avtorji / Authors: Bajt Leban Mirjam, Kuhar Viljem, Kosec Tadeja, Legat Andraž
	Tipologija	1.04 Strokovni članek
4.	COBISS ID	YY Vir: vpis v poročilo
	Naslov	<i>SLO</i> Aplikativni projekt Korozija bakra v bentonitu
		<i>ANG</i> Applicative project Corrosion of copper in bentonite
	Opis	<i>SLO</i> Aplikativni projekt je del raziskav povezanih z odlagališcem izrabljenega jedrskega goriva skupaj s švedskim partnerjem.Tri leta in pol smo spremljali korozijsko hitrost čistega bakra z namestitvijo električnih uporovnih senzorjev v bentonitu, nasičenim s slano podtalnico. V bentonitu smo dokazali oksidativne pogoje. Naredili smo vrsto meritev elektrokemijske impedančne spktroskopije kot tudi meritve zmanjševanja debeline na uporovnih senzorjih iz bakra. EIS meritve so pokazale postopno zmanjševanje korozijske hitrosti bakra, skladno z pričakovanji. Po treh letih in pol izpostave bakrenih senzorjev bentonitu smo izmerili korozijske hitrosti med 0.4 do 0.7 µm/leto, vrednosti pa so primerljive z merjenjem izgube debeline, kjer je bila korozijska hitrost izmerjena 1.0 µm/leto.
		<i>ANG</i> Applied project is research project on spent nuclear fuel nuclear waste management for disposal in Sweden. Corrosion of copper has been followed by the use of copper electrical resistance sensors that were placed in bentonite for 3 years and a half. Oxic conditions were confirmed by continuous monitoring. Different measurement techniques were applied: thickness measurements and electrochemical impedance spectroscopy. Both measurements showed the decreasing corrosion rate of copper ER sensors. After exposure the

		corrosion rates estimated by EIS are 0.4-0.7 micro M/year and around 1 micoM/year with thickness measurement.
Šifra	F.17	Prenos obstoječih tehnologij, znanj, metod in postopkov v prakso
Objavljeno v	Electrochimica Acta	
Tipologija	1.01	Izvirni znanstveni članek

9. Drugi pomembni rezultati projektne skupine⁸

Predstavljamo še druge vrste delovanja vodje projekta:

OTMAČIĆ ĆURKOVIĆ, Helena, KOSEC, Tadeja, LEGAT, Andraž, STUPNIŠEK LISAC, Ema. Improvement of corrosion stability of patinated bronze. Corros. eng. sci. technol., 2010, vol. 45, no. 5, str. 327-333, ilustr. [COBISS.SI-ID 1700967]
 KOSEC, Tadeja, OTMAČIĆ ĆURKOVIĆ, Helena, LEGAT, Andraž. Investigation of the corrosion protection of chemically and electrochemically formed patinas on recent bronze. Electrochim. acta. 2010, vol. 56, issue 2, str. 722-731, [COBISS.SI-ID 1700711]
 MILOŠEV, Ingrid, KOSEC, Tadeja, BELE, Marjan. The formation of hydrophobic and corrosion resistant surfaces on copper and bronze by treatment in myristic acid. J. Appl. Electrochem., jul. 2010, vol. 40, no. 7, str. 1317-1323, [COBISS.SI-ID 1665639]
 BAJT LEBAN, Mirjam, KUCHAR, Viljem, KOSEC, Tadeja, LEGAT, Andraž. Corrosion investigation of the Prešeren monument in Ljubljana = Korozijska preiskava Prešernovega spomenika v Ljubljani. Mater. tehnol., 2010, letn. 44, št. 5, str. 265-269 [COBISS.SI-ID 829098]
 KOSEC, Tadeja, LEGAT, Andraž, MILOŠEV, Ingrid. The comparison of organic protective layers on bronze and copper. Prog. org. coat. 2010, vol. 69, no. 2, str. 199-206, [COBISS.SI-ID 1677927]
 Bo Rosborg, Tadeja Kosec, Andrej Kranjc, Jinshan Pan, Andraz Legat, Electrochemical impedance spectroscopy of pure copper exposed in bentonite under oxic conditions, Electrochim. acta. (2011)vol. 56, issue 23, 7862-7870 [COBISS.SI-ID 1756007]
 Erika Švara, Tadeja Kosec, Viljem Kuhar, Andraž Legat, Corrosion stability of different bronzes in simulated urban rain = Korozijska stabilnost različnih bronov v umetnem kislem dežju. Mater. tehnol., 2011, letn. 45, št. 6, str. 585-591. [COBISS.SI-ID 1844583]

10. Pomen raziskovalnih rezultatov projektne skupine⁹

10.1. Pomen za razvoj znanosti¹⁰

SLO

Projekt »Karakterizacija tribokorozijskih procesov« v celoti sovпада s prednostnimi nacionalnimi raziskovalnimi cilji, saj povezuje področje naprednih materialov in nanotehnologije s tehnološkim razvojem za trajnostno gospodarstvo. Novi kovinski materiali imajo namreč izboljšane posamezne mehanske lastnosti in splošno korozijsko obstojnost, ob specifičnih pogojih okolja pa so lahko podvrženi intenzivnim degradacijskim procesom. Kompleksni korozijski procesi so običajno izrazito lokalni, njihov razvoj pa relativno hiter, zato jih težko detektiramo. Takšni procesi so sinergija posameznih mehanskih in elektrokemijskih dogodkov (napetostno-korozijsko pokanje, korozijsko utrujanje, tribokorozijski procesi) in so najbolj izraziti pri kovinskih materialih, ki tvorijo stabilne pasivne filme (titanove zlitine in nerjavna jekla). Glede na to, da so taki materiali v osnovi zelo obstojni in se uporabljajo v najzahtevnejših industrijskih in medicinskih sistemih, je ključno definirati pogoje in parametre, kjer je njihova trajnost lahko bistveno zmanjšana. Nenadna odpoved industrijskih in medicinskih sistemov namreč poleg velike gospodarske škode lahko povzroči tudi ekološke katastrofe in neposredne človeške žrtve. Industrijsko najrazvitejše države intenzivno povezujejo temeljna in tehnološka znanja, pri čemer je ključno tudi povezovanje različnih področij (multidisciplinarnost). V Sloveniji je bilo povezovanje na omenjenih segmentih že večkrat ocenjeno kot pomanjkljivo, zato je tudi

eksplicitno omenjeno v Nacionalnem raziskovalnem in razvojnem programu (NRRP) kot slabost, ki jo je potrebno odpraviti. Pri raziskavah uporabljamo in povezujemo znanje iz različnih področij (kemija, fizika, strojništvo, metalurgija, medicina) in na različnih nivojih (raziskovalna sfera, industrijski tehnološko-razvojni centri).

Glede na to, da je tribokorozija relativno nova veda, ter na naše dosedanje uspešno povezovanje različnih znanstvenih in tehničnih področij, pričakujemo objave v revijah najvišjega znanstvenega nivoja. S sodelovanjem s strokovnjaki iz drugih institucij in industrije smo zagotovili tudi sprotni prenos naših rezultatov v prakso, oziroma čimprejšnji začetek usmerjenih tehnoloških raziskav za reševanje specifičnih industrijskih problemov.

S primerjavo različnih elektrokemijskih in fizikalnih metod bomo določili optimalno metodologijo za ocenjevanje in karakterizacijo tribokorozijskih procesov. Z uporabo omenjenih merilnih metod in ustrezno analizo smo dopolnili temeljno znanje o posameznih fazah procesov korozije in obrabe, ter njihovega medsebojnega vplivanja. Pri izbranih sistemih kovina/elektrolit smo tudi določili kritične parametre omenjenih procesov.

Dosedanje intenzivne mednarodne aktivnosti vseh sodelujočih partnerjev so tudi osnova za tesnejše mednarodno sodelovanje na ožjem področju tribokorozije. Na ta način smo v domači prostor uspešno prenesli posamezne mednarodne izkušnje, oziroma dopolnili naše raziskave in pridobljeno znanje. Pričakujemo, da se bo del znanja prelil tudi v učne programe posameznih fakultet: FS, FKKT in MF, UL.

ANG

Newly developed materials can have better mechanical characteristics and/or corrosion resistance, but suffer from intensive deterioration process under certain aggressive environment (s). Complex corrosion processes are usually localized and quickly initiated, which makes it difficult to detect. In most cases, the processes are combined actions of both mechanical and electrochemical events (stress corrosion cracking and tribocorrosion). It is usually observed in materials that form stable oxide films (stainless steels and titanium alloys). It was of great importance to set the limiting operation conditions and parameters to ensure the longer lifespan of such alloys, because they are important technological and biomedical materials that are used in a wide range of applications. Namely, sudden failure of technological and medical systems can result in vast damages leading to ecological catastrophe and human deaths (victims of circumstances).

The optimal methodology for estimation and characterization of tribocorrosion processes will be chosen after evaluation of different electrochemical and physical methods.

We expect that the collection of proposed techniques will supplement the fundamental knowledge on different stages of corrosion processes, wear, and their synergistic effect. The critical parameters will be determined at the chosen metal/electrolyte systems.

Tribocorrosion is a relatively new scientific research area. It is expected that our results will be published in journals of high impact factors. Collaborating with scientists and experts from the field at other research and technology institutes, we assured the results to be applied in practice. The rationale being to start the implementation of technological research to resolve problems of high industry impact.

There was an intensive international collaboration with the partners (scientific communities) involved in the past and present. The conclusions were for continuous research, dialogue, and collaboration within these communities towards the selected scientific field of tribocorrosion. These experiences were implemented in our own research field, which lead to a better research and knowledge. We aim to implement knowledge of tribocorrosion as special courses at different faculties; such as Faculty for Civil Engineering, Faculty for Chemistry and Chemical Engineering, and Medical Faculty.

10.2. Pomen za razvoj Slovenije¹¹

SLO

V tehnološko najrazvitejših podjetjih se že dalj časa zavedajo pomena pravilne izbire materialov in optimalnih konstrukcijskih rešitev, saj je to pogoj za ustrezno kvaliteto njihovih proizvodov. Eno od glavnih meril je zagotavljanje ustrezne trajnosti pri izbranih pogojih okolja (kombinacija mehanskih, fizikalnih in kemijskih obremenitev), pri čemer korozija velikokrat predstavlja kritični degradacijski proces. Podobni pogoji nastopajo tudi pri kovinskih vsadkih v človeško

telo, saj so poleg agresivnega vpliva okoljskega tkiva v večini primerov prisotne tudi relativno velike mehanske obremenitve. Zaradi uporabe novih materialov (posebni kovinski materiali in prevleke, novi načini spajanja materialov, različna maziva, dodajanje inhibitorjev) in višjih mehanskih zahtev, so raziskave na tem kompleksnem področju korozije nujne.

Raziskave tribokorozijskih procesov so bile sicer definirane kot temeljni projekt, vendar so rezultati nujni za nadaljnje industrijske in medicinske aplikacije. V kolikor želimo definirati natančne pogoje raziskav za avtomobilsko industrijo (batni in ležajni deli, zavore), sistemi v parnih generatorjih (korozija pod vplivom toka) in potrebne lastnosti vsadkov v človeško telo (dentalni in ortopedski implantati), smo morali definirati osnovne tribološke procese, predvsem pa metodologijo (merilne tehnike in postopke) za njihovo karakterizacijo. Za rezultate naših raziskav so izrazili zanimanje ključni člani ACS (slovenskega avtomobilskega grozda: HIDRIA), Medicinska fakulteta, UL, NEK in Institut za materiale in tehnologije-IMT. Pri naših raziskavah smo povezali z sodelujočimi institucijami (Center za tribologijo in tehnično diagnostiko, Institut za materiale in tehnologije-IMT in Institut Jožef Stefan).

Poudariti je prav tako potrebno, da je tribokorozija kot veda še zelo mlada in da se v Evropi trenutno ukvarjajo s to tematiko le maloštevilne skupine. S podporo Agencije za raziskovalno dejavnost smo tako lahko segli in doprinesli slovensko znanje v mednarodni prostor. Slovenska tribološka znanost je zelo močna in prepoznavna, z dodatnim znanjem na področju kemijskega vpliva na korozijsko propadanje materialov med obrabljanjem pa le-ta predstavlja dodano vrednost.

ANG

An important condition to achieve quality products, leading companies are aware of the importance in choosing good, quality materials and constructions. One basic criteria is the assurance for sustainable durability of materials at the chosen environment (combination of mechanical, physical and chemical wear) where the corrosion itself represents the critical deterioration process. Similar conditions can be found in the case of biomedical materials used in orthopaedics and dental surgeries. In vivo degradation of metallic biomaterials due to combined wear and corrosion processes results in the formation of particulate and ionic metallic debris, which can lead to failures.

Thus, the tribocorrosion research represents an important scientific field due to increased number of new materials (special alloys and coatings, new conjunction systems, use of lubricants and inhibitors) and higher mechanical demands.

These particular tribocorrosion studies proposed in this project are basic research studies, which are needed for further technological and biomedical research studies. There are great needs for defining tribocorossion processes as well as the developement of methodology for the testing. The reasons are to define the field of research for certain applications for automotive industry (pistons, bearings, and brakes) and biomedicine (dental screw and hip implants). There is great interest, for the implementation of the research results in some Slovenian automobile industries (HIDRIA) and the Faculty of Medicine. We will collaborate with different research groups at the Centre for Tribology and Technical Diagnostics, Institute for Metals and technologies and Department for Thin Coatings and Surfaces at Jozef Stefan Institute.

Tribocorrosion is a relatively young scientific field and there are very few scientific groups in Europe that are involved in this type of research. With the help of Slovenian research Agency there we were able to present international public the Slovenian knowledge. Slovenia is very strong and recognizable in tribology as a science. Combination of tribology and tribocorrosion science thus represents the added value to general knowledge for sustainable corrosion protection of materials.

11. Samo za aplikativne projekte!

Označite, katerega od navedenih ciljev ste si zastavili pri aplikativnem projektu, katere konkretne rezultate ste dosegli in v kakšni meri so doseženi rezultati uporabljeni

Cilj		
F.01	Pridobitev novih praktičnih znanj, informacij in veščin	
	Zastavljen cilj	☒ DA ☐ NE

	Rezultat	
	Uporaba rezultatov	
F.02	Pridobitev novih znanstvenih spoznanj	
	Zastavljen cilj	☐ DA ☐ NE
	Rezultat	
	Uporaba rezultatov	
F.03	Večja usposobljenost raziskovalno-razvojnega osebja	
	Zastavljen cilj	☐ DA ☐ NE
	Rezultat	
	Uporaba rezultatov	
F.04	Dvig tehnološke ravni	
	Zastavljen cilj	☐ DA ☐ NE
	Rezultat	
	Uporaba rezultatov	
F.05	Sposobnost za začetek novega tehnološkega razvoja	
	Zastavljen cilj	☐ DA ☐ NE
	Rezultat	
	Uporaba rezultatov	
F.06	Razvoj novega izdelka	
	Zastavljen cilj	☐ DA ☐ NE
	Rezultat	
	Uporaba rezultatov	
F.07	Izboljšanje obstoječega izdelka	
	Zastavljen cilj	☐ DA ☐ NE
	Rezultat	
	Uporaba rezultatov	
F.08	Razvoj in izdelava prototipa	
	Zastavljen cilj	☐ DA ☐ NE
	Rezultat	
	Uporaba rezultatov	
F.09	Razvoj novega tehnološkega procesa oz. tehnologije	
	Zastavljen cilj	☐ DA ☐ NE
	Rezultat	
	Uporaba rezultatov	
F.10	Izboljšanje obstoječega tehnološkega procesa oz. tehnologije	
	Zastavljen cilj	☐ DA ☐ NE
	Rezultat	
	Uporaba rezultatov	

F.11	Razvoj nove storitve	
	Zastavljen cilj	☐ DA ☐ NE
	Rezultat	
	Uporaba rezultatov	
F.12	Izboljšanje obstoječe storitve	
	Zastavljen cilj	☐ DA ☐ NE
	Rezultat	
	Uporaba rezultatov	
F.13	Razvoj novih proizvodnih metod in instrumentov oz. proizvodnih procesov	
	Zastavljen cilj	☐ DA ☐ NE
	Rezultat	
	Uporaba rezultatov	
F.14	Izboljšanje obstoječih proizvodnih metod in instrumentov oz. proizvodnih procesov	
	Zastavljen cilj	☐ DA ☐ NE
	Rezultat	
	Uporaba rezultatov	
F.15	Razvoj novega informacijskega sistema/podatkovnih baz	
	Zastavljen cilj	☐ DA ☐ NE
	Rezultat	
	Uporaba rezultatov	
F.16	Izboljšanje obstoječega informacijskega sistema/podatkovnih baz	
	Zastavljen cilj	☐ DA ☐ NE
	Rezultat	
	Uporaba rezultatov	
F.17	Prenos obstoječih tehnologij, znanj, metod in postopkov v prakso	
	Zastavljen cilj	☐ DA ☐ NE
	Rezultat	
	Uporaba rezultatov	
F.18	Posredovanje novih znanj neposrednim uporabnikom (seminarji, forumi, konference)	
	Zastavljen cilj	☐ DA ☐ NE
	Rezultat	
	Uporaba rezultatov	
F.19	Znanje, ki vodi k ustanovitvi novega podjetja ("spin off")	
	Zastavljen cilj	☐ DA ☐ NE
	Rezultat	
	Uporaba rezultatov	
F.20	Ustanovitev novega podjetja ("spin off")	

	Zastavljen cilj	☐ DA ☐ NE
	Rezultat	
	Uporaba rezultatov	
F.21	Razvoj novih zdravstvenih/diagnostičnih metod/postopkov	
	Zastavljen cilj	☐ DA ☐ NE
	Rezultat	
	Uporaba rezultatov	
F.22	Izboljšanje obstoječih zdravstvenih/diagnostičnih metod/postopkov	
	Zastavljen cilj	☐ DA ☐ NE
	Rezultat	
	Uporaba rezultatov	
F.23	Razvoj novih sistemskih, normativnih, programskih in metodoloških rešitev	
	Zastavljen cilj	☐ DA ☐ NE
	Rezultat	
	Uporaba rezultatov	
F.24	Izboljšanje obstoječih sistemskih, normativnih, programskih in metodoloških rešitev	
	Zastavljen cilj	☐ DA ☐ NE
	Rezultat	
	Uporaba rezultatov	
F.25	Razvoj novih organizacijskih in upravljavskih rešitev	
	Zastavljen cilj	☐ DA ☐ NE
	Rezultat	
	Uporaba rezultatov	
F.26	Izboljšanje obstoječih organizacijskih in upravljavskih rešitev	
	Zastavljen cilj	☐ DA ☐ NE
	Rezultat	
	Uporaba rezultatov	
F.27	Prispevek k ohranjanju/varovanje naravne in kulturne dediščine	
	Zastavljen cilj	☐ DA ☐ NE
	Rezultat	
	Uporaba rezultatov	
F.28	Priprava/organizacija razstave	
	Zastavljen cilj	☐ DA ☐ NE
	Rezultat	
	Uporaba rezultatov	
F.29	Prispevek k razvoju nacionalne kulturne identitete	
	Zastavljen cilj	☐ DA ☐ NE
	Rezultat	

	Uporaba rezultatov	
F.30	Strokovna ocena stanja	
	Zastavljen cilj	☐ DA ☐ NE
	Rezultat	
	Uporaba rezultatov	
F.31	Razvoj standardov	
	Zastavljen cilj	☐ DA ☐ NE
	Rezultat	
	Uporaba rezultatov	
F.32	Mednarodni patent	
	Zastavljen cilj	☐ DA ☐ NE
	Rezultat	
	Uporaba rezultatov	
F.33	Patent v Sloveniji	
	Zastavljen cilj	☐ DA ☐ NE
	Rezultat	
	Uporaba rezultatov	
F.34	Svetovalna dejavnost	
	Zastavljen cilj	☐ DA ☐ NE
	Rezultat	
	Uporaba rezultatov	
F.35	Drugo	
	Zastavljen cilj	☐ DA ☐ NE
	Rezultat	
	Uporaba rezultatov	

Komentar

--

12.Samo za aplikativne projekte!**Označite potencialne vplive oziroma učinke vaših rezultatov na navedena področja**

	Vpliv	Ni vpliva	Majhen vpliv	Srednji vpliv	Velik vpliv	
G.01	Razvoj visoko-šolskega izobraževanja					
G.01.01.	Razvoj dodiplomskega izobraževanja	☐	☐	☐	☐	
G.01.02.	Razvoj podiplomskega izobraževanja	☐	☐	☐	☐	
G.01.03.	Drugo:	☐	☐	☐	☐	
G.02	Gospodarski razvoj					
G.02.01	Razširitev ponudbe novih izdelkov/storitev na trgu	☐	☐	☐	☐	
G.02.02.	Širitev obstoječih trgov	☐	☐	☐	☐	

G.02.03.	Znižanje stroškov proizvodnje	☐	☐	☐	☐	
G.02.04.	Zmanjšanje porabe materialov in energije	☐	☐	☐	☐	
G.02.05.	Razširitev področja dejavnosti	☐	☐	☐	☐	
G.02.06.	Večja konkurenčna sposobnost	☐	☐	☐	☐	
G.02.07.	Večji delež izvoza	☐	☐	☐	☐	
G.02.08.	Povečanje dobička	☐	☐	☐	☐	
G.02.09.	Nova delovna mesta	☐	☐	☐	☐	
G.02.10.	Dvig izobrazbene strukture zaposlenih	☐	☐	☐	☐	
G.02.11.	Nov investicijski zagon	☐	☐	☐	☐	
G.02.12.	Drugo:	☐	☐	☐	☐	
G.03	Tehnološki razvoj					
G.03.01.	Tehnološka razširitev/posodobitev dejavnosti	☐	☐	☐	☐	
G.03.02.	Tehnološko prestrukturiranje dejavnosti	☐	☐	☐	☐	
G.03.03.	Uvajanje novih tehnologij	☐	☐	☐	☐	
G.03.04.	Drugo:	☐	☐	☐	☐	
G.04	Družbeni razvoj					
G.04.01	Dvig kvalitete življenja	☐	☐	☐	☐	
G.04.02.	Izboljšanje vodenja in upravljanja	☐	☐	☐	☐	
G.04.03.	Izboljšanje delovanja administracije in javne uprave	☐	☐	☐	☐	
G.04.04.	Razvoj socialnih dejavnosti	☐	☐	☐	☐	
G.04.05.	Razvoj civilne družbe	☐	☐	☐	☐	
G.04.06.	Drugo:	☐	☐	☐	☐	
G.05.	Ohranjanje in razvoj nacionalne naravne in kulturne dediščine in identitete	☐	☐	☐	☐	
G.06.	Varovanje okolja in trajnostni razvoj	☐	☐	☐	☐	
G.07	Razvoj družbene infrastrukture					
G.07.01.	Informacijsko-komunikacijska infrastruktura	☐	☐	☐	☐	
G.07.02.	Prometna infrastruktura	☐	☐	☐	☐	
G.07.03.	Energetska infrastruktura	☐	☐	☐	☐	
G.07.04.	Drugo:	☐	☐	☐	☐	
G.08.	Varovanje zdravja in razvoj zdravstvenega varstva	☐	☐	☐	☐	
G.09.	Drugo:	☐	☐	☐	☐	

Komentar**13.Pomen raziskovanja za sofinancerje¹²**

Sofinancer				
1.	Naziv			
	Naslov			
	Vrednost sofinanciranja za celotno obdobje trajanja projekta je znašala:		EUR	
	Odstotek od utemeljenih stroškov projekta:		%	
	Najpomembnejši rezultati raziskovanja za sofinancerja		Šifra	
		1.		
		2.		
		3.		
		4.		
		5.		
Komentar				
Ocena				

C. IZJAVE

Podpisani izjavljam/o, da:

- so vsi podatki, ki jih navajamo v poročilu, resnični in točni
- se strinjamo z obdelavo podatkov v skladu z zakonodajo o varstvu osebnih podatkov za potrebe ocenjevanja ter obdelavo teh podatkov za evidence ARRS
- so vsi podatki v obrazcu v elektronski obliki identični podatkom v obrazcu v pisni obliki
- so z vsebino zaključnega poročila seznanjeni in se strinjajo vsi soizvajalci projekta

Podpisi:

*zastopnik oz. pooblaščen oseba
raziskovalne organizacije:*

in

vodja raziskovalnega projekta:

Zavod za gradbeništvo Slovenije

Tadeja Kosec

ŽIG

Kraj in datum: Ljubljana 9.3.2012

Oznaka prijave: ARRS-RPROJ-ZP-2012/29

¹ Zaradi spremembe klasifikacije je potrebno v poročilu opredeliti raziskovalno področje po novi klasifikaciji FOS 2007 (Fields of Science). Prevaljna tabela med raziskovalnimi področji po klasifikaciji ARRS ter po klasifikaciji FOS 2007 (Fields of Science) s kategorijami WOS (Web of Science) kot podpodročji je dostopna na spletni strani agencije (<http://www.arrs.gov.si/sl/gradivo/sifranti/preslik-vpp-fos-wos.asp>). [Nazaj](#)

² Napišite povzetek raziskovalnega projekta (največ 3.000 znakov v slovenskem in angleškem jeziku) [Nazaj](#)

³ Napišite kratko vsebinsko poročilo, kjer boste predstavili raziskovalno hipotezo in opis raziskovanja. Navedite ključne ugotovitve, znanstvena spoznanja, rezultate in učinke raziskovalnega projekta in njihovo uporabo ter sodelovanje s tujimi partnerji. Največ 12.000 znakov vključno s presledki (približno dve strani, velikosti pisave 11). [Nazaj](#)

⁴ Realizacija raziskovalne hipoteze. Največ 3.000 znakov vključno s presledki (približno pol strani, velikosti pisave 11) [Nazaj](#)

⁵ V primeru bistvenih odstopanj in sprememb od predvidenega programa raziskovalnega projekta, kot je bil zapisan v

Zaključno poročilo o rezultatih raziskovalnega projekta - 2012

predlogu raziskovalnega projekta oziroma v primeru sprememb, povečanja ali zmanjšanja sestave projektne skupine v zadnjem letu izvajanja projekta (obrazložitev). V primeru, da sprememb ni bilo, to navedite. Največ 6.000 znakov vključno s presledki (približno ena stran, velikosti pisave 11). [Nazaj](#)

⁶ Znanstveni in družbeno-ekonomski dosežki v programu in projektu so lahko enaki, saj se projektna vsebina praviloma nanaša na širšo problematiko raziskovalnega programa, zato pričakujemo, da bo večina izjemnih dosežkov raziskovalnih programov dokumentirana tudi med izjemnimi dosežki različnih raziskovalnih projektov.

Raziskovalni dosežek iz obdobja izvajanja projekta (do oddaje zaključnega poročila) vpišete tako, da izpolnite COBISS kodo dosežka – sistem nato sam izpolni naslov objave, naziv, IF in srednjo vrednost revije, naziv FOS področja ter podatek, ali je dosežek uvrščen v A'' ali A'. [Nazaj](#)

⁷ Znanstveni in družbeno-ekonomski dosežki v programu in projektu so lahko enaki, saj se projektna vsebina praviloma nanaša na širšo problematiko raziskovalnega programa, zato pričakujemo, da bo večina izjemnih dosežkov raziskovalnih programov dokumentirana tudi med izjemnimi dosežki različnih raziskovalnih projektov.

Družbeno-ekonomski rezultat iz obdobja izvajanja projekta (do oddaje zaključnega poročila) vpišete tako, da izpolnite COBISS kodo dosežka – sistem nato sam izpolni naslov objave, naziv, IF in srednjo vrednost revije, naziv FOS področja ter podatek, ali je dosežek uvrščen v A'' ali A'.

Družbenoekonomski dosežek je po svoji strukturi drugačen, kot znanstveni dosežek. Povzetek znanstvenega dosežka je praviloma povzetek bibliografske enote (članka, knjige), v kateri je dosežek objavljen.

Povzetek družbeno ekonomsko relevantnega dosežka praviloma ni povzetek bibliografske enote, ki ta dosežek dokumentira, ker je dosežek sklop več rezultatov raziskovanja, ki je lahko dokumentiran v različnih bibliografskih enotah. COBISS ID zato ni enoznačen izjemoma pa ga lahko tudi ni (npr. v preteklem letu vodja meni, da je izjemen dosežek to, da sta se dva mlajša sodelavca zaposlila v gospodarstvu na pomembnih raziskovalnih nalogah, ali ustanovila svoje podjetje, ki je rezultat prejšnjega dela ... - v obeh primerih ni COBISS ID). [Nazaj](#)

⁸ Navedite rezultate raziskovalnega projekta iz obdobja izvajanja projekta (do oddaje zaključnega poročila) v primeru, da katerega od rezultatov ni mogoče navesti v točkah 7 in 8 (npr. ker se ga v sistemu COBISS ne vodi). Največ 2.000 znakov vključno s presledki. [Nazaj](#)

⁹ Pomen raziskovalnih rezultatov za razvoj znanosti in za razvoj Slovenije bo objavljen na spletni strani: <http://sicris.izum.si/> za posamezen projekt, ki je predmet poročanja [Nazaj](#)

¹⁰ Največ 4.000 znakov vključno s presledki [Nazaj](#)

¹¹ Največ 4.000 znakov vključno s presledki [Nazaj](#)

¹² Rubrike izpolnite / prepisite skladno z obrazcem "izjava sofinancerja" <http://www.arrs.gov.si/sl/progproj/rproj/gradivo/>, ki ga mora izpolniti sofinancer. Podpisan obrazec "Izjava sofinancerja" pridobi in hrani nosilna raziskovalna organizacija – izvajalka projekta. [Nazaj](#)

Obrazec: ARRS-RPROJ-ZP/2012 v1.00

65-CA-04-BE-FF-65-72-0F-FC-81-83-46-12-AD-3E-C6-7D-D2-B7-5E

Manuscript Number:

Title: The tribocorrosion behaviour of NiTi alloy

Article Type: Full-Length Article

Keywords: NiTi, microstructure, simulated saliva, tribo-corrosion, passive film

Corresponding Author: Dr Tadeja Kosec,

Corresponding Author's Institution: .

First Author: Tadeja Kosec, PhD

Order of Authors: Tadeja Kosec, PhD; Petra Močnik; Andraž Legat, assoc. Prof, PhD

Abstract: NiTi alloys as important technological material finds its wide application in different fields. Due to shape memory and superelastic properties it is widely used in biomedical applications. Generally, nickel titanium alloys are known for their good corrosion resistance, but in some circumstances they suffer from pitting and crevice corrosion. Beside corrosion, the wear resistance of this alloy is of critical concern in many applications. Since dental NiTi archwires experience severe failures in applications, it is assumed that their performance is affected also by their microstructure. In our study, the microstructural properties of NiTi alloy samples were investigated: NiTi plate and NiTi dental wire with and without surface oxide in as-received state, were compared. The electrochemical properties of NiTi wires and sheets was compared by the use of different electrochemical techniques. The tribocorrosion properties were studied in artificial saliva. Wear rate was determined as well as its chemical and tribological contribution. The variation of corrosion performance in artificial saliva was greater for specimens covered with surface oxide films. Tribocorrosion studies showed that the total wear of the NiTi alloy is greater when corrosion is combined with the wear. It was confirmed that microstructure has an influential effect on electrochemical and triboelectrochemical properties. As a result, it is noteworthy to distinguish that electrochemical properties of the exposed working surface varies in dependence of microstructural properties of the studied alloy material.

WEAR

Confirmation of Authorship

Please save a copy of this MS Word file, complete and upload as the “Confirmation of Authorship” file.

As corresponding author, Tadeja Kosec, hereby confirm on behalf of all authors that:

- 1) The authors have obtained the necessary authority for publication.
- 2) The paper has not been published previously, that it is not under consideration for publication elsewhere, and that if accepted it will not be published elsewhere in the same form, in English or in any other language, without the written consent of the publisher.
- 3) The paper does not contain material which has been published previously, by the current authors or by others, of which the source is not explicitly cited in the paper.

Upon acceptance of an article by the journal, the author(s) will be asked to transfer the copyright of the article to the publisher. This transfer will ensure the widest possible dissemination of information.

Novelty statement

Hereby, as a corresponding and first author, I confirm that the paper entitled “The tribocorrosion behaviour of NiTi alloy” by the authors Tadeja Kosec, Petra Močnik, Andraž Legat represents significance and novelty of the work presented in the present manuscript.

Tadeja Kosec

The tribocorrosion behaviour of NiTi alloy

Tadeja Kosec*, Petra Močnik, Andraž Legat

Slovenian National Building and Civil Engineering Institute,
Dimičeva 12, SI - 1000 Ljubljana, Slovenia

Abstract

NiTi alloys as important technological material finds its wide application in different fields. Due to shape memory and superelastic properties it is widely used in biomedical applications. Generally, nickel titanium alloys are known for their good corrosion resistance, but in some circumstances they suffer from pitting and crevice corrosion. Beside corrosion, the wear resistance of this alloy is of critical concern in many applications. Since dental NiTi archwires experience severe failures in applications, it is assumed that their performance is affected also by their microstructure.

In our study, the microstructural properties of NiTi alloy samples were investigated: NiTi plate and NiTi dental wire with and without surface oxide in as-received state, were compared. The electrochemical properties of NiTi wires and sheets was compared by the use of different electrochemical techniques. The tribocorrosion properties were studied in artificial saliva. Wear rate was determined as well as its chemical and tribological contribution. The variation of corrosion performance in artificial saliva was greater for specimens covered with surface oxide films. Tribocorrosion studies showed that the total wear of the NiTi alloy is greater when corrosion is combined with the wear. It was confirmed that microstructure has an influential effect on electrochemical and triboelectrochemical properties. As a result, it is noteworthy to distinguish that electrochemical properties of the exposed working surface varies in dependence of microstructural properties of the studied alloy material.

Keywords: NiTi, microstructure, simulated saliva, tribo-corrosion, passive film

1. Introduction

There have been numerous studies conducted on nickel titanium alloy as the most representative example of the shape memory alloy that is most used material in practice. The studies can be roughly divided into different areas of the interest: basic corrosion and electrochemical studies [1–6], mechanical and material property studies [7-11] and surface treatment studies [12–18].

* corresponding author: T. Kosec: tadeja.kosec@zag.si, tel. 00 386 1 2804547

Among extensive corrosion studies on nickel titanium alloy [1-6], Rondelli made a comparison of NiTi with other implant materials in body simulating fluids [1]. It was shown that passive films on NiTi are inferior to those formed on TiAlV alloys, but are comparable to those formed on stainless steels [1]. The pitting potentials lower than 250 mV were found on NiTi in simulated body fluid at pH 7 °C, and they were dependant on surface modification procedures, with which it was possible to increase the pitting potential to values exceeding 800 mV [3]. Figueira et al. have recently studied NiTi, and compared it to Ti, Al, 316L in Hank's solution and in Eagle's minimum essential medium, also at 37 °C [4]. It was found that NiTi is subjected to crevice corrosion, and that the passive films are thinner in amino acid containing environment [4]. Among different drawbacks of the use of NiTi such as its subjection to pitting corrosion [3], failures are reported like stress corrosion cracking in orthodontic NiTi wires [8] and extensive Ni release [7]. Since nickel can cause hypersensitive reactions in the human body, a vast choice of surface treatments have been proposed and implemented in order to reduce the content of nickel in surface oxide film [12], among which ion implantation [12], mechanical polishing, chemical etching and selective oxidation [13] were proposed and investigated. It was found that corrosion properties were improved by chemical etching that provided depletion of nickel in surface compact oxide film, whereas oxidation at 530 °C as a part of shape setting procedure negatively affected the corrosion performance [13]. Higher corrosion resistance of austenitic grown oxide film was determined [5]. Also alloying with Nb and Co exchanging the content of Ni in NiTi alloy was studied. Corrosion properties were improved as well as hardness of the alloy [14].

Many studies involve evaluation of different coatings on NiTi alloy, from hydroxyapatite [17] to hard coatings like TiN [15,16,19]. Corrosion resistance of NiTi was significantly improved by almost 60 times by electrodeposition of the hydroxyapatite/zirconia composite coating. The drawback of such system is that it can not be used in load bearing applications [17]. Water plasma immersion ion implantation on NiTi surface also enhanced corrosion resistance of such oxide film [18]. Surface of NiTi was modified by implementation of N⁺ and/or Ar⁺ ion to produce Nickel free surface on NiTi to improve biocompatibility, as evaluated by cell culture experiments [11].

Concerning tribological behaviour of NiTi alloys, there are several studies done in dry conditions [9–11], but there is a huge lack in tribocorrosion studies on NiTi alloys [6]. Tribological behaviour of NiTi alloy against steel and WC at elevated temperatures was studied in order to get data of tribological behaviour where superelasticity and shape memory effect might be lost [9]. The reduction of wear rate on NiTi/steel contact at elevated temperature was observed. It was attributed to tribological layer on the wear surface of NiTi [9Abedini]. Another study by the same authors showed that NiTi in austenitic state had higher wear resistance as compared to martensitic state, where also higher coefficient of friction was measured as a result of lower strength of martensitic state [10]. Also, sliding wear of superelastic NiTi was studied in dry conditions [11]. It was shown that wear resistance of superelastic TiNi alloy is about 30 and 10 times higher

than pure Ti and Ni, respectively. The dominant wear mechanisms observed for TiNi were abrasion and delamination of subsurface cracks as a result of cyclic loading. Moreover, dry tribological tests were done on plasma source ion implanted NiTi samples in austenitic and martensitic state, as well [6]. It was shown that the wear was reduced by 38 % for austenitic state in dry conditions and down to 79 % in the lubricated conditions. The closest study to tribocorrosion investigation of NiTi alloy was done by Rondelli [1]. The localized corrosion tests where the passive film was abruptly damaged showed that the characteristics of the passive film on NiTi were inferior to those of TiAlV and in some cases even to stainless steels [1].

Since most tribological studies on NiTi alloy was done in dry conditions and only effect of mechanical wear was studied, there is a great demand in recognizing properties of NiTi alloy at simultaneous process of wear and corrosion in aggressive media. The aim of the present study is to evaluate and compare electrochemical and triboelectrochemical properties of nickel titanium alloys of two different microstructural shapes in simulated saliva: dental archwire and superelastic Nickel titanium sheet.

Polarization curves were measured to evaluate electrochemical behaviour in a simulated saliva. Tribocorrosion tests were carried out at open circuit potential. Wear rate of the two microstructural alloys (archwire and sheet) and the two different surface pre-treatments step (oxidized as received form and polished) was studied. Optical and microscopic investigation of surface modifications after wear tests was investigated as well.

2. Experimental

2.1. Preparation of the samples

Two samples were chosen for the study, namely:

1) Superelastic, alloy BB NiTi 2 mm sheet, flat annealed, surface oxide free (pickled), Memry GMBH alloy,

2) NiTinol orthodontic wire (3M), superelastic, 0.019×0.025 in (0.48×0.64 mm), Orthoform III Ovoid Upper.

Samples (i.e. working electrodes) for electrochemical tests were cut from the sheet in the form of discs with a diameter of 15 mm and from the archwire at the straight part in the full length of 5 cm. Samples for triboelectrochemical tests were cut from the sheet with electro discharge machining in the shape of 50×10 mm. The electrical contact was attached and the back and the sides of the sample as well as electrical contact were protected by epoxy coating, so that the exposed surface measured 4.5 cm². Samples for triboelectrochemical tests from archwire were prepared from the flat part of the archwire in the total length

of 40 mm, moulded in an acrylate mould with the electrical contact attached. It was subsequently grinded and polished in order to get surface free oxide film of NiTi dental wire.

Two different surface finishes were studied: the first were samples without oxide film, which were prepared by grinding and polishing in order to investigate the effect of microstructure. The second surface finish was oxide film in as received state (with the suppliers' finish) in order to investigate the actual sample that comes into use in realistic environment (i.e. dental archwire in saliva). For oxide film removal the samples were abraded with 800 and 1000-grid SiC paper. Samples were ultrasonically cleaned in ethanol for 3 min and then well dried.

2.2. Micro-structural examination

Samples for metallographic investigation were etched in a solution of 10 vol. % HF, 40 vol. % HNO₃ and 50 vol. % H₂O for 2 min. Shortly after, the optical microscopy study was conducted at different magnifications.

2.3. Electrochemical measurements

The choice of adequate saliva solution was made by testing Nickel titanium alloy in various solution compositions. The one that most closely represents natural saliva was chosen for further experiments, similarly as the tested choice of salivas by Duffo et al. [20]. Thus, the electrochemical measurements were performed in a solution of 0.60 g/L NaCl, 0.72 g/L KCl, 0.22 g/L CaCl₂·2 H₂O, 0.68 g/L KH₂PO₄, 0.856 g/L Na₂HPO₄·12 H₂O, 0.060 g/L KSCN, 1.5 g/L KHCO₃ and 0.03 g/L citric acid, pH=6.5 in order to simulate saliva (this solution was designated: "simulated saliva"), as proposed by Duffo et al [20].

In the case of flat disc electrode, a three-electrode corrosion cell was used, with a volume of 350 cm³. The working electrode was embedded in a Teflon holder, and had an exposed area of 0.785 cm². In the case of the wire electrodes, the area exposed to the solution was 1.0 cm². An Autolab PGStat 100, Floating version expanded with Nova software 6 was used.

Electrochemical testing was executed in the following order: 2-hour stabilization at open circuit potential (OCP), linear polarization measurements at ± 20 mV vs. OCP at a scan rate 0.1 mV/s were performed. Potentiodynamic measurements were then performed starting from -0.25 V vs. OCP, and progressing in the anodic direction up to $+2.0$ V at a scan rate of 1 mV/s. For cyclic polarization measurement the reverse potential was chosen at the potential 1.4 V in order to provide the definite unknown to all of the tested samples. Average current densities at potential of 1.4 V varied from 0.4 to 1 mA cm⁻². All potentials are reported with respect to the SCE scale.

At least three measurements were performed to fulfil electrochemical testing statistical requirement [21]. After estimating the mean values of logarithm results of corrosion resistance, the measurement that had the closest value to the mean value from the set, was chosen to be presented.

2.4 Triboelectrochemical measurements

The wear tests were performed on a reciprocal tribometer (Tribotechnic, pin on disc + reciprocating tribometer, 2009, France) with a 6-mm Al_2O_3 ball as a counter body.

The test parameters that were evaluated for triboelectrochemical experiments are denoted in each figure. The normal loads in tests varied from 1 N to 5 N at average sliding speed 5 mm/s. The wear length was 10 mm. In all of the experiments the friction force and friction coefficient were followed by time. Ball counter body with a 6 mm diameter was made from Al_2O_3 . Triboelectrochemical three-electrode cell, made of Teflon, consisted of: working electrode with electrical contact, platinum wire counter electrode and Ag/AgCl reference electrode.

Electrochemical and tribocorrosion experiments were executed at room temperature. The reason for that is that tribocorrosion experiments do not enable test conditions at elevated temperatures. Moreover, electrochemical experiments were also executed at elevated temperatures and no in the pitting potential was detected.

2.5. SEM/EDS, profilometer and hardness analysis

A low-vacuum JEOL 5500 LV, JEOL, JAPAN (*Japan*) scanning electron microscope, equipped with energy dispersive spectroscopy (EDX) Oxford Inca (*Oxford Instrument Analytical, UK*), was used to observe the surface products formed using an accelerating voltage of 20 kV.

A Taylor Hobson profilometer Taylor Hobson precision, Surtronic 25 (France, 2010) was used for wear scar analysis.

The Vickers Hardness was determined by tester Frank Finotest 38542 using an indenter at loads of 9.8 N at microscopic enlargement of 40.

3. Results and discussion

3.1 Metallographic examination

Both samples, NiTi sheet and NiTi archwire in cross section and longitudinal direction were metallographically examined. They are presented in Figure 1. NiTi sheet (Figure 1 a and b) has martensitic structure. The not well defined crystal grains are of 40–50 μm in cross-sectional and longitudinal view.

Grains are uniformly oriented in all directions due to thermal procedures. There are several bigger inclusions of diameter 2–5 μm found in cross section view (Fig 1a). There is smaller number of inclusions in longitudinal direction (Fig 1b, the exposed working surface at electrochemical and tribocorrosion experiments).

The martensitic microstructure of NiTi archwire in cross section view and longitudinal view was very difficult to reveal (Fig 1c and d). Crystal grain size in cross-section (Fig 1c) are relatively small (less than 40 μm) being elongated in longitudinal direction (Fig 1d, exposed surface for electrochemical testing) due to technological procedure that includes cold drawing. There are many small inclusions (less than 1 μm) in the microstructure of the wire that occupy 8.8 % of the total area in cross-section and 4.3 % of the total area in longitudinal view. The inclusions are elongated in the pulling direction. They measure from 10–200 μm in length. Unfortunately, it was impossible to exactly locate area of inclusions in SEM microscope, so their consistency could not be determined. It was thus reported that the inclusions are both TiC and Ti_2NiO_x [22].

Fig. 1. Microstructural examination of NiTinol superelastic sheet a) cross-section and b) longitudinal view and NiTi archwire c) cross-section and d) longitudinal view.

3.2 Potentiodynamic measurements

In order to estimate pitting susceptibility, cyclic polarization measurements at a scan rate 1 mV/s were executed for polished NiTi sheet and wire, as well as for NiTi sheet and wire with surface oxide films in as-received state. Repassivation properties were determined, both for NiTi sheet and wire.

Fig. 2. Cyclic polarization scans for NiTi sheets and wires: a) without surface oxide film, b) with oxide film, in simulated saliva at a scan rate 1 mV/s.

NiTi sheet without surface oxide film evidently showed that NiTi was not susceptible to pitting corrosion as negative hysteresis was observed for NiTi sheet in reversed anodic scan in simulated saliva. The corrosion current density is 74 nA/cm^2 . The forward scan, in which a low passive current density of approximately $3 \text{ }\mu\text{A/cm}^2$ was measured, was consistent with a passive behaviour. A sharp increase in current density marked the breakdown potential at 1.10 V in the forward scan. The potential applied to the electrode was reversed and scanned in reverse direction at potential 1.4 V , where approximate current of 1 mA/cm^2 was reached. The reverse scan evidenced currents, lower than currents in the passive forward scan. Under conditions studied, the polished NiTi electrode could successfully repassivate.

For a NiTi dental wire without oxide film a shape of CP curve is similar to NiTi sheet, while the forward corrosion current density is lower (45.9 nA/cm^2) and E_{corr} is more positive (-0.267 V) than the one for NiTi sheet. The passive current in forward scan is similar to the NiTi sheet sample, while in the reversed scan it is smaller for NiTi wire. The breakdown potential was evidenced at 1.2 V (Table 1). The repassivation potentials for both samples were relatively high, 0.9 V for a sheet and 0.86 V for a wire sample. Polarization resistance, as a good measure for corrosion susceptibility, since the scan rates are lower, showed that NiTi sheet without surface oxide film is smaller, $0.824 \text{ M}\Omega \text{ cm}^2$ than the one for NiTi dental wire without surface oxide film, $1.19 \text{ M}\Omega \text{ cm}^2$.

Comparing the two different samples without surface oxide film it can be concluded that micro-structural characteristics of dental wire exhibited better corrosion properties than NiTi sheet sample. This can be attributed to the fact that the exposed metal surface of dental wire has fewer inclusions 4.3% , relatively small number of elongated crystal grains in nominal area. It is also microstructurally less susceptible to corrosion attack that could experience its counterpart of dental wire- cross section with 8.8% of inclusions and much smaller crystal grains.

This fact is important when interpreting and comparing results with previously published ones.

Aziz Kerrzo studied cross section of the Ti-45Ni surface, where the pitting potential was as low as 250 mV (vs. SCE) in phosphate buffer solution at $37 \text{ }^\circ\text{C}$ [3]. In another study, pitting potentials of 800 mV were found by Rondelly in deaerated physiological solution for NiTi flat specimen [1]. Cross sections of two different dimensions of the rod were tested (2 and 8 mm), where it was found that low diameter electrode experienced onset of crevice corrosion at potentials 250 mV vs. SCE, while for larger specimen at 1000 mV in Hank's solution at $37 \text{ }^\circ\text{C}$. Beside susceptibility of crevice corrosion for the samples mounted in resins, there is probably the effect of microstructure that plays a major role in different pitting susceptibility properties of NiTi alloy. It is believed that dental wire in cross-section would show the worst corrosion characteristics.

For a realistic evaluation of the corrosion properties of the metal alloy it is important to study their characteristics in the "as received" state, with a surface oxide film as achieved from technological

procedure. The electrochemical properties of NiTi sheet with surface oxide film are better than NiTi wire with surface oxide film (Figure 1, Table 1). The corrosion potential for NiTi sheet with surface oxide film is more negative (-0.207 V) than the one for NiTi wire with oxide film (-0.143 V), both were more positive than in the case of without oxide film, as described in previous case. Corrosion current density for NiTi sheet with surface oxide is as low as 15.4 nA/cm² (see values in Table 1). Passive current densities are comparable, while in the case of NiTi sheet with surface oxide film, the breakdown potential is much higher, at 1.27 V. Scanning in the reverse direction showed negative hysteresis pointing at good repassivation properties of investigated samples in the environment and conditions studied. Repassivation potentials in this case are lower (0.32 V for NiTi sheet and 0.06 for NiTi wire) when compared to samples without oxide film. The reverse current density for wire exhibits numerous oscillations in anodic current path, pointing at possible metastable passive state. With the surface oxide film present it can be concluded that NiTi sheet exhibited better corrosion properties when compared to NiTi dental wire samples. Polarization resistance measurements prove that observation, R_p of NiTi sheet with surface oxide film is 2.57 M Ω cm² and 1.38 M Ω cm² for NiTi dental wire with surface oxide film.

Higher values for anodic current densities and positive hysteresis in the reverse scan were reported for NiTi wire electrode which is in contradiction with our observation. The possible explanations for such a difference are the following: higher experiment temperatures, at body temperature, 37 °C [3], higher content of chlorides in phosphate buffer solution (PBS, pH 7.4 contains 8.77 g/L NaCl, 1.42 g/L Na₂HPO₄ and 2.72 g/L KH₂PO₄) and the cross sectioned part of the exposed polished NiTi archwire. Namely, as it was reported by Aziz Kerrzo et al. [3], surface modification techniques did not influence the repassivation kinetics- which is in contradiction with the results obtained in our experiments. But comparing the content of total chloride in PBS solution, used by Aziz Kerrzo et al. [3], and chloride in simulated saliva, as suggested by Duffo and Castillo [20], it can be expected that the difference arises from chloride content, thus, 0.15 M chloride content induces the pitting corrosion in simulated body fluids but showed repassivation characteristics in artificial saliva solutions (chloride content 0.123 M), both for polished NiTi wire and polished sheet. Also, the cross-section in comparison to exposure of the whole longitudinal surface of the archwire might have given a rise to pitting susceptibility and lower corrosion properties of cross sectioned NiTi sample. The microstructure might have such a big influence, as already reported by authors in the case of steel wires in pore water [23]. In the previous case, the delicate edges of microstructural grains that were exposed as cross-section are more intense corrosion-wise than the elongated grains and its surface when the sides of the wire are exposed.

Fig. 3. Potentiodynamic curves for NiTi dental wire a) and NiTi sheet b), at different long term exposure times in simulated saliva solution at a scan rate 1 mV/s.

Long term exposure to corrosive environment of simulated saliva gave insight to possible different behaviour of the studied samples with and without oxide film and are presented in Figure 3. The time of exposure varied in the length, from 48 h to 72 h.

For NiTinol dental wire the corrosion current of the freshly polished wire was the smallest, 16 nA/cm^2 in comparison with as-received wire, where corrosion current density was slightly higher 81 nA/cm^2 . Corrosion potential of freshly polished wire was more positive ($E_{\text{corr}} = -0.17 \text{ V}$) than for as received wire ($E_{\text{corr}} = -0.54 \text{ V}$). Freshly polished surface of NiTinol wire exhibited well defined passive region with approximate current at around $40 \text{ } \mu\text{A/cm}^2$, where the breakdown potential in simulated saliva was at 0.98 V . For as received wire the passive range extended through wider range with some current fluctuation in voltage range from 0.7 V to 1.4 V vs. SCE. Breakdown potential was estimated at around 1.3 V . Anodic current for as received wire was higher than for freshly polished wire, it drifted from $6 \text{ } \mu\text{A/cm}^2$ to $80 \text{ } \mu\text{A/cm}^2$.

However, electrochemical behaviour of NiTi sheet of as received surface finish and polished electrode was similar. Corrosion current densities and corrosion potentials for as received surface finish and polished NiTi sheet electrode are similar, reaching value of $61 \text{ } \mu\text{A/cm}^2$ and $13 \text{ } \mu\text{A/cm}^2$ and -0.18 V and -0.12 V , respectively. Anodic currents are similar for as received NiTi sheets and freshly polished electrode. Breakdown potentials for as received and polished samples were 1.2 V and 1.15 V , respectively.

To conclude, electrochemical behaviour of NiTi sheet in two different surface finish is more similar than electrochemical behaviour of as received wire and polished wire. Electrochemical behaviour of as received wire thus, is very different from NiTi sheets in both forms and polished dental NiTi wire, respectively. Microstructural characteristics of alloy as well as surface finish had a great effect on electrochemical and corrosion properties of NiTinol in studied environment.

When comparing cyclic polarization tests and tests after long term exposure (48 h), it can be concluded that electrochemical properties of wire without oxide film has better electrochemical properties than NiTi sheet without oxide film. However, there is some discrepancy noticed between the two experiments for the samples with its as received oxide film: after 48 h NiTi wire exhibits better properties than NiTi sheet as observed from lower corrosion current densities for the wire, but after CP tests, NiTi sheet exhibited lower corrosion current densities and higher R_p than NiTi wire with surface oxide film present. Thus, it is important, which microstructural plane is studied, what sample (microstructural characteristics), surface finish, length of the corrosion tests and nature of experiment.

3.3 Tribocorrosion tests

Since NiTi alloy undergoes different modes of wear during its operation, it is very important to study corrosion properties of the alloy simultaneously with its wear. In situ information of the surface state of the NiTi alloy at open circuit potential can be followed when combining wear in simulated saliva solution. The mechanical and chemical data acquired before after and during sliding tests is very useful for getting a better understanding of the tribocorrosion processes that take place on samples with and without oxide film. Coefficient of friction (COF), corrosion potential measurement (E_{corr}), versus time curves for for NiTi sheet with and without surface oxide film and for dental archwire without oxide film at speed 5 mm/s and different normal loads in simulated saliva are shown in Fig. 4. The normal load was varied from 1 N, 2 N to 5 N. Each measurement was repeated at least twice and very repetitive measurements were obtained.

For tribocorrosion experiments on NiTi sheet without surface oxide film (Figure 4 a), the normal load affected the changes in corrosion potential: the higher the force, the more negative changes in corrosion potentials during rubbing were observed. The variation of the corrosion potential value during rubbing is higher for higher applied loads. It was previously reported that during wear (sliding), lowering of the open circuit potential is frequently experienced, as well as with increasing normal loads and/or sliding velocity [24]. Also, it was observed, that the higher the load, the quicker was the run-in period to the stable coefficient of friction for NiTi without surface oxide film in simulated saliva solution. COF was as high as 0.80 for the load 1 N and 0.7 for the loads 2 and 5 N, respectively. The repassivation is dependent on the wear regime in the wear track. It was 30 s at the load 1 N, 60 s for 2 N and 100 s for the normal load 5 N. The different repassivation times are though affected by the exposed, newly uncovered surface after wear.

In general, the coefficient of friction curves for all tested materials show similar overall shapes (Fig. 4a). COF curves were characterized by two friction regimes; a run-in period, represented by a rapid increase in the value of the coefficient of friction followed by a steady state where the coefficient of friction became independent of time.

Figure 4b shows the decrease of measured potentials on NiTi sheet with oxide film once the rubbing had started. The higher the force, the lower the measured corrosion potential during rubbing. Initially lower measured OCP potential for the sample worn with 1 N force, has decreased for approximately 200 mV, but relatively high fluctuations in measured potential were observed. It is assumed that the normal force 1 N was that low that did not damaged the surface film through entire rubbing period. Once rubbing had stopped, the open circuit potential returned to the initial equilibrium electrochemical potential in 20 s. It was observed that the initial OCP potential was reached more quickly for less worn surface, thus it was the quickest for sample worn with 1 N (20 s) force, then 2 N (70 s) and for sample worn with 5 N force (100 s).

Coefficient of friction was very high, as high as 0.7 for the normal loads 2 N and 5 N. The run in period is smaller for NiTi sheet samples with the surface oxide film when compared to samples without surface oxide

film (Figure 4 b). COF increased in the first minutes of rubbing for smaller normal forces as there is evident difference in coefficient of friction on oxide film and base underlying alloy. Once the alloy matrix is reached, the coefficient of friction stayed the same during the entire rubbing period.

Special behaviour was observed when a low normal force of 1 N was used. The coefficient of friction increased in the first cycles of rubbing, it was constant for 500 s, than it was decreased again after 600 s of rubbing. At the same time, the increase of the measured corrosion potential was detected. Repetitive measurements always showed similar characteristics. Namely, the applied normal force is low enough not to damage surface oxide film on the wear track. As it was not destructive, the surface film was quickly repaired, as could be observed from the decrease in coefficient of friction and from the increase in electrochemical potential during the rubbing in simulated saliva with 1 N normal force.

Fig. 4. OCP potential, friction coefficient and friction force vs. time for NiTi sheet without surface oxide film (a), with surface oxide film (b) and dental wire without surface oxide film (c) against Al₂O₃ ball counterbody at different applied normal forces in simulated saliva

The fixation of the sample was a difficult so that the experiment for dental wire enabled investigation only for dental wire without surface oxide film with two different applied loads, 1 N and 2 N. The tribocorrosion study is presented on Figure 4 c. During the rubbing, the coefficient of friction is as high as 0.8 for load 1 N and 0.7 for load 2 N. It varied more for the 1 N applied load. The run in period is shorter for the higher applied load in the case of dental wire. The electrochemical potential lowered to a great extent for 0.25 V for 1 N and 0.30 V for the load 2 N. The variation of potential during rubbing is very smooth when comparing to sheet samples without oxide film. Passive film recovered in 30 s after stopping the rubbing and the potential reached the initial value.

3.4. Wear track analysis

The wear tracks were observed by SEM and the wear volume loss of the samples was determined by measuring the cross section of the wear tracks by contact profilometry (Figure 5 and 6).

It can be seen that the wear tracks were different in dependence of the load used, the type of the sample and type of media (ambient air, saliva).

Fig. 5. Wear track of NiTi sheet without oxide film after tribological wear ($F_N = 5$ N) in ambient conditions a) and in simulated saliva b)

Fig. 6. Wear track of NiTi sheet with oxide film (as received) after tribological wear ($F_N = 5$ N) in ambient conditions a) and in simulated saliva b)

A wear track width and wear track depth increases with the applied normal force. Wear track observation pointed at two possible wear mechanisms, one being abrasion and the other delamination. The wear track consisted of parallel grooves as a result of sliding of Al_2O_3 ball against the investigated sample. The material was displaced to the edges forming topography observed as extruded ridges (Figure 6). General observation of the investigated samples showed that the amount of wear debris increases with the applied normal force. Wear debris sizes of delamination plates are of 20-150 μm for the samples where the applied load was 5 N (Figure 6). Such delamination is a result of harder asperity on soft surface which induces plastic deformation. At repeated loading, microcracks eventually propagate to critical length, become unstable and sheet like wear debris is generated. The number of wear debris for tribocorrosion tests are smaller (Figure 6b) than the number for the wear in atmospheric conditions (Figure 6a). Also, the sizes of delamination particles became larger with the applied normal force. Similar wear mechanisms and type of damage was observed for TiNi alloys, investigated by sliding wear experiments in dry conditions [11].

EDS analysis outside the track, in the track and on particular inclusions showed different atomic structures (Table 2). Only results for tribocorrosion wear for NiTi sheet with and without surface oxide film in simulated saliva are presented and discussed.

The composition of the passive film on the samples with surface oxide film outside the track (area No. 1, Figure 5a) is as follows: Ti and Ni almost at atomic equilibrium and 24.0 % of oxygen. Composition changes in the wear track. It becomes richer in oxygen and also aluminium is detected in small percentage (2.46 %) as a residue of wear with Al₂O₃ ball counterpart (area No. 2, Fig 5 a). Inclusion consists of Ti and Ni at equilibrium and a relatively high percentage of oxygen and aluminium (Table 2). Similar observations were found for polished samples (without oxide film). The composition outside the track gave values for NiTi composition of the alloy with no detected oxygen. In the track the amount of oxygen was increased and some traces of aluminium were found, while on the biggest inclusions the amount of oxygen and aluminium were very high pointing at high abrasive wear of Al₂O₃ counterpart body against NiTi sample. EDS analysis showed similar composition at the comparable positions on NiTi wear track in dependence of different loads applied.

The hardness was also measured outside and inside the wear track, as well as on the inclusions.

After tribocorrosion experiments, the results for NiTi sheet without surface oxide film, loaded with 2 N normal load, in simulated saliva showed that the hardness was lower outside the wear track (311 HV) and was increased in the wear track to 339 HV. This increase in surface hardening is a result of rubbing, and has been observed previously on other materials [25]. Hardness in the wear track thus is a result of work hardening, induced internal stresses during oxide film growth, stress release due to dissolution or other changes during corrosion processes. Since the hardness in the wear track after tribological wear in ambient air was lower (331 HV) than the one after tribocorrosion wear in the solution, it could be observed that wear in corrosive environment affects hardness to different extent than in ambient air. The hardness, measured on inclusions was as high as 395 HV on inclusions measured on samples without surface film and 430 HV on samples with surface oxide film. The high hardness of inclusions are worn debris from Al₂O₃ counterbody that immersed into wear track during tribocorrosion wear. The hardness was measured also on NiTi archwire without surface oxide film (345 HV) and it was higher than on NiTi sheet (315 HV). The higher hardness resulted in shallower wear profile (not shown) on dental archwires. Also, the inclusions were not detected in the wear track of NiTi archwire. The mechanical resistance of dental archwire is greater and wear is lower for these harder polished archwire samples.

The wear rate was determined according to mechanistic approach by measuring the wear volume [26]. The total wear is a sum of mechanical and corrosion wear:

$$V_{\text{tot}} = V_{\text{mech}} + V_{\text{chem}} \quad \text{Eq. (1)}$$

Wear volumes were determined from profiles and the lengths of wear tracks, where the wear volume is defined as volume wear in a definite measure of time. The wear rates are presented in Table 3, where total

wear is defined by tribocorrosion experiments, mechanical wear is a contribution due to tribological wear in ambient air, whereas chemical wear is deduced from the equation above.

At lower load forces (1 N), the total chemical wear could not be defined, since the wear rate in dry conditions is higher than wear rate in simulated saliva. Wear rate was higher for NiTi sheet with surface oxide film present. Similarly was found previously, where the wear rate was more severe on annealed 316L samples compared to polished samples [27]. It was explained that large accumulation of strain occurred at passive potentials which then facilitated crack formation at microstructural defects [27]. At conditions studied, the chemical wear presents a smaller contribution to the total wear rate than mechanical wear, probably due to very good repassivating properties of the studied alloy. The highest contribution of chemical wear was detected at loads of 2 N, where chemical wear contribution was around 33 % (Table 3). Thus, at higher loads, the mechanical wear dominates the chemical wear. It was found with our experiments and in published literature [27], that for passive materials, the wear rate is increased at passive potentials when compared to cathodic potentials. NiTi alloy at open circuit potentials represent passive potentials, where repassivation is enabled and thus wear rate of such material is of great concern.

4. Conclusions

Metallographic, electrochemical, tribocorrosion experiments, as well as surface analysis were performed on the two microstructurally different NiTi alloys with and without surface oxide film in order to study the effect of microstructure on chemical and physical properties in artificial saliva.

NiTi sheet in cross section and longitudinal plane is microstructurally different from NiTi dental archwire.

It is important whether the sample investigated is longitudinal plane of the sheet alloy or cross section or longitudinal plane of the wire (rod).

Cyclic polarization tests showed that it is very important to know the state and the microstructural plane of the sample that is being studied, especially when results are compared to previously reported ones.

- Our experiments showed that electrochemical parameters, such as corrosion potential, corrosion current density, breakdown potential and repassivation potentials of NiTi sheet samples and longitudinal exposed surface of NiTi archwire without surface oxide films are very similar, but with distinguishing polarization resistances. With surface oxide film in as received state, the NiTi sheet samples showed better corrosion properties.

- Electrochemical results in simulated saliva showed good repassivation properties of the investigated microstructural planes and surface states of NiTi alloy.

- However, after long term exposure the electrochemical properties of samples without oxide film are comparable to cyclic polarization results but wire in as received form exhibited better corrosion properties than as-received NiTi sheet, which means that in long term performance, oxide film formed on wire is more corrosion resistant than one on NiTi sheet.

- Tribocorrosion experiments confirmed synergistic effect of combined wear and chemical process observed as higher wear rate of NiTi alloy in simulated saliva compared to dry tribological wear.

- All investigated samples showed very good repassivation properties after tribological wear in simulated saliva.

- During tribological wear in simulated saliva plastic deformation in wear track occurs with many inclusions of the worn surface film and counterbody parts in the wear track. The hardness of the wear track is increased while coefficient of friction vary in dependence of the hardness of the material. The coefficient of friction increases in the first cycles of wear and then stays stable for all tested loads.

As an overall conclusion it can be said that tribocorrosion studies on exposed surfaces (longitudinal plane of sheet sample and longitudinal surface of the wire) do not enable to differentiate between microstructural

effect on tribocorrosion properties. Corrosion contribution to total wear is bigger for samples with oxide film. Thus, in the case of possible damage when handling dental wire, cross-section of the wire with many inclusions would show the weaker corrosion properties, leading to quicker corrosion and mechanical failure. These findings have to be confirmed in future studies.

Acknowledgements

This work has been sponsored by Slovenian Research Agency grant No Z2-2298. Help of laboratory staff-Viljem Kuhar and Monika Prosenc is gratefully acknowledged.

References

- [1] G. Rondelli, Corrosion resistance tests on NiTi shape memory alloy, *Biomaterials* 17 (1996) 2003–2008.
- [2] S. Rosi, F. Deflorian, A. Pegoretti, D. D’Orazio, S. Gialanella, Chemical and mechanical treatments to improve the surface properties of shape memory NiTi wires, *Surf. Coat. Technol.* 202 (2008) 2214–2222.
- [3] M. Aziz-Kerrzo, K. G. Conroy, A. M. Fenelon, S. T. Farrell, C. B. Breslin, *Biomaterials* 22 (2001) 1531–1539.
- [4] N. Figueira, T.M. Silva, M.J. Carnezim, J.C.S. Fernandes, Corrosion behaviour of NiTi alloy, *Electrochim. Acta* 54 (2009) 921–926.
- [5] A. Michiardi, C. Aparicio, J.A. Planell, F.J. Gil, Electrochemical behaviour of oxidized NiTi shape memory alloys for biomedical applications, *Surf. Coat. Technol.* 201 (2007) 6484–6488.
- [6] L.Tan, R.A. Dood, W.C. Crone, Corrosion and wear corrosion behaviour of NiTi modified by plasma source ion implantation, *Biomaterials* 24 (2003) 3931–3939.
- [7] D. Vojtěch, M. Voděrová, J. Fojt, P. Novák, T. Kubásek, Surface structure and corrosion resistance of short-time heat treated NiTi shape memory alloy, *Appl. Surf. Sci.* 257 (2010) 1573–1582.
- [8] J. Wang, N. Li, G. Rao, E. Han, W. Ke, Stress Corrosion cracking of NiTi in artificial saliva, *Dental Materials* 23 (2007) 133–137.
- [9] M. Abedini, H.M. Ghasemi, M. Nili Ahmadabadi, Tribological behaviour of NiTi alloy against 52100 steel and WC at elevated temperatures, *Materials Characterization* 61 (2010) 689–695.
- [10] M. Abedini, H.M. Ghasemi, M. Nili Ahmadabadi, Tribological behavior of NiTi alloy in martensitic and austenitic states, *Materials and Design* 30 (2009) 4493–4497.
- [11] C. Zhang, Z.N. Farhat, Sliding wear of superelastic TiNi alloy, *Wear* 267 (2009) 9394–9400.
- [12] N. Shevchenko, M-T. Pham, M.F. Maitz, Studies of surface modified NiTi alloy, *Appl. Surf. Sci.* 235 (2004) 126–131.
- [13] D. Vojtěch, J.Fojt, L. Joska, P. Novák, Surface treatment of NiTi shape memory alloy and its influence on corrosion behaviour, *Surf. Coat. Technol.* 204 (2010) 3895–3901.

- [14] K.W. Ng, H.C. Man, T.M. Yue, Characterization and corrosion study of NiTi laser surface alloyed with Nb or Co, *Appl. Surf. Sci.* 257 (2011) 3269–3274.
- [15] D. Starosvetsky, I. Gotman, TiN coating improves the corrosion behavior of superelastic NiTi surgical Alloy, *Surface and Coatings Technology* 148 (2001) 268–276.
- [16] A. Kumar, D. Kaur, Nanoidentation and corrosion studies of TiN/NiTi thin films for biomedical applications, *Surf. Coat. Technol.* 204 (2009) 1132–1136.
- [17] D. Oui, A.Wang, Y.Yin, Characterization and corrosion behaviour of hydroxyapatite/zirconia composite coating on NiTi fabricated by electrochemical deposition, *Appl. Surf. Sci.* 257 (2010) 1774–1778.
- [18] X.M. Liu, S.L. Wu, Paul K. Chu, C.Y. Chung, C.L. Chu, K.W.K. Yeung, W.W. Lu, K.M.C. Cheung, K.D.K. Luk, Effects of water plasma immersion ion implantation on surface electrochemical behaviour of NiTi shape memory alloys in simulated body fluids, *Appl. Surf. Sci.* 253 (2007) 3154–3159
- [19] L. Neelakantan, S. Swaminathan, M. Spiegel, G. Eggeler, A.W. Hassel, Selective surface oxidation and nitridation of NiTi shape memory alloys by reduction annealing, *Corros. Sci.* 51 (2009) 635–641.
- [20] G.S. Duffo, Q. Castillo, Development of artificial saliva solution for studying the corrosion behaviour of dental alloys, *Corrosion* 60 (2004) 594–602.
- [21] W. Stephen Tait, *An Introduction to electrochemical corrosion testing for practicing Engineers and scientists*, 1994, USA.
- [22] http://en.wikipedia.org/wiki/Nickel_titanium (11.2.2012)
- [23] J. Kovač, M. Bajt Leban, A. Legat, Detection of SCC on prestressing steel wire by the simultaneous use of electrochemical noise and acoustic emission measurements. *Electrochim. acta.* 52 (2007) 7607–7616.
- [24] J-P- Celis, P. Ponthiaux, F. Wenger, Tribo-corrosion of materials: Interplay between chemical, electrochemical and mechanical reactivity of surfaces, *Wear* 261 (2006) 939–946.
- [25] S. Mishler, A. Spiegel, M. Stemp, D. Landolt, Influence of passivity on the tribocorrosion of carbon steel in aqueous solutions, *Wear* 251 (2001) 1295–1307.
- [26] S. Mischler, Triboelectrochemical techniques and interpretation methods in tribocorrosion: A comparative evaluation, *Tribology International* 41 (2008) 573–583.
- [27] A. Bidiville, M. Favero, P. Stadelmann, S. Mischler, Effect of surface chemistry on the mechanical response of metals in sliding tribocorrosion systems, *Wear* 263 (2007) 207–217.

Figure Captions

Fig. 1: Microstructural examination of NiTi_{inol} superelastic sheet a) cross-section and b) longitudinal view and NiTi archwire c) cross-section and d) longitudinal view.

Fig. 2: Cyclic polarization scans for NiTi sheets and wires: a) without surface oxide film, b) with oxide film, in simulated saliva at a scan rate 1 mV/s.

Fig. 3: Potentiodynamic curves for NiTi dental wire a) and NiTi sheet b), at different long term exposure times in simulated saliva solution at a scan rate 1 mV/s.

Fig. 4: OCP potential, friction coefficient and friction force vs. time for NiTi sheet without surface oxide film (a), with surface oxide film (b) and dental wire without surface oxide film (c) against Al₂O₃ ball counterbody at different applied normal forces in simulated saliva.

Fig. 5: Wear track of NiTi sheet without oxide film after tribological wear ($F_N = 5$ N) in ambient conditions a) and in simulated saliva b).

Fig. 6: Wear track of NiTi sheet with oxide film after tribological wear ($F_N = 5$ N) in ambient conditions a) and in simulated saliva b).

Table 1: Electrochemical parameters for NiTi dental wire and sheet (E_{corr} and j_{corr} estimated from CP curves, $\nu=1$ mV/s, R_p from linear polarization measurements, $\nu=0.1$ mV/s)

	sheet	wire	NiTi sheet as received	NiTi wire With surface oxide film
E_{corr} [V]	-0.291	-0.267	-0.207	-0.143
j_{corr} [A/cm ²]	$74.0 \cdot 10^{-9}$	$45.9 \cdot 10^{-9}$	$15.4 \cdot 10^{-9}$	$44.2 \cdot 10^{-9}$
R_p [M Ω cm ²]	0.824	1.19	2.57	1.38
E_b [V]	1.10	1.20	1.27	1.05
E_{tp} [V]	0.9	0.86	0.32	0.06

Table 2: EDS analysis at different spots after tribocorrosion testing in simulated saliva, load force 5 N (Figure 5 a and 6a)

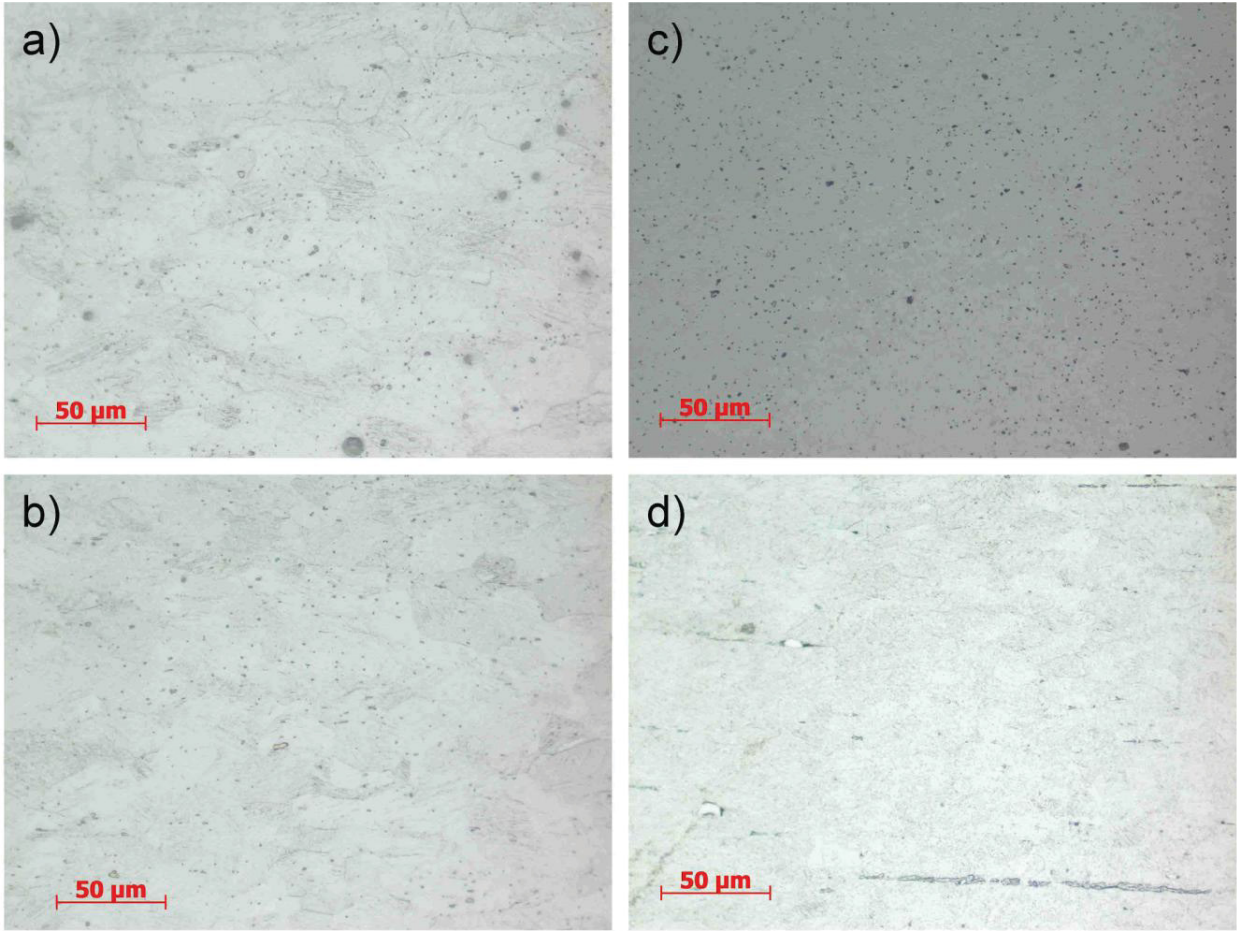
	Ti	Ni	O	Al
NiTi sheet without surface oxide film				
Out of the track	50.	50		
In the track	42.5	43.0	13.8	0.7
inclusion	18.8	18.7	52.5	10.0

NiTi sheet with surface oxide film				
Out of the track	38.8	37.2	24.0	
In the track	33.6	33.8	30.1	2.5
inclusion	19.0	17.9	54.1	9.0

Table 3: Wear rate [cm³/s] during tribocorrosion and tribological wear of NiTi sheet samples

	NiTi sheet without surface oxide film			NiTi sheet with oxide film		
	<i>Total wear</i>	<i>Mechanical wear</i>	<i>Corrosion wear</i>	<i>Total wear</i>	<i>Mechanical wear</i>	<i>Corrosion wear</i>
1 N	$0.045 \cdot 10^{-8}$	$0.18 \cdot 10^{-8}$		$0.14 \cdot 10^{-8}$	$0.41 \cdot 10^{-8}$	
2 N	$0.61 \cdot 10^{-8}$	$0.40 \cdot 10^{-8}$	$0.21 \cdot 10^{-8}$ (34 %)	$0.99 \cdot 10^{-8}$	$0.66 \cdot 10^{-8}$	$0.33 \cdot 10^{-8}$ (33 %)
5 N	$1.63 \cdot 10^{-8}$	$1.43 \cdot 10^{-8}$	$0.20 \cdot 10^{-8}$ (12 %)	$1.75 \cdot 10^{-8}$	$1.67 \cdot 10^{-8}$	$0.08 \cdot 10^{-8}$ (4.6 %)

Figure 1:



* corresponding author: T. Kosec: tadeja.kosec@zag.si, tel. 00 386 1 2804547

Figure 2:

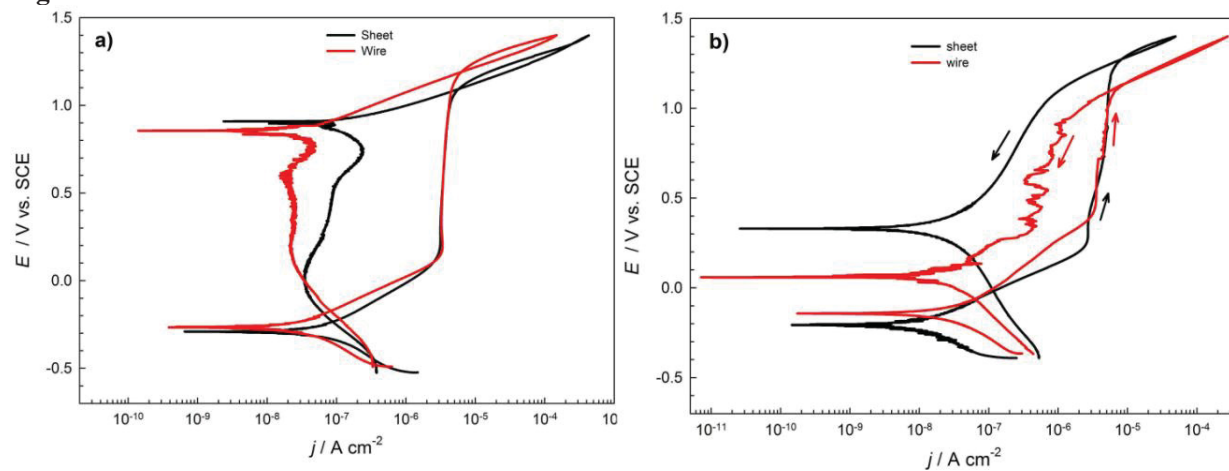
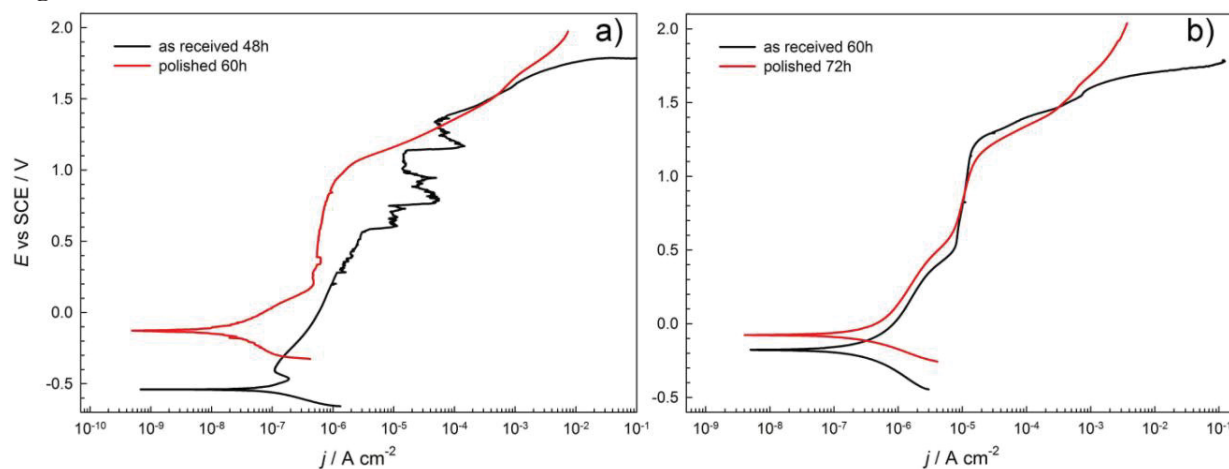


Figure 3:



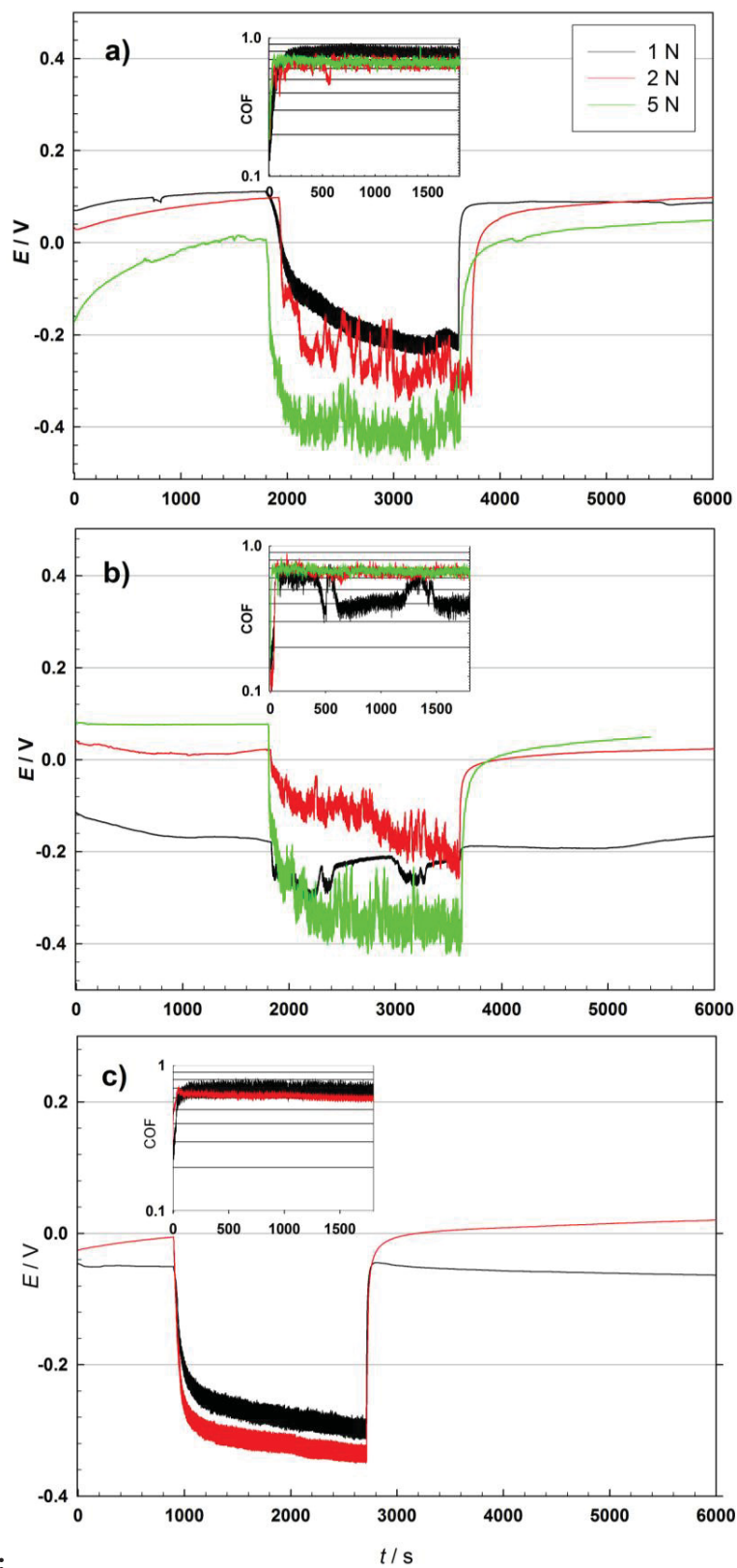
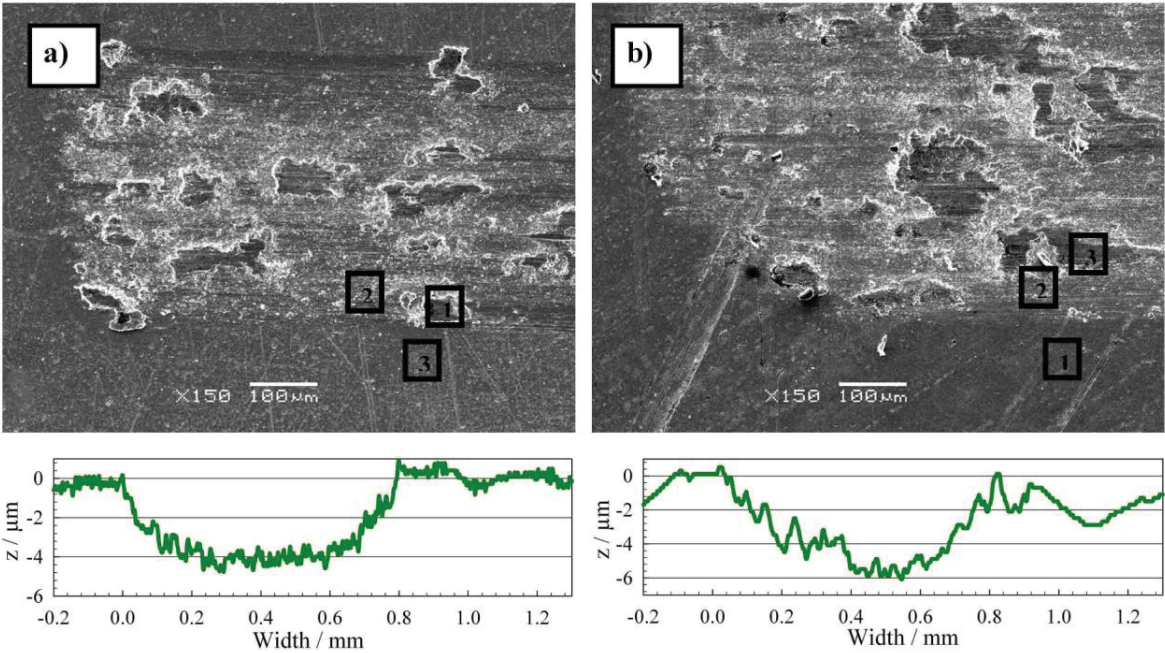


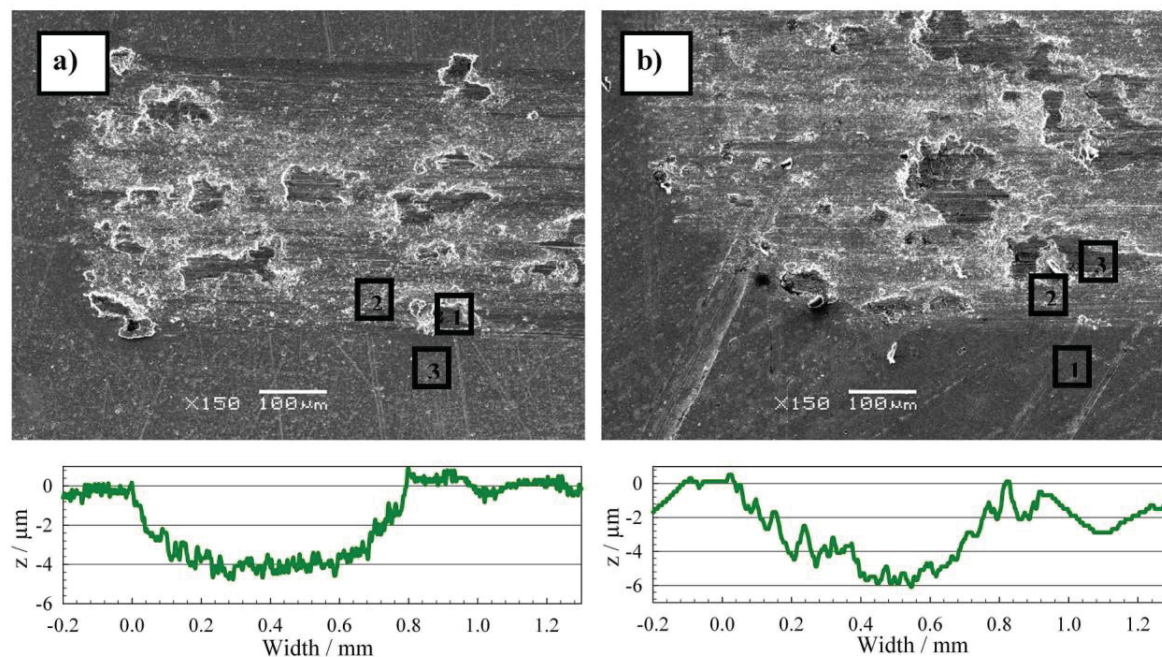
Figure 4:

Figure 5:



* corresponding author: T. Kosec: tadeja.kosec@zag.si, tel. 00 386 1 2804547

Figure 6:



***Suggested Reviewers**

Possible reviewer:

Stefano Mischler,
Ecole Polytechnique Federale de Lausanne (EPFL), Laboratory for Metallurgical Chemistry,
CH-1015 Lausanne, Switzerland
Tel.: +41 21 693 2954; fax: +41 21 693 3946.
Stefano.mishler@epfl.ch

***Highlights**

Highlights

- Tribocorrosion of NiTi alloys is investigated in simulated saliva.
- Two microstructurally different alloys are investigated: dental archwire and NiTi sheet.
- Synergistic effect of combined wear and chemical process observed as higher wear rate of NiTi alloy is reported.

Tribokorozija in tribokorozijsko preskušanje

Tadeja Kosec

Zavod za gradbeništvo Slovenije, Dimičeva 11, 1000 Ljubljana

Povzetek

V prispevku so predstavljene osnove tribokorozijskih procesov. Tribokorozijski proces je korozijski proces, ki nastane ob sočasnem drgnjenju ali obrabi materiala. Zaradi odstranjevanja oksidnih plasti je korozijski proces zato največkrat pospešen. Za spremljanje korozijskih procesov potrebujemo posebno preskuševališče - tribometer, predelan za možnost spremljanja elektrokemijskih procesov v troelektrodni korozijski celici. Seznanimo se z različnimi možnostmi tribokorozijskega preskušanja, možnimi metodami za tribokorozijsko spremljanje procesov ter predstavimo tipične primere tribokorozijskega preskušanja.

Abstract

Basic introduction to tribocorrosion processes is given. Tribocorrosion process is a corrosion process which results from simultaneous rubbing, fretting of metals. Corrosion process is in most cases accelerated process due to removal of oxide films.

For tribocorrosion study a special tribocorrosion system is needed-it consists of tribometer with specially constructed three-electrode electrochemical cell. Different setups for possible tribocorrosion study are presented as well as different electrochemical techniques that enable to study tribocorrosion processes. Different case studies are presented as well.

1. Splošno o tribokoroziji

Pri relativnem gibanju kontaktnih površin je tribološki kontakt zelo zapleten proces, saj vključuje simultan proces trenja, deformacije in obrabe. Meja med mehanizmi na makro in mikro nivoju je težko določljiva, saj so med seboj prepleteni in povezani. V kolikor je pri procesih prisoten elektrolit (npr. oksidirano mazivo, kondenz, tkivo, slina) se mehanski procesi obrabe kombinirajo s korozijskimi. Tribološki proces vključuje tako spremembo materiala in spremembe, ki nastanejo kot rezultat skupnega delovanja obrabe in korozije. V splošnem omenjena kombinacija ni vsota, temveč sinergija obeh vrst procesov, zato so vplivi posameznih parametrov pri skupnih tribokorozijskih procesih izrazito nelinearni in nestacionarni.

Za uspešno poznavanje tribokorozijskega obnašanja materiala ni dovolj zgolj poznavanje tribološkega delovanja brez upoštevanja korozivnih razmer, kot tudi ni dovolj poznavanje kemijskega vedenja brez poznavanja vplivov obrabe. Zato tribokorozija kot veda zahteva interdisciplinarno obravnavo. V zadnjem času je povečano zanimanje za razumevanje uporabe različnih materialov in

njihovih kombinacij, kar sili tako raziskovalce kot inženirje k sodelovanju zaradi znanstvenih, ekonomskih in praktičnih interesov. Pridobivanje temeljitega vpogleda v mehanizme in določevanje kritičnih mehanskih in kemijskih vplivov na tribološki proces ima zelo velik pomen. Določene zakonitosti pri uporabi posameznih materialov v izbranih okoljih in določenih obremenitvah so sicer poznane, vendar je povezovanje znanj s področja tribologije in korozije materialov še vedno relativno neraziskano področje. Glavna vzroka za to sta težavnost simuliranja realnih pogojev in nestacionarnost procesov.

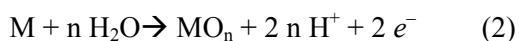
1.1 Opredelitev problema

Večina korozijskih procesov je po naravi elektrokemijskih. To vključuje prenos elektronov. Oksidacija kovine poteče na sledeč način:

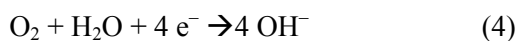


kjer je M kovina (*angl.* Metal) in n število izmenjanih elektronov na atom kovine. Na anodi se kovina raztaplja (reakcija 1) in prehaja iz oksidacijskega stanja 0 v n^{+} (tj. aktivna kovina).

Če pa se v elektrolitu tvori oksid (tj. pasivna kovina), poteče reakcija po enačbi (2)



Partnerska katodna reakcija je lahko sproščanje vodika, ki je favorizirana v kislem okolju, ter redukcija kisika, ki je favorizirana v bazičnem okolju in zračenih raztopinah. Pri tem potečejo reakcije po (3)–(5):

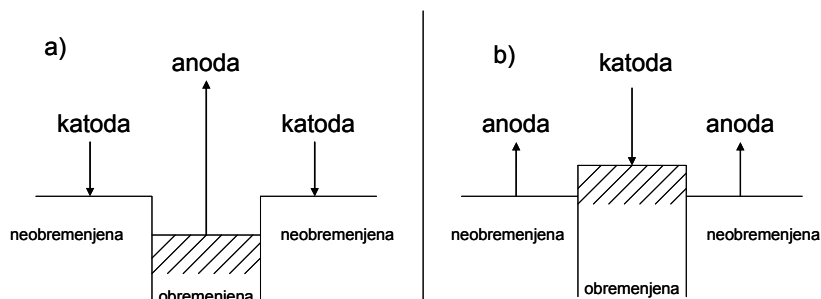


Pri običajnih korozijskih razmerah je reakcija (1) v ravnotežju z eno ali več redukcijskih reakcij po enačbi (3)–(5). Ko sta katodni in anodni tok enaka, govorimo o korozijskem potencialu, E_{kor} .

Tako je bilo razvitih nekaj vrst elektrokemijskih tehnik za spremljanje in kontroliranje korozijskega potenciala. Prav tako so jih uporabili v tribokorozijskih eksperimentih za spremljanje procesov med drgnjenjem. Največkrat uporabljene elektrokemijske tehnike so meritve korozijskega potenciala, potenciostatske ter potenciodinamske meritve. To pomeni, da je uporabnost konvencionalnih elektrokemijskih tehnik, ki so sicer primerne za napoved splošne korozijske obstojnosti, pri triboloških procesih delno omejena zaradi nestacionarnih razmer med tribološko obrabo. Zato je ovrednotenje elektrokemijskega vpliva pri sinergijski kombinaciji z mehanskimi procesi problematično, posledično pa je nezanesljivo tudi modeliranje teh procesov. Za spremljanje triboelektrokemijskih procesov je potrebno razviti in vključiti tudi druge elektrokemijske tehnike.

2. Korozijski in mehanski procesi

Drgnjenje materiala lahko vodi k lokalnem odstranjevanju pasivne plasti. Posledično lahko nastopi korozijska obraba, ki v kontaktnem področju spremeni lastnosti materiala. Pri tem se lahko v kontaktnem področju nalagajo korozijski produkti (prisotnost tretjega telesa, *angl.* Third Body), ki vplivajo na nadaljnji proces obrabe.



Slika 1: Grafični prikaz dveh različnih razmer pri drgnjenju, ko obremenjeni material deluje kot a) anoda ali kot b) katoda.

Mehanska obremenitev in hitrost drgnjenja vplivata različno na različne materiale (nepasivni materiali kot je baker in pasivni materiali kot nerjavno jeklo). V večina primerov obrabljen material deluje kot anoda (slika 1 a) in redkeje kot katoda (slika 1 b). To lahko spremljamo z ocenjevanjem procesa depasivacije.

Glavno zanimanje v tribokorozijskih študijah je ravno izbira pravih korozijskih razmer, saj drgnjenje ustvarja nestacionarne elektrokemijske razmere v kontaktnem področju. Omejitve pri določanju katodnih in anodnih mest (slika 1) lahko zaobidemo s tehnikami in kombinacijo metod. Elektrokemijske tehnike v splošnem zahtevajo stacionarne pogoje med potekom meritve. Dinamične in tranzientne razmere v kontaktnem področju vplivajo na dobljene rezultate. Iskanje metodologij za karakterizacijo osnovnih tribokorozijskih procesov oziroma študij medsebojnega vplivanja mehanskih in elektrokemijskih procesov predstavlja velike izzive za raziskovalce iz različnih področij. Poseben izziv predstavlja nadgradnja tranzientnih elektrokemijskih tehnik (elektrokemijski šum z akustično emisijo, metoda merjenja delnih tokov z mikroelektrodami), ki so bile v preteklosti razvite pri študiju drugih lokalnih oblik korozije (napetostno-korozijsko pokanje, špranjska korozija, korozija jekla v betonu) [1–3].

Tribokorozijske raziskave zaobjemajo tista področja, kjer lahko v agresivnih okoljih pride do korozijskih procesov, hkrati pa so vsi mehanski stiki tudi obrabno obremenjeni. To so materiali, katerih trajnost je problematična: pogonski agregati in materiali v procesni industriji (orodna jekla, siva litina) ter v biomedicini (nerjavna jekla, titanove zlitine in različni steliti). V splošnem je potrebno poznati osnovne parametre in njihov vpliv na tribokorozijske procese problematičnih kovinskih materialov pri tipičnih pogojih okolja (mehanska obremenitev, elektrolit). Potrebno je izdelati in proučiti primerne tehnike, ki bodo v bodoče lahko služile kot orodje za napoved tribokorozijskih

lastnosti določenih materialov pri realnih problemih: npr. uporaba biogoriv, lubrikantov, evalvacija učinkovitosti inhibitorjev, trajnost različnih vrst vsadkov.

3. »State of the art«

Tribološka obraba, ki poteče v prevodnem elektrolitu ob kontroliranih elektrokemijskih razmerah, je definirana kot triboelektrokemijski eksperiment. Definicija tribokorozije je bila prvič prikazana in omenjena v klasični tribološki knjigi med rezultati, ki jih je predstavil Barker [4]. Prvi standard, ki upošteva tako obrabo kot korozijo, je standard ASTM G119 – Standardna navodila za določanje sinergije med obrabo in korozijo, ki je izšel leta 1995 in bil kasneje dopolnjen [5].

Mehanizem obrabe, sinergistični učinek med obrabo in korozijo na tribokorozijske procese ter na drugi strani fenomen tretjega telesa priteguje v zadnjem času precej zanimanja [6–9]. Tako je Stack s sodelavci izdelala različne režime za prepoznavanje prevladujočega mehanizma med tribokorozijskim procesom. Za boljše razumevanje sinergističnega delovanja je določila koeficient K_c/K_w ter opredelila različne načine obrabe in korozije. Koeficient K_c/K_w , pri čemer je K_c obraba zaradi korozije in K_w tribološka obraba, služi kot kriterij za ocenjevanje medsebojne odvisnosti korozije in obrabe [6,7]. Če je koeficient K_c/K_w manjši od 0,01, je prevladujoč mehanizem obraba, če pa je koeficient manjši od $K_c/K_w \geq 10$, proces narekuje korozija. Med potekom drgnjenja prihaja do akumuliranja delcev, ki se sproščajo zaradi obrabe teles med kontaktom. Obrabljata se lahko en ali oba materiala v stiku. Landolt je s sodelavci poskušal opisati vplive delcev, nastalih zaradi obrabe (*angl.* Third Body), katerih vpliv je preiskoval z elektrokemijskimi eksperimenti [9,10]. Opazili so, da imajo delci, nastali zaradi obrabe, velik vpliv na tribokorozijske procese.

Različne tribološke obrabe, od ponavljajočih gibanj, enosmernih premikov, drgnjenja ter spinninga so študirali z različnimi triboelektrokemijskimi tehnikami. Odvisno od načina obrabe in kontaktne geometrije je lahko pričakovati različne odzive oz. načine obnašanja. In-situ analize tribološke obrabe v področju dentalne protetike so pokazale, da je obremenitev v kombinaciji s premiki majhne frekvence zelo zahteven process [11]. Študije so zelo raznolike, s tribološkega stališča so preiskovali sistem jezik/nebo [12]. Zelo kompleksen način kombinacije obrabe in korozijskega procesa lahko povzroča tvorbo obrabnih delcev in raztopljenih kovin, kar lahko povzroči krajšo življenjsko dobo kolčne proteze [13].

Med materiali za temeljne študije je najbolj pogosto izbran material nerjavno jeklo (tip 304L in 316L skupaj z sestavnimi kovinami, Cr, Ni) [14–16], biokompatibilni materiali, kot so kobaltove zlitine (Stelliti) [17,18] in titanove zlitine, med katerimi prevladuje TiAlV [13, 19–21]. V zadnjem času se je povečalo zanimanje po tribokorozijskem obnašanju tankih prevlek [22–24]. Bayon je s sodelavci proučeval PVD prevleke v prestavnih sistemih [22]. Prav tako je veliko objav s področja obrabe [23], upoštevajoč korozijo, ki pa ni povezana z njeno elektrokemijsko naravo. Med procesom obrabe in trenja so kemijske in strukturne spremembe, ki se dogajajo na DLC prevlekah med obrabo v

prisotnosti mineralnih olj študirali z Ramansko in X-žarkovno spektroskopijo [23]. Druga študija obravnava vplive trdote, debeline in strukture TiCO tankih plasti na tribokorozijsko vedenje [24]. Ocenjena sta tako posamezni kot medsebojni vpliv obrabe in korozije.

Prav tako, kot so študije razdeljene po različnih obravnavanih materialih, lahko razdelimo tribokorozijske študije glede na njihovo uporabo; nekatere so temeljne študije, druge so študije tribokorozijske v biomedicinske namene kot tudi študije trih tankih in proti obrabi odpornih prevlek.

Nekatere tehnike in metode so pogosto uporabljene, medtem ko so nekatere poredko. Med zadnjimi objavami S. Mischlerja se lahko spoznamo s kritično obravnavo glavnih elektrokemijskih tehnik ter metod za razumevanje tribokorozijskih procesov s posebnim poudarkom na procese drsenja in trenja pri študiju pasivnih kovin [25].

V skladu s prej omenjeno pregledno študijo [25] lahko tehnike razdelimo na tehnike spremljanja korozijskega potenciala, galvanske celice ter potenciodinamske tehnike.

Na podlagi potenciostatskih tehnik so nekateri avtorji razvili modele za napoved elektrokemijskega odziva pasivnih kovin na tribokorozijski process. Landolt je s sodelavci razvil model za pasivne kovine, ki se obrabljajo, in opisal tok, ki se spreminja med drgnjenjem kot funkcija hitrosti depasivacije in repasivacije [26]. Hitrost depasivacije je odvisna od obremenitve, hitrosti, trdote kovine, površinske topografije in kontaktne geometrije [26]. Tudi Olsson in Stemp sta izdelala model za napoved repasivacijske kinetike med drgnjenjem [27].

Pontiaux poudarja, da je glavni problem pri tribokorozijskih procesih ta, da pri dvosmernem sistemu obrabe, obrabna konica ustvarja nestalne (angl. non-steady) elektrokemijske razmere v področju kontakta [15]. Jemmely s sodel. je ugotovil, da se je vrednost toka med časom, ko material ni bil v procesu obrabe, zmanjševal zaradi repasivacije in se ponovno povečal, ko je obrabna konica potovala nazaj v primeru uporabe ponavljajočega dvosmernega tribometra [10]. Mnoge elektrokemijske tehnike pa zahtevajo stacionarne razmere med samo meritvijo. Dinamične in prehodne razmere v področju kontakta tako lahko drastično vplivajo na dobljene rezultate [15].

Le nekaj je objav, te so zelo redke, ki kot možno tehniko za proučevanje tribokorozijske uporabljajo elektrokemijski šum in elektrokemijsko impedančno spektroskopijo [15, 16]. Elektrokemijsko impedančno spektroskopijo so uporabljali le kot dodatno tehniko pred procesom obrabe in po njem [24]. Monticelli s sodelavci [20] pa je ugotovil, da je splošna stabilnost TiAlV zlitine v korozijskih razmerah dovolj stabilna, da so lahko izmerili impedančne spektre. Impedanca depasiviranega področja namreč prevlada nad celotno impedanco elektrode. Tudi merjenje z mrežo galvansko povezanih elektrod še ni bilo uporabljeno v triboelektrokemijskih študijah. Metoda merjenja delnih tokov z mikroelektrodami smo razvili študiju drugih lokalnih oblik korozije, kjer razlike med anodnimi in katodnimi mesti vplivajo na potek korozije [3]. Kot je poudaril Cellis s sodel., obremenjeno področje materiala, ki je podvržen drgnjenju, lahko deluje kot anoda ali kot katoda [28]. Tako uporaba mreže galvansko povezanih elektrod z uporabo elektrokemijskega šuma in akustične emisije predstavlja velik izziv v znanju na področju tribokorozijske.

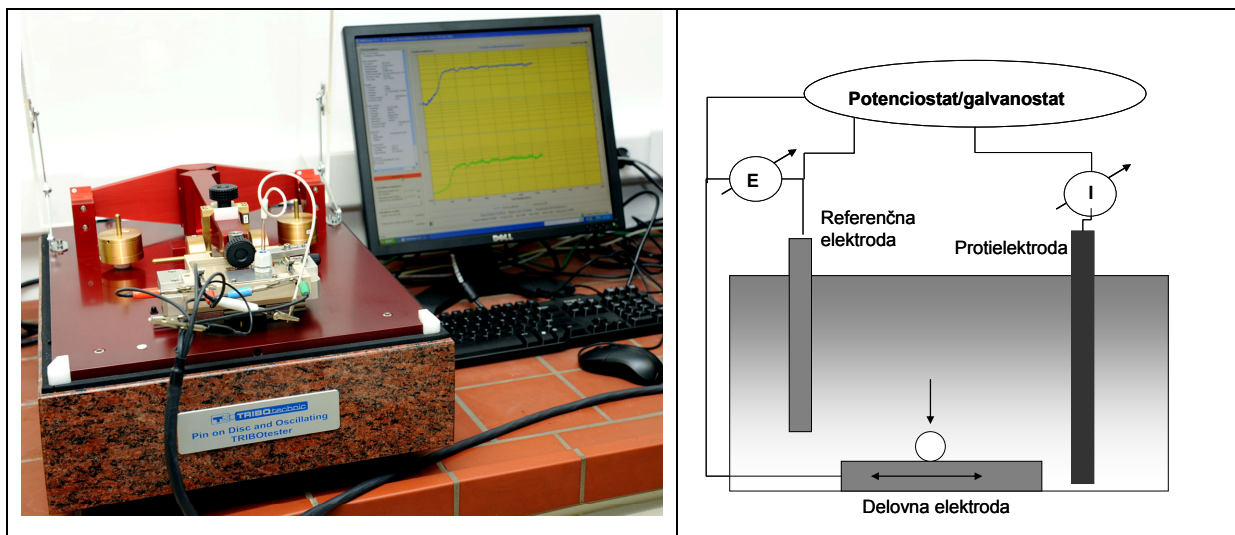
Poudariti je potrebno, da obstaja velika potreba po temeljnih raziskavah in kritičnemu ovrednotenju posameznih elektrokemijskih tehnik, ki se uporabljajo za tribokorozijske preiskave. Če povzamemo, večina temeljnih študij uporablja poteciostatsko tehniko v 80 % izbranih literaturnih virih. Druga najbolj uporabljena tehnika je bila merjenje korozijskega potenciala v 50 % primerih. V 10 % preiskane literature so uporabili potenciodinamsko tehniko kot orodje za spremljanje elektrokemijskih procesov, ta pa je problematična za uspešno interpretacijo rezultatov zaradi nestacionarnih pogojev, ki jih ta tehnika zahteva. Prav tako je nekajkrat uporabljena tehnika galvanskega člana.

Večina raziskav uporablja eno ali dve tehniki med opisanimi najpogostejše uporabljenimi tehnikami za spremljanje tribokorozijskih eksperimentov. Kot je bilo že bilo poudarjeno, le nekaj raziskav uporablja elektrokemijski šum in impedančno elektrokemijsko spektroskopijo pri študiju tribokorozijskih lastnosti, pri čemer mreža elektrod in akustična emisija kot dodatna tehnika k elektrokemijskemu šumu, še ni bila uporabljena. Tako lahko ugotovimo, da je na področju nadaljnjih in temeljnih študij možnih tehnik za študij tribokorozijskih procesov še veliko odprtih problemov in izzivov.

4. Tribokorozijsko preskuševališče

Tribokorozijsko preskuševališče je sestavljeno iz tribometra ter posebej za korozijske meritve predelano korozijsko celico. Prav slednja predstavlja velik problem za dejansko realizacijo tribokorozijskih preiskav. Na tržišču so dostopni različni tribometri (CSM instruments, Phoenix instruments) za raznovrstne tribološke študije trenja in obrabe materialov z ali brez prisotnosti lubrikantov. Obstajajo tudi bolj specializirane različice za testiranje pri nižjih ali višjih temperaturah ali v vakuumu. Aparat za tribokorozijske meritve mora biti ustrezno predelan ali pa posebno izdelan.

Prilagojen tribometer za elektrokemijske preiskave mora imeti nekatere njemu slične karakteristike, ki imajo prednost pred komercialnimi aparati. Te so: obremenitev na vzorec za natančno določeno silo, kontrolo parametrov, kot so hitrost drgnjenja, frekvenca in čas ter razpon sile nekaj N do nekaj mN ter materiali v stiku s korozijsko raztopino. Materiali morajo biti električno neprevodni: nosilec za obrabno telo, ohišje korozijske celice, nosilci za pritrditev vzorca. Najpomembnejša značilnost je elektrokemijska celica za spremljanje tribokorozijskih procesov, kjer predstavljajo kontakti za delovno elektrodo (preiskovan material), referenčno elektrodo (ponavadi nameščena na posebnem nosilcu) ter proti-elektrodo) poseben tehničen izziv.



Slika 2: Slika linearnega recipročnega tribometra z elektrokemijsko celico ter shema tipičnega tribokorozijskega preskuševališča

Na sliki 2 je prikazan linearni recipročni tribometer z elektrokemijsko celico ter shema tipičnega tribokorozijskega preskuševališča. Na spodnji sliki 3 pa sta predstavljena najpogostejša načina tribokorozijskega eksperimenta, glede na uporabljeno vrsto tribometra: pin on disk ali pa dvosmerni linearni tribometer.



Slika 3: Prikaz različnih obrab in načinov gibanja na tribokorozijskih sistemih: a) pin-on disc tribokorozijska obraba in b) linearna dvosmerna (*angl.* Reciprocating) obraba

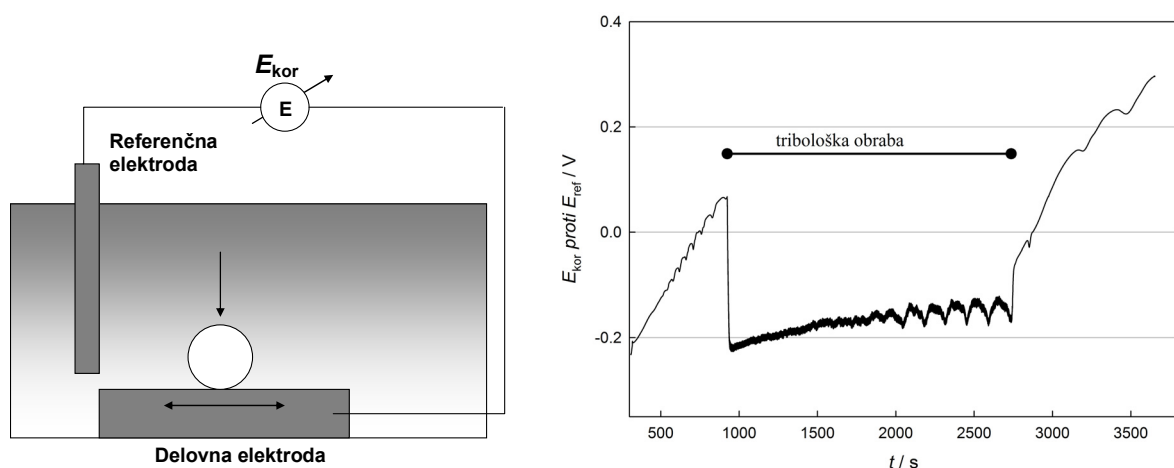
5. Elektrokemijske metode za tribokorozijsko preskušanje

Pri tribokorozijskih eksperimentih se med procesom obrabe posamezno uporabljajo naslednje elektrokemijske tehnike: merjenje korozijskega potenciala, galvanske celice, potenciostatske ter potenciodinamske meritve. Največkrat uporabljeni tehniki sta potenciostatska in tehnika s spremljanjem korozijskega potenciala.

Merjenje korozijskega potenciala med tribokorozijsko obrabo je zelo preprosta tehnika. Z njo pridobimo informacijo o stanju površine med drgnjenjem. Korozijski potencial, E_{kor} merimo med delovno in referenčno elektrodo (Slika 4). Ko se med obrabo odkriva kovina (obrabljena površina), je neto potencial elektrode spremenjen. Med tribološko obrabo potencial pade na nižje vrednosti, temu

pravimo katodna sprememba (*angl.* cathodic shift). Po končani tribološki obrabi se potencial zopet pomakne na višje začetne vrednosti. Na obrabljeni površini se v odvisnosti od narave kovinskega materiala različno hitro lahko tvori pasivna plast.

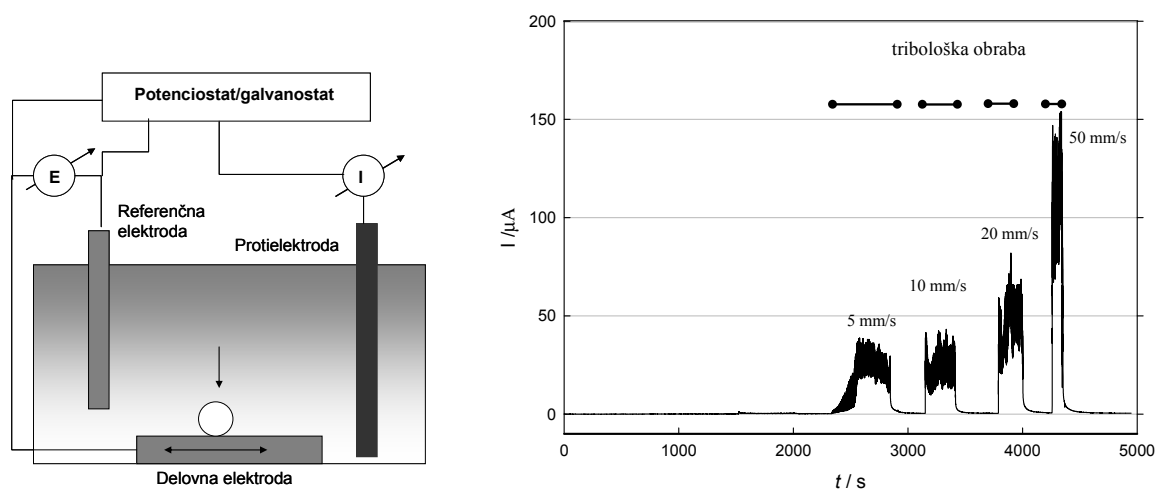
Slabost te tehnike je, da pri njeni uporabi ne dobimo nikakršnih podatkov o kinetiki reakcij, ki nastopajo med drgnjenjem oz. obrabo.



Slika 4: Primer elektrokemijskega spremljanja korozijskega potenciala

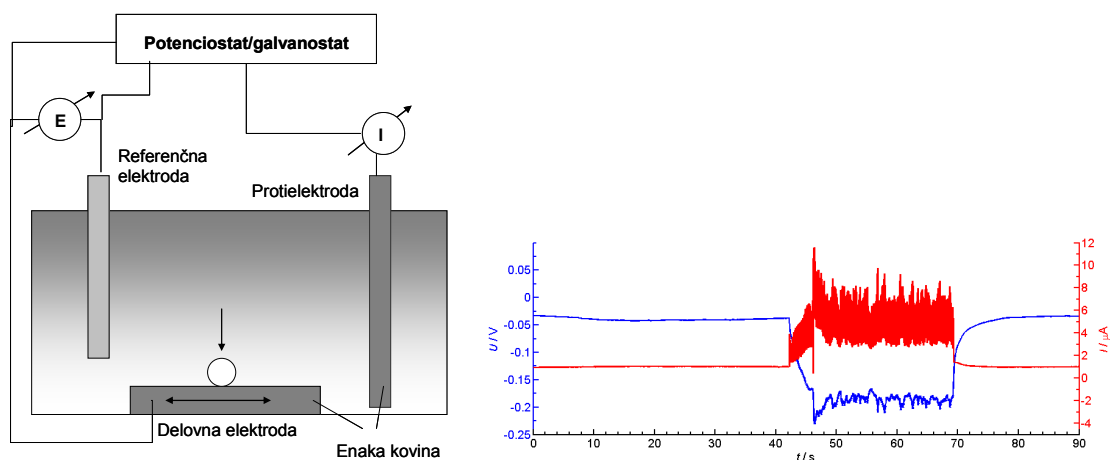
a) shema eksperimenta, b) primer tribokorozijskega preskušanja nerjavnega jekla 316 L v 0,5 M H_2SO_4

Potentiostatski tribokorozijski test je test, pri katerim delovno elektrodo držimo na izbranem potencialu v troelektrodni elektrokemijski celici. Elektrode so povezane s potencistatom, ki vzdržuje potencial med delovno in referenčno elektrodo. Pri stalni napetosti merimo tok v odvisnosti od časa in s tem spremljamo kinetiko reakcij, ki potekajo na elektrodi (Slika 5).



Slika 5: Primer potenciostatskega tribokorozijskega testa

a) shema eksperimenta, b) primer tribokorozijskega preskušanja nerjavnega jekla 316 L v 0,5 M H_2SO_4 pri različnih hitrostih obrabe



Slika 6: Primer tribokorozijskega preskušanja z galvansko celico oz. elektrokemijskim šumom shema eksperimenta a), primer tribokorozijskega preskušanja nerjavnega jekla 316 L v 0,5 M H_2SO_4 b)

Tok med elektrodama, I_{cell} merimo z nizko ohmskim predočajevalcem (*angl.* zero-resistance ammeter, ZRA), priključen na preiskovan kovinski material (delovna elektroda), pri čemer je protielektroda iz istega materiala kot delovna elektroda s podobno izpostavljeno površino. Tem delu eksperimenta rečemo merjenje galvanske celice.

Glavna prednost opisane metode EŠ pred drugimi klasičnimi elektrokemijskimi metodami je dejstvo, da meritev elektrokemijskega šuma poteka v prostokorodirajočih sistemih brez od zunaj vzbujenih signalov. To nam omogoča, da z metodo EŠ zaznavamo naravni (nemoten) razvoj korozijskih procesov in tako na podlagi hitrih sprememb (tranzientov) v merjenem toku in napetosti detektiramo iniciacijo in razvoj korozijskih procesov.

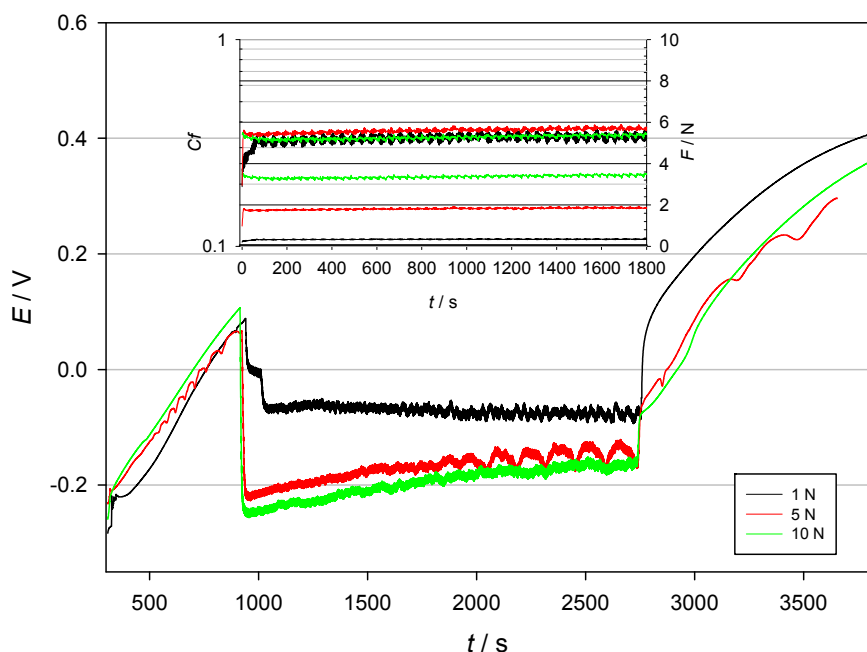
Korozijski dogodki na posamezni elektrodi se odražajo v izmerjenem toku in napetosti. Če so vse tri elektrode enake, med delovno in referenčnima elektrodama ni toka in napetosti. Kadar pa se lokalna korozijska poškodba anodnega značaja (poškodba pasivnega filma, nastanek nove korozijske jamice, pojavi na delovni elektrodi, se to pozna tako na tokovni kot tudi na napetostni krivulji kot premik (zasuk) signala v t.i. anodno smer. Pri tem nastali elektroni potujejo iz delovne na referenčni elektrodi. Če se lokalna korozijska poškodba anodnega značaja pojavi na tokovni referenčni elektrodi, se to odraža kot premik toka v nasprotno smer – katodna smer (elektroni potujejo iz tokovne elektrode) in premik napetosti v anodno smer. Pri nastanku anodne poškodbe na napetostni referenčni elektrodi se to opazi kot premik napetosti v katodno smer. Torej je sočasen tokovni in napetostni odziv v anodni smeri pogoj za detekcijo korozijskega dogodka na delovni elektrodi.

Če je merilni sistem sestavljen iz ohmskega predočajevalca in visokoimpedančnega predočajevalca, lahko omogočimo hkratno spremljanje tudi potenciala, ki ga merimo med referenčno elektrodo in delovno elektrodo. Ob uporabi 18-bit A/D pretvornika lahko dosežemo resolucijo za tok nekaj nA, za meritve napetosti pa μV . Tovrstnemu eksperimentu, ki je za tribokorozijsko preskušanje zelo redko, pravimo meritve elektrokemijskega šuma.

Pri **potenciodynamskih meritvah** različno hitro spreminjamo potencial. S to metodo lahko opazujemo vpliv trenja na različne reakcije, ki potekajo med drgnjenjem. Ta vpliv se lahko opazi le, če je razmerje med obrabljeno in neobrabljeno površino dovolj veliko.

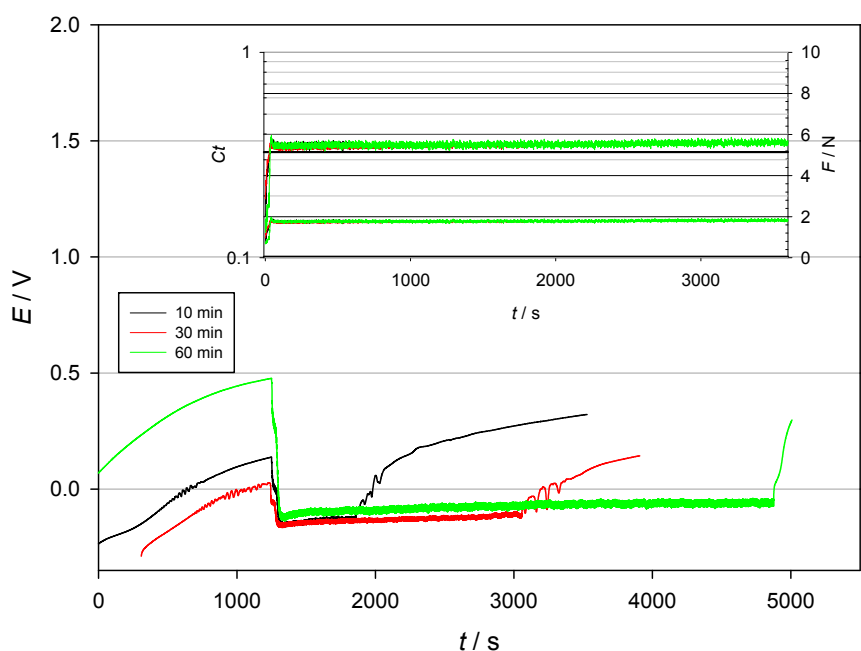
6. Primeri tribokorozijskega preskušanja

Tribokorozijske lastnosti izbranega materiala v korozivni raztopini preskušamo s klasičnim tribološkim spremljanjem obrabe, povezanim s hkratnim elektrokemijskim eksperimentom. Povezovanje mehanskih in elektrokemijskih metod omogoča hkratno spremljanje koeficientov in sile trenja pri definiranih korozijskih razmerah. Na slikah 7–9 so prikazani tribokorozijski eksperimenti na ploščici iz nerjavnega jekla 316L v raztopini 0,5 M H_2SO_4 . Predstavljeni eksperimenti so narejeni pri potencialu odprtega kroga (*angl.* Open circuit potential) brez zunanje narinjene napetosti.



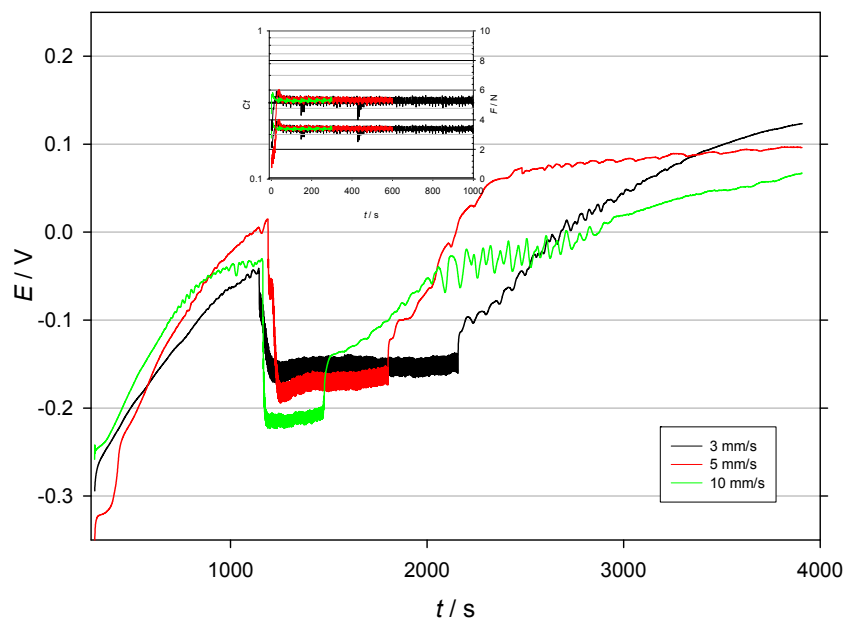
Slika 7: Spremljanje korozijskega potenciala nerjavnega jekla 316 L pri različnih silah obremenitve med tribološko obrabo

Nas sliki 7 lahko spremljamo odvisnost uporabljene sile pri drgnjenju. Večja, ko je sila, večja je sprememba v zmanjšanju korozijskega potenciala elektrode iz nerjavnega jekla tipa 316 L. Vidimo lahko, da so potenciali pri silah 5 in 10 N podobni, iz česar lahko sklepamo, da sila 1 N ni zadosti velika, da bi povsem odstanila pasivno plast na obrabni poti. Zato je korozijski potencial pri sili 1 N nekoliko bolj pozitiven med časom obrabe. Po končani obrabi se potencial povrne nazačetno vrednost v različnih časih, to je čas, ki ga kovina potrebuje, da se ponovno pasivira.



Slika 8: Spremljanje korozijskega potenciala nerjavnega jekla 316 L pri različnih poteh med tribološko obrabo

Nas sliki 8 lahko spremljamo vpliv časa obrabe v raztopini 0,5 M H_2SO_4 pri konstantni sili obremenitve. Korozijski potencial elektrode se ob začetku tribološke obrabe zmanjša in ostaja konstantne vrednosti pri vseh neodvisno od časa obrabe. Po koncu obrabe se potencial začne povečevati. Čas repasivacije je odvisen od več dejavnikov in je različen za tri različna preskušanja.



Slika 9: Spremljanje korozijskega potenciala nerjavnega jekla 316 L pri različnih hitrostih tribološke obrabe

Nas sliki 9 je predstavljena odvisnost korozijskega potenciala od hitrosti obrabe pri konstantni sili in poti obrabe za sistem nerjavno jeklo 316 L v 0,5 M raztopini H_2SO_4 . Večja, ko je hitrost, večja je sprememba v zmanjšanju korozijskega potenciala. Prav tako hitrost obrabe vpliva na repasivacijo elektrode. Opazimo lahko, da se po koncu obrabe potencial začne pomikati k bolj pozitivnim vrednostim. Ta čas je najdaljši pri največji hitrosti obrabe. Predvidimo lahko, da je opažena lastnost posledica dejstva, da so se korozijske razmete tik ob elektrodi bistveno spremenile, saj je hitro drgnjenje povzročilo večje spremembe v električni dvoplasti in celotnem okoliškem korozijskem sistemu. Do vzpostavitve ravnovesnega stanja in repasivacije je potrebno več časa, kar lahko opazimo s počasnim večanjem korozijskega potenciala.

7. Sklep

Kovine so v agresivnem okolju izpostavljene korozijskem propadanju. V mnogih primerih lahko korozijsko stanje kovinskega materiala poslabša hkratna obraba, kar povzroča še izrazitejše propadanje kovinskih površin. Področje uporabe kovin je zelo široko, zato je poznavanje tribokorozijskih procesov in njihove kontrole velikega pomena.

Ker je propadanje kovine elektrokemijski proces, lahko njegove lastnosti spremljamo z uporabo različnih elektrokemijskih tehnik. Za spremljanje tribokorozijskih lastnosti pa potrebujemo posebno preskuševališče, ki je sestavljeno iz tribometra ter posebej predelane korozijske celice, ki vsebuje tako delovno, referenčno ter števno elektrodo.

Korozijo kovinskega materiala med obrabo lahko spremljamo na več različnih načinov.

V prispevku so predstavljeni različni primeri tribokorozijskega preskušanja nerjavnega jekla 316 L v 0,5 M raztopini žveplove(VI) kisline pri potencialu odprtega kroga v odvisnosti od velikosti sile obrabe, časa oziroma poti obrabe ter hitrosti obrabe.

8. Literatura:

- [1] A. Legat, M. Bajt Leban, Ž. Bajt, *Electrochim. acta.* 49 (2004) 2741–2751.
- [2] M. Bajt Leban, Ž. Bajt, A. Legat, *Electrochim. acta.* 49(2004) 2795–2801.
- [3] A. Legat, *Electrochim. Acta* 52 (2007) 7590–7598.
- [4] F. P. Bowden, D. Tabor, *The Friction and Lubrication of Solids*, Oxford, Clarendon Press, 1986.
- [5] ASTM G119 - 04 Standard Guide for Determining Synergism between Wear and Corrosion.
- [6] M.M. Stack, N. Pungwiwat, *Wear* 256 (2004) 565–576.
- [7] M. Stack, N. Pungwiwat, *Tribol. Int.* 35 (2002) 681–689.
- [8] M.M. Stack, S. Zhou, R.C. Newman, *Mater. Sci. Technol.* 12 (1996) 261–268.
- [9] D. Landolt, S. Mischler, M. Stemp, S. Barril, *Wear* 256 (2004) 517–524.
- [10] P. Jemmely, S. Mischler, D. Landolt, *Tribol. Int.* 32 (1999) 295–303.
- [11] C. Rapijko, S. Fouvry, B. Grosgeat, B. Wendler, *Wear* 266 (2009) 850–858.
- [12] H. Ranc, C. Cervaix, P.-F. Chauvy, S. Debaud, S. Mischler, *Trib. Int.* 39 (2006) 1518–1526.
- [13] S. Horimoto, S. Mischler, *Wear* 261 (2006) 1002–1011.
- [14] P. Ponthiaux, F. Wenger, J. Galland, G. Lederer, M. Calati, *Materiaux et Techniques* (1997) 43–46.
- [15] Ponthiaux P, F. Wenger, D. Drees, J.P. Celis, *Wear* 256 (2004) 459–468.
- [16] P.-Q. Wu, J.-P. Celis, *Wear* 256 (2004) 480–490.
- [17] Y. Yan, A. Neville, D. Dowson, *J. Phys. D., Appl. Phys.* 39 (2006) 3200–3205.
- [18] F. Contu, B. Elsener, H. Bohni, *Corros. Sci.* 47 (2005) 1863–1875.
- [19] S. Barril, N. Debaud, S. Mischler, D. Landolt, *Wear* 252 (2002) 744–754.
- [20] C. Monticelli, F. Zucchi, A. Tampieri, *Wear* 266 (2009) 327–336.
- [21] A.C. Vieira, A.R. Ribeiro, L.A. Rocha, J.P. Celis, *Wear* 261 (2006) 994–1001.
- [22] E. Bayon, A. Igartua, X. Fernandez, R. Martinez, R.J. Rodrigues, J.A. Garcia, A. De Frutos, M.A. Arenas, J. deDamborenea, *Tribology International* 42 (2009) 591–599.
- [23] M. Kalin, E. Roman, J. Vizintin, *Thin Solid Films* 515 (2007) 3644–3652.
- [24] M.T. Mathew, E. Ariza, L.A. Rocha, A.C. Fernandes, F. Vaz, *Tribol. Inter.* 41 (2008) 603–615.
- [25] S. Mischler, *Tribology Inter.* 41 (2008) 573–583.
- [26] D. Landolt, S. Mischler, M. Stemp, *Electrochim. Acta* 46 (2001) 3913–3929.
- [27] C-OA. Olsson, M. Stemp, *Electrochim. Acta* 49 (2004) 2145–2154.
- [28] J.-P. Celis, P. Ponthiaux, F. Wenger, *Wear* 261 (2006) 939–946.