

RAZISKAVE PASIVNIH PLASTI NA DVEH KOBALTOVIH ZLITINAH IN NJUNIH KOVINSKIH KOMPONENTAH Z ELEKTROKEMIJSKO IMPEDANČNO SPEKTROSKOPIJO

STUDIES OF PASSIVE FILMS FORMED ON TWO COBALT-BASED ALLOYS AND THEIR METAL COMPONENTS BY ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

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Raziskovali smo tvorbo pasivne plasti na površini kobaltonih zlitin in kovinskih komponent z elektrokemijsko impedančno spektroskopijo (EIS) v simulirani fiziološki raztopini in v prisotnosti dveh kompleksantov: EDTA in citrata. Ugotovili smo, da je zlitina Co-Cr-Mo bolj korozijsko odporna, kar dokazujejo večje vrednosti polarizacijskih upornosti, predvsem v pasivnem območju.

Ključne besede: kobaltove zlitine, impedanca, fiziološka raztopina

The formation of passive layer on the surface of cobalt-based alloys in physiological solution and in the presence of complexing agents, EDTA and citrate was studied by electrochemical impedance spectroscopy. Studies showed better corrosion resistance of Co-Cr-Mo alloy due to higher Rp values, especially in passive region.

Key words: cobalt-based alloys, impedance, physiological solution

1 UVOD

Človeško telo je zaradi visoke koncentracije kloridnih ionov in kompleksantov relativno agresivno okolje za kovinske materiale. Kljub dobrim korozijskim in mehanskim lastnostim kobaltonih zlitin prihaja do sproščanja kovinskih ionov in delcev v okoliško tkivo. Sproščeni kovinski ioni lahko tvorijo med drugim kloride, okside, hidrokside in organokovinske komplekse, ki se s telesnimi tekočinami izločijo iz telesa ali pa se raznašajo po organizmu in kopičijo v nekaterih organih, kot so bezgavke, pljuča, jetra in vranica¹. Povečana koncentracija kovinskih ionov v bezgavkah in omenjenih notranjih organih lahko povzroči nekrozo². Milijoni sproščenih mikro- in submikrometrskih delcev, ki nastajajo pri mehanski obrabi, se kopičijo v tkivu ob protezi, kjer lahko sprožijo proces fagocitoze. Fagocitirani delci v makrofagih sprožijo verižno reakcijo, ki privede do omajanja in posledično do menjave proteze.

Zaradi navedenih razlogov so raziskave korozijskega vedenja kobaltonih zlitin in možnosti sproščanja korozijskih produktov v človeško telo zelo pomembne. Namen našega dela je bil raziskati elektrokemijske lastnosti pasivne plasti na površini zlitin Co-Cr-Mo in Co-Ni-Cr-Mo, zlitini medsebojno primerjati in poiskati skupne točke z njunimi kovinskimi komponentami, kobaltom, kromom, nikljem in molibdenom, v simulirani

1 INTRODUCTION

Surgical-grade Co-based alloys are widely used for the manufacture of prosthetic devices. Their extensive use is based on their superior resistance to corrosion and biodegradation and to their good mechanical properties, including high ultimate tensile and fatigue strengths combined with sufficient elongation at the point of fracture¹. Implanted metal was submitted to the simultaneous effects of mechanical and chemical interactions². In the course of time the alloy and its corrosion products react directly with the surrounding tissues, being transported by the bloodstream to distant organs or being partially eliminated by body fluids. During the long-term accumulation of metal corrosion products in internal organs, such as liver and kidney, the tolerance level can be exceeded, leading to conditions under which certain diseases can begin to develop².

The natural, aggressive environment of the human body is difficult to simulate. In the present work Co-Cr-Mo and Co-Ni-Cr-Mo alloys and their individual metal components (Co, Cr, Ni, and Mo) were studied in a simulated physiological solution (SPS), with and without the addition of the complexing agents EDTA and citrate. The latter simulated the influence of biomolecules, which *in vivo* can act as complexing agents for metal ions. The study was conducted using electro-

fiziološki raztopini, to je v Hankovi raztopini, pri pH = 7,8. Raziskovali smo tudi vpliv dodatka dveh kompleksantov: EDTA in citrata, na korozijsko vedenje omenjenih materialov. Pri tem smo uporabili elektrokemijsko impedančno spektroskopijo (EIS).

Impedančna spektroskopija je zelo razširjena metoda za preučevanje elektrokemijskih sistemov, ki omogoča določitev ionske in elektronske prevodnosti ter študij osnovnih elementarnih procesov³. Odlikujeta jo natančnost in možnost ločevanja posameznih elementarnih transportnih procesov, ki potekajo v materialih. Pri določevanju električnih lastnosti materialov navadno uporabljamo trielektrodne celice. V takih sistemih poteka več različnih transportnih procesov, npr. transport električnega naboja v notranjosti materiala, prenos naboja na fazni meji in v raztopini. Procesi se odzivajo v različnih frekvenčnih območjih, če potekajo "zaporedno", in z različnimi relaksacijskimi časi. V takih primerih lahko posamezne transportne procese ločimo med seboj.

Elektrokemijski sistem vzbujamo z nizko napetostjo sinusne oblike, impedančni odziv pa dobimo z merjenjem razmerja med vzbujevalno napetostjo U in tokovnim odzivom I kot funkcijo krožne frekvence ω . Vrednost $Z(\omega)$ pri izbrani frekvenci ω_0 imenujemo impedanca in jo po navadi predstavimo v kompleksni ravnini v obliki Nyquistovega diagrama (Z_{img} proti Z_{real}) ali v obliki Bodejevega diagrama ($|Z|$ proti ω).

V kompleksni ravnini impedanco določata $Z' = \text{Re}(Z) = |Z| \cos \phi$ na abscisni osi in $Z'' = \text{Im}(Z) = |Z| \sin \phi$ na ordinati. Teoretično je impedančni odziv, predstavljen v kompleksni ravnini, sestavljen iz enega ali več polkrogov s centri na abscisni osi, vendar pri realnih meritvah dobimo polkroge s centri pod realno osjo.

Obdelava impedančnih spektrov poteka na osnovi modelov nadomestnih vezij, sestavljenih iz uporov in kondenzatorjev. Elementom nadomestnega vezja pripišemo fizikalni pomen in izračunamo parametre modela. Pri enostavnem korozijskem procesu, ko ima impedančni odziv notranjosti materiala obliko enega polkroga, lahko električno dvojno plast primerjamo s kondenzatorjem, ki ima fiksno in gibljivo ploščo, kot jo sicer tvori fiksna zunanja Helmholtzova plast z gibljivo difuzijsko plastjo. Elektrokemijska celica ima enake elektrokemijske lastnosti kot enostavno električno vezje, sestavljeno iz kondenzatorja in uporov. Vzoredno vezan upor R_p pomeni korozijsko upornost, imenovano polarizacijska upornost ali upornost prenosa naboja, medtem ko zaporedno vezan upor R_e pomeni upornost elektrolita. Kapaciteta električne dvoplasti je predstavljena kot kondenzator s kapacitivnostjo C_{dl} , ki jo imenujemo kapacitivnost dvoplasti. Simbol Q se uporablja za prikazovanje neidealne kapacitivnosti za kompenzacijo nehomogenosti sistema in je okrajšava za "constant phase element" – CPE.

chemical techniques of cyclic voltammetry, anodic potentiodynamic measurements and linear polarization, and electrochemical impedance spectroscopy (EIS).

EIS has been successfully applied to the study of corrosion systems for thirty years and has proven to be a powerful and an accurate method for measuring corrosion rates³. An important advantage of EIS over other laboratory techniques is the possibility of using very small amplitude signals without significantly disturbing the properties being measured. Like resistance, impedance is a measure of the ability of a circuit to resist the flow of electrical current.

Electrochemical impedance is usually measured by applying an AC potential to an electrochemical cell and measuring the current through the cell. The applied potential is sinusoidal and the response to this potential is an AC current signal containing the excitation frequency and its harmonics. This current signal can be analyzed as a sum of sinusoidal functions (a Fourier series). Electrochemical impedance is normally measured using a small excitation signal, so that the cell response is pseudo-linear.

The expression for the impedance $Z(\omega)$ is composed of a real and an imaginary part. In a Nyquist plot the real part is plotted on the Z axis and the imaginary part on the Y axis of a chart. A semicircle is characteristic of a single "time constant". Electrochemical impedance plots often contain several time constants. However, often only a portion of one or more of their semicircles is seen. Capacitors in EIS experiments often do not behave ideally. Instead, they act like a constant phase element (CPE).

EIS data is generally analyzed in terms of an equivalent circuit model. The analyst tries to find a model whose impedance matches the measured data.

The type of electrical components in the model and their interconnections control the shape of the model's impedance spectrum. The model's parameters (i.e., the resistance value of a resistor) control the size of each feature in the spectrum. Both these factors affect the degree to which the model's impedance spectrum matches a measured EIS spectrum.

2 EXPERIMENTAL

The pure metal components, Co, Cr, Ni and Mo (all 99.9 wt. %), were obtained from Metalle und Materialien GmbH, Nürnberg, Germany. The alloys were cut from original prostheses (Protek, Sulzer, Bern, Switzerland). The alloy compositions were confirmed by energy-dispersive X-ray analysis (EDA) as follows: 27.9 at. % Cr, 3.4 at. % Mo, 1.6 at. % Si, 0.7 at. % Fe and the remainder Co, denoted as the Co-Cr-Mo alloy; and 23 at. % Cr, 36 at. % Ni, 6.1 at. % Mo, 1 at. % Ti, 0.5 at. % Fe and the remainder Co, denoted as the Co-Ni-Cr-Mo alloy.

2 EKSPERIMENTALNI DEL

Pri svojem delu smo uporabljali čiste kovine Co, Cr, Ni in Mo (masna čistota 99,9 %, proizvajalec Metalle und Materialien GmbH, Nürnberg, Nemčija) ter dve kobaltovi zlitini, ki sta bili izrezani iz originalnih protez proizvajalca Protek, Sulzer, Bern, Švica. Kemijska sestava zlitin je bila določena s spektroskopsko analizo energijske porazdelitve rentgenskih žarkov (EDS) na Odseku za nanostrukturne materiale IJS. Zlitina Co-Cr-Mo je vsebovala naslednje atomske deleže: 66,4 % Co, 27,9 % Cr in 3,4 % Mo, zlitina Co-Ni-Cr-Mo pa 33,4 % Co, 36 % Ni, 23 % Cr in 6,1 % Mo.

Preiskovani vzorci so bili izdelani v obliki okroglih ploščic premera 15 mm in debeline 2 mm. Pred elektrokemijskimi meritvami smo vzorce mehansko zbrusili na SiC-brusnem papirju gradacije 600, 800 in 1000 ter sprali z destilirano vodo. Meritve smo izvajali v Hankovi raztopini, simulirani fiziološki raztopini (SFR) s pH = 7,8 pri 37 °C. Osnovni fiziološki raztopini smo dodali kompleksanta EDTA in Na-citrat.

Za meritve elektrokemijske impedančne spektroskopije (EIS) smo uporabili analizator frekvenčnega odziva Solartron 1250 s potenciostat/galvanostat Solartron 1286 in računalniškima programoma ZPlot in ZView. Meritve impedance smo izvedli v frekvenčnem območju 10 kHz do 1 mHz pri amplitudi napetosti 10 mV. Pred merjenjem impedance smo preiskovane vzorce polarizirali 15 min pri potencialih, ki smo jih izbrali glede na značilnosti cikličnih voltamogramov. Izbrani potenciali so podani v **tabeli 1**. Meritve smo izvedli v SFR, ter z dodatkom 50 mM EDTA in 50 mM citrata. Za določitev polarizacijske upornosti (R_p) iz impedančnih meritev smo izmerjenim krivuljam prilagodili teoretično krivuljo z nadomestno shemo, sestavljeno iz serijskega upora (R_s), ki pomeni upornost elektrolita (R_e) in enega RQ člena, ali pa dveh zaporedno ali vzporedno vezanih RQ členov. V prvem primeru je polarizacijska upornost R člena pri zaporedni vezavi $R_p = R_1 + R_2$, pri vzporedni vezavi pa $1/R_p = 1/R_1 + 1/R_2$.

3 REZULTATI

Z elektrokemijsko impedančno spektroskopijo smo preučevali potek nastajanja in raztapljanja pasivne plasti na obeh zlitinah in čistih kovinah v SFR ter v prisotnosti 50 mM citrata ali EDTA v povezavi s karakteristikami cikličnih voltamogramov. Pogoji, pri katerih smo izvajali meritve, so podani v eksperimentalnem delu.

Pri kobaltu impedančni odziv pri potencialu $-0,9$ V predstavlja visokofrekvenčni odsek na abscisni osi in nizkofrekvenčni polkrog, ki smo ju opisali z nadomestno shemo, sestavljeno iz serijskega upora (R_e), ki pomeni odsek na abscisni osi, in iz dveh zaporedno vezanih RQ členov, ki pomenita odziv na fazni meji kovina/elektrolit (**slika 1a**). Upornost pasivne plasti R_p je v SFR 11,5 $k\Omega/cm^2$, v prisotnosti citrata je 4,5 $k\Omega/cm^2$, v prisotnosti

The experiments were carried out at 37 °C in Hank's solution, a simulated physiological solution (SPS), which contained 8 g L⁻¹ NaCl, 0,40 g L⁻¹ KCl, 0,35 g L⁻¹ NaHCO₃, 0,25 g L⁻¹ NaH₂PO₄×2H₂O, 0,06 g L⁻¹ Na₂HPO₄×2H₂O, 0,19 g L⁻¹ CaCl₂×2H₂O, 0,41 g L⁻¹ MgCl₂×6H₂O, 0,06 g L⁻¹ MgSO₄×7H₂O and 1 g L⁻¹ glucose. Complexing agents, EDTA (ethylenediaminetetraacetic acid disodium salt dihydrate) and citrate (tri-sodium citrate dihydrate), were added to concentrations of 0.1 mM, 5 mM and 50 mM. In all cases the pH values were adjusted to a physiological pH of 7.8. All the chemicals were from Merck, Darmstadt, Germany.

The test specimens were cut into discs of 15 mm diameter. The specimens were abraded with SiC emery paper down to 1000-grit and rinsed with distilled water. The specimens were then embedded in a Teflon PAR holder and employed as a working electrode. The reference electrode was a saturated calomel electrode (SCE, 0,242 V vs. SHE) and the counter electrode was a high-purity graphite rod.

Electrochemical impedance spectroscopy (EIS) measurements were made using a frequency-response analyzer (Solartron 1250) combined with a potentiostat/galvanostat (Solartron 1286) and ZPlot computer program. The impedance spectra were measured for both the alloys and the pure metals. The working electrode (the tested specimen) was polarized at the selected potentials in correlation with the cyclic voltammograms (**Table 1**). A quasi steady-state current was usually attained within 15 minutes. The potential was then raised to the value of interest and the impedance spectra collected within the frequency range of 10 kHz to 1 mHz, with an excitation signal amplitude of 10 mV.

Tabela 1: Potenciali polarizacije vzorcev pred meritvami z elektrokemijsko impedančno spektroskopijo

Table 1: Polarization potentials of the samples before the EIS measurements.

vzorec/ sample	Co-Cr- Mo	Co-Ni- Cr-Mo	Cr	Co	Ni	Mo
poten- cial	-0,7 V	-0,7 V	-0,7 V	-0,9 V	-0,75 V	-0,7 V
	-0,3 V	-0,3 V	-0,3 V	-0,7 V	-0,4 V	-0,4 V
	0,1 V	0,1 V	0,1 V	-0,3 V	0 V	-0,1 V
	0,6 V	0,6 V	0,6 V			
	0,8 V	0,8 V	0,8 V			

3 RESULTS

The processes of formation and dissolution of the passive films on both the alloys and the pure metals in a simulated physiological solution containing 50 mM citrate or EDTA were studied using EIS. The experimental parameters are described in Section 2. The impedance data were fitted using an equivalent circuit model in order to get the best approximation between the fitted and the measured data. The values of R_1 , R_2 , Q_1 and Q_2 are related to the polarization resistances and the

EDTA pa $2 \text{ k}\Omega/\text{cm}^2$ (slika 7). Iz tega izhaja potrditev ugotovitve dosedanjih meritev (anodna polarizacija, ciklični voltamogrami), da se v prisotnosti kompleksantov zmanjša korozijska odpornost najbolj izrazito v EDTA ^{4,5}.

Pri potencialu polarizacije $-0,7 \text{ V}$ je impedančni odziv pri kobaltu sestavljen iz visokofrekvenčnega odseka na abscisni osi in nizkofrekvenčnega polkroga, ki smo ju opisali z nadomestno shemo, predstavljeno na sliki 1b. V tem primeru je pasivna plast že debelejša, kar se kaže v povečanju polarizacijske upornosti, ki je $60 \text{ k}\Omega/\text{cm}^2$ v SFR, $12 \text{ k}\Omega/\text{cm}^2$ v citratu in $4 \text{ k}\Omega/\text{cm}^2$ v EDTA (slika 7).

Pri potencialu polarizacije $-0,3 \text{ V}$ je impedančni odziv pri kobaltu sestavljen iz odseka na abscisni osi in dveh polkrogov v primeru SFR in v prisotnosti EDTA ter enega polkroga v prisotnosti citrata (slika 1c). Opisali smo ga z nadomestno shemo, sestavljeno iz serijskega upora (R_c) in kombinacijo dveh vzporednih RQ -elementov. V tej nadomestni shemi visokofrekvenčna kapacitivnost (Q_1) pomeni kapacitivnost dvojne plasti, visokofrekvenčni upor (R_1) pa upornost reakcije prenosa naboja. Nizkofrekvenčni odziv je povezan z difuzijskim in adsorpcijskim procesom reaktantov. Vrednosti polarizacijske upornosti so $2,7 \text{ k}\Omega/\text{cm}^2$ v SFR, $100 \Omega/\text{cm}^2$ v citratu in $20 \Omega/\text{cm}^2$ v EDTA (slika 7). Te vrednosti so precej nižje kot pri $-0,9 \text{ V}$ in $-0,7 \text{ V}$, kar kaže na postopno razgradnjo pasivne plasti, in sicer bolj intenzivno v prisotnosti kompleksantov, kjer že nastopi območje transpasivne oksidacije. V SFR je kobalt pri potencialu $-0,3 \text{ V}$ še v pasivnem območju, vendar se zaščitna plast že tanjša, kar je razvidno iz nižje vrednosti polarizacijske upornosti v primerjavi s tistima pri $-0,9 \text{ V}$ in $-0,7 \text{ V}$.

Pri kromu je impedančni odziv pri potencialu polarizacije $-0,7 \text{ V}$ v vseh treh raztopinah sestavljen iz odseka na abscisni osi in polkroga (slika 2a). Pri tem potencialu se za krom začne pasivno območje, zato so polarizacijske upornosti precej visoke: $90 \text{ k}\Omega/\text{cm}^2$ v SFR, $38 \text{ k}\Omega/\text{cm}^2$ v citratu in $33 \text{ k}\Omega/\text{cm}^2$ v EDTA (slika 7).

Pri potencialu polarizacije $-0,3 \text{ V}$ je impedančni odziv za krom sestavljen iz odseka na abscisi in nedokončanega polkroga (slika 2b). Pri tem potencialu je krom na sredini pasivnega območja, vrednosti polarizacijske upornosti pa so reda velikosti $10^5 \Omega/\text{cm}^2$ (slika 7).

Pri potencialu polarizacije $0,1 \text{ V}$ smo izmerili podoben impedančni odziv kot pri $-0,3 \text{ V}$ in smo ga enako tudi opisali (slika 2c). Tu je krom še vedno v pasivnem območju, vrednosti polarizacijske upornosti so reda velikosti $10^5 \Omega/\text{cm}^2$ (slika 7), dodatek kompleksanta pa zaradi naraščajoče debeline pasivne plasti bistveno ne vpliva na impedančno odzivnost kroma.

Pri potencialu $0,6 \text{ V}$ krom že prehaja v območje transpasivne oksidacije, kjer se pasivna plast začne

capacitances of the elements in the equivalent circuit model.

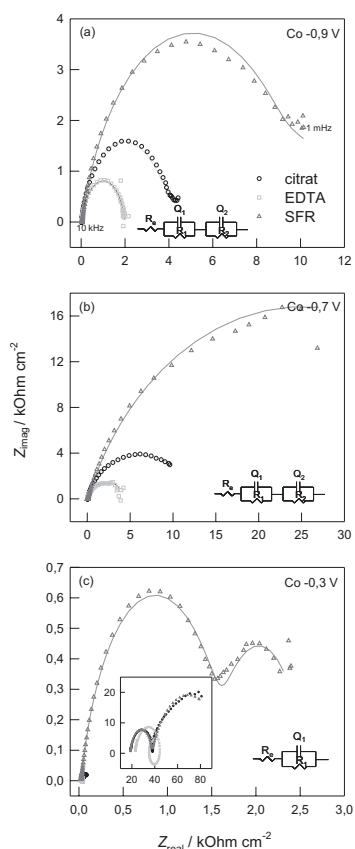
The impedance spectra for Co at -0.9 V consisted of a high-frequency intercept and a low-frequency arc, which were described with an equivalent circuit consisting of two RQ elements in series with R_c (resistance of the electrolyte, Figure 1a). The resistance of the passive layer in the SPS was $11.5 \text{ kW}/\text{cm}^2$, in the SPS containing citrate it was $4.5 \text{ kW}/\text{cm}^2$, and in the SPS containing EDTA it was $2 \text{ kW}/\text{cm}^2$ (Figure 7). Therefore, the corrosion resistance of the Co was reduced in the presence of the complexing agents, especially the EDTA, which is in accordance with the results from our previous electrochemical measurements (anodic polarisation, cyclic voltammetry) ^{4,5}.

The impedance response for Co at a potential of -0.7 V combined a high-frequency intercept and a low-frequency arc, which was described with the equivalent circuit presented in Figure 1b. The passive layer was thicker than at a potential of -0.9 V , which is shown by an increasing polarization resistance, i.e., $60 \text{ kW}/\text{cm}^2$ in the SPS, $12 \text{ kW}/\text{cm}^2$ in the citrate, and $4 \text{ kW}/\text{cm}^2$ in the EDTA (Figure 7).

The impedance response for Co at a potential of -0.3 V combined a high-frequency intercept and two low-frequency arcs in the case of the SPS and the EDTA, and one low-frequency arc in the case of the citrate (Figure 1c). The equivalent circuit consisted of the R_c and two RQ elements in parallel. A high-frequency capacitance Q_1 represents the capacitance of the double layer, and the high-frequency resistance R_1 is related to the resistance of the charge transfer. A low-frequency response is related to the diffusion and the adsorption processes of the reactants. The values of the polarization resistances were $2.7 \text{ kW}/\text{cm}^2$ in the SPS, $100 \text{ W}/\text{cm}^2$ in the citrate and $20 \text{ W}/\text{cm}^2$ in the EDTA (Figure 7). These values are much lower than in the case of the potentials of -0.9 V and -0.7 V , which indicates a progressive decomposition of the passive layer, especially in the presence of the complexing agents due to the crossing to the region of transpassive oxidation. The Co in the SPS at a potential of -0.3 V is still in the passive region; however, the passive layer is thinner due to the lower values of the polarization resistance with regard to the values at -0.9 V and -0.7 V .

The impedance response for Cr at a potential of -0.7 V in all three electrolytes consisted of a high-frequency intercept and a low-frequency arc (Figure 2a). At that potential the Cr entered into the passive region, and consequently the values of the polarization resistance were relatively high, i.e., $90 \text{ kW}/\text{cm}^2$ in the SPS, $38 \text{ kW}/\text{cm}^2$ in the citrate and $33 \text{ kW}/\text{cm}^2$ in the EDTA (Figure 7).

The impedance response for Cr at a potential of -0.3 V consisted of a high-frequency intercept and a low-frequency unfinished arc (Figure 2b). At that potential the Cr was in the middle of the passive region



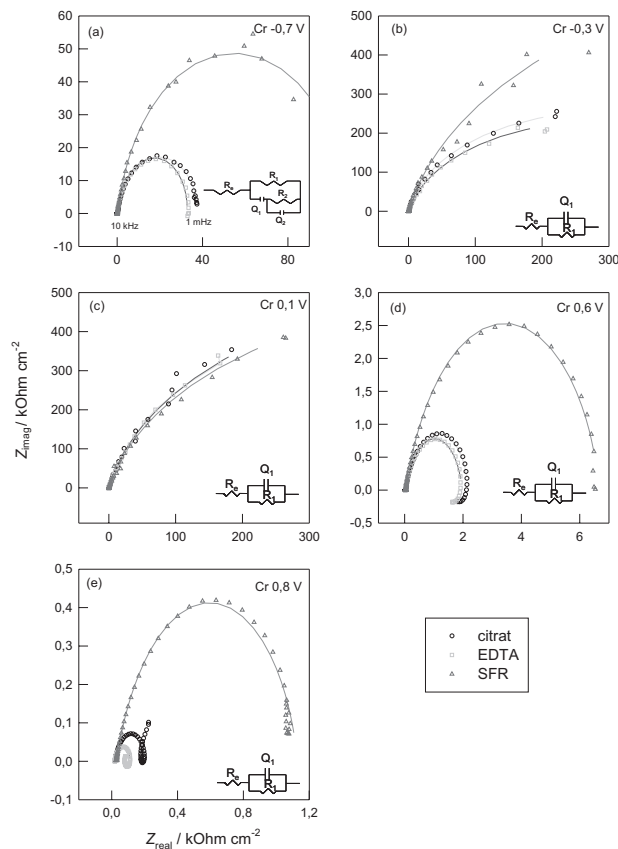
Slika 1: Nyquistovi diagrami za Co pri (a) -0.9 V, (b) -0.7 V in (c) -0.3 V v SFR in v prisotnosti 50 mM EDTA ali 50 mM citrata z ustreznimi nadomestnimi shemami

Figure 1: Nyquist plot recorded for Co at (a) -0.9 V, (b) -0.7 V and (c) -0.3 V in SPS and SPS containing 50 mM EDTA or citrate. The equivalent circuit models are inserted in the figure

raztapljati (slika 2d). Impedančni odziv je v obliki odseka na abscisi in polkroga, ki pri nizkih frekvencah že nakazuje obliko polža, ki je značilna za korozijske procese. Opisali smo ga z nadomestno shemo, sestavljeno iz serijskega upora (R_e) in enega RQ -elementa. Ta nadomestna shema natančno ne opiše procesa pri nizkih frekvencah, ker ne upošteva delnih anodnih in katodnih reakcij, vendar to ne vpliva na meritve polarizacijskih upornosti, ker so te neodvisne od oblike reaktivne komponente in bi bila uporaba kompleksnega modela nepotrebna⁶. Polarizacijske upornosti so v primerjavi s pasivnim območjem mnogo manjše, in sicer: $6,5 \text{ k}\Omega/\text{cm}^2$ v SFR, $2,2 \text{ k}\Omega/\text{cm}^2$ v citratu in $1,8 \text{ k}\Omega/\text{cm}^2$ v EDTA (slika 7).

Pri potencialu $0,8$ V, kjer so gostote toka že precej visoke, je impedančni odziv v obliki polža zelo izražen (slika 2e). Opisali smo ga tako kot pri $0,6$ V. Polarizacijske upornosti so v skladu z višjimi gostotami toka⁴ še nižje: $1,7 \text{ k}\Omega/\text{cm}^2$ v SFR, $200 \text{ }\Omega/\text{cm}^2$ v citratu in $110 \text{ }\Omega/\text{cm}^2$ v EDTA (slika 7).

Pri niklju je impedančni odziv pri potencialu polarizacije $-0,75$ V sestavljen iz odseka na abscisi in polkroga (slika 3a). Polarizacijske upornosti so 36



Slika 2: Nyquistovi diagrami za Cr pri (a) -0.7 V, (b) -0.3 V, (c) $0,1$ V, (d) $0,6$ V in (e) $0,8$ V v SFR in v prisotnosti 50 mM EDTA ali 50 mM citrata z ustreznimi nadomestnimi shemami

Figure 2: Nyquist plot recorded for Cr at (a) -0.7 V, (b) -0.3 V, (c) 0.1 V, (d) 0.6 V and (e) 0.8 V in SPS and SPS containing 50 mM EDTA or citrate. The equivalent circuit models are inserted in the figure

and the values of the polarization resistance were around $10^5 \text{ W}/\text{cm}^2$ (Figure 7).

The results at a potential of 0.1 V for Cr are similar to the case of -0.3 V; the same equivalent circuits were used (Figure 2c). Chromium was still in the passive region, and the values of the polarization resistance were around $10^5 \text{ W}/\text{cm}^2$ (Figure 7). The addition of the complexing agents did not affect the impedance response due to the increasing thickness of the passive layer on the Cr.

At a potential of 0.6 V the Cr entered into the region of transpassive oxidation where the dissolution of the passive layer started (Figure 2d). The impedance response consisted of a high-frequency intercept and a low-frequency arc, which bent into a spiral characteristic for the corrosion processes (Figure 2b). The equivalent circuit combined one RQ element in series with the R_e . The scheme did not describe the processes at low frequencies that are related to partial anodic and cathodic reactions. However, that did not influence the measurements of the polarization resistance due to their independence of the form of the reactive component and, therefore, the application of a more complex model

$\text{k}\Omega/\text{cm}^2$ v SFR, $35 \text{ k}\Omega/\text{cm}^2$ v citratu in $25 \text{ k}\Omega/\text{cm}^2$ v EDTA (slika 7).

Pri potencialu $-0,4 \text{ V}$ prihaja do oksidacije niklja v NiO, kar je razvidno na cikličnih voltamogramih iz pojava vrha (slika 3b). Impedančni odziv je sestavljen iz odseka na abscisi in lepo izraženega polkroga. Vrednost polarizacijske upornosti v SFR je podobna kot pri $-0,75 \text{ V}$, v prisotnosti kompleksantov pa se zmanjša, predvsem v EDTA, in je $17,5 \text{ k}\Omega/\text{cm}^2$ v citratu in $5,5 \text{ k}\Omega/\text{cm}^2$ v EDTA (slika 7). V prisotnosti kompleksantov pride do kompleksacije ionov Ni^{2+} , ki nastajajo pri oksidaciji Ni, in s tem posledično do tanjše zaščitne plasti.

Pri potencialu 0 V je nikelj v pasivnem območju, impedančni odziv je sestavljen iz odseka na abscisi in polkroga (slika 3c). Polarizacijske upornosti so reda velikosti $10^5 \Omega/\text{cm}^2$, so višje kot pri drugih dveh polarizacijskih potencialih, iz česar sklepamo na tvorbo debelejšje zaščitne plasti.

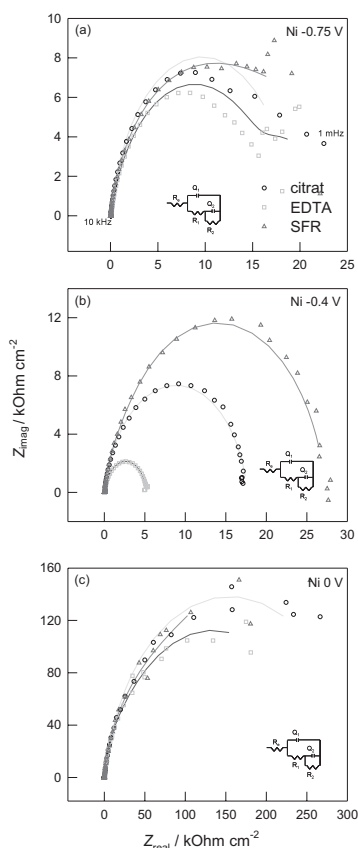
Pri molibdenu je impedančni odziv pri potencialu $-0,7 \text{ V}$ v SFR in citratu sestavljen iz odseka na abscisi in polkroga, v prisotnosti EDTA pa se pri nizkih frekvencah pojavi difuzija (slika 4a). Polarizacijska upornost je bila v SFR okrog $40 \text{ k}\Omega/\text{cm}^2$, v citratu $35 \text{ k}\Omega/\text{cm}^2$ in v EDTA $20 \text{ k}\Omega/\text{cm}^2$ (slika 7).

would be unnecessary⁶. The values of the polarization resistance were lower compared with the passive region, i.e., $6.5 \text{ kW}/\text{cm}^2$ in the SPS, $2.2 \text{ kW}/\text{cm}^2$ in the citrate and $1.8 \text{ kW}/\text{cm}^2$ in the EDTA (Figure 7).

At a potential of 0.8 V the current densities were higher than at a potential of 0.6 V ; therefore, the impedance response in the form of a spiral was more pronounced (Figure 2e). The equivalent circuit combined one RQ element in series with the R_p . The values of the polarization resistance were, in accordance with higher current densities⁴, even lower, i.e., $1.7 \text{ kW}/\text{cm}^2$ in the SPS, $200 \text{ W}/\text{cm}^2$ in the citrate and $110 \text{ W}/\text{cm}^2$ in the EDTA (Figure 7).

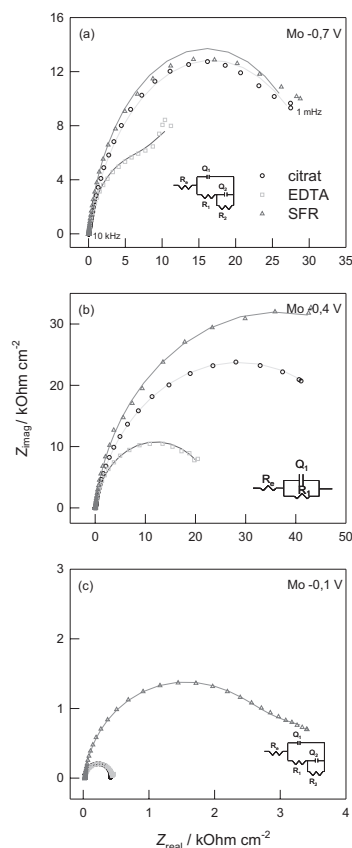
The impedance response for Ni at a potential of -0.75 V consisted of a high-frequency intercept and a low-frequency arc (Figure 3a). The polarization resistance values were $36 \text{ kW}/\text{cm}^2$ in the SPS, $35 \text{ kW}/\text{cm}^2$ in the citrate and $25 \text{ kW}/\text{cm}^2$ in the EDTA (Figure 7).

At a potential of -0.4 V the oxidation of Ni to NiO started. The impedance response consisted of a high-frequency intercept and a low-frequency arc (Figure 3b). The polarization resistance values in the SPS were similar to the values at -0.75 V , with the addition of the complexing agent the values decreased, especially in the



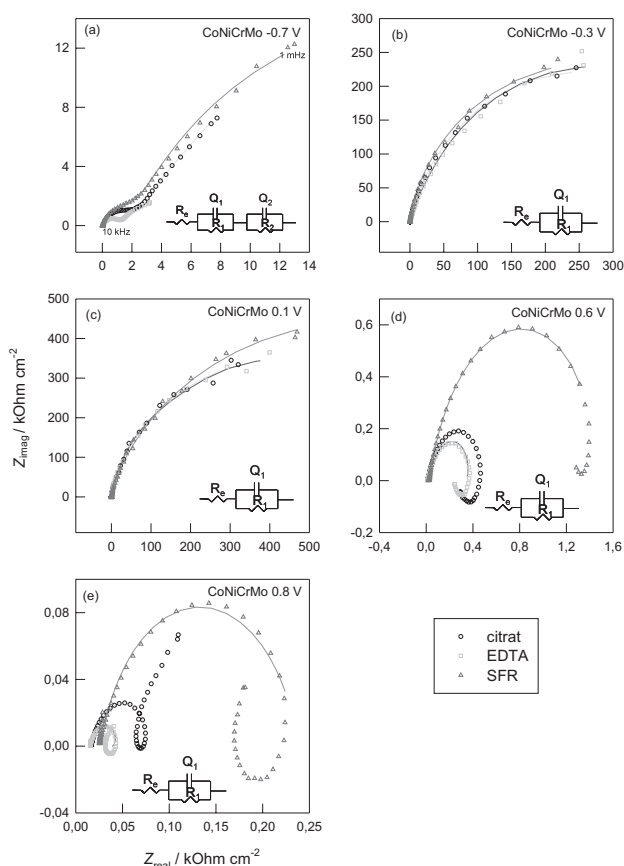
Slika 3: Nyquistovi diagrami za Ni pri (a) $-0,75 \text{ V}$, (b) $-0,4 \text{ V}$ in (c) 0 V v SFR in v prisotnosti 50 mM EDTA ali 50 mM citrata z ustreznimi nadomestnimi shemami

Figure 3: Nyquist plot recorded for Ni at (a) -0.75 V , (b) -0.4 V and (c) 0 V in SPS and SPS containing 50 mM EDTA or citrate. The equivalent circuit models are inserted in the figure



Slika 4: Nyquistovi diagrami za Mo pri (a) $-0,7 \text{ V}$, (b) $-0,4 \text{ V}$ in (c) $-0,1 \text{ V}$ v SFR in v prisotnosti 50 mM EDTA ali 50 mM citrata z ustreznimi nadomestnimi shemami

Figure 4: Nyquist plot recorded for Mo at (a) -0.7 V , (b) -0.4 V and (c) -0.1 V in SPS and SPS containing 50 mM EDTA or citrate. The equivalent circuit models are inserted in the figure



Slika 5: Nyquistovi diagrami za zlitino Co-Ni-Cr-Mo pri (a) $-0,7$ V, (b) $-0,3$ V, (c) $0,1$ V, (d) $0,6$ V in (e) $0,8$ V v SFR in v prisotnosti 50 mM EDTA ali 50 mM citrata z ustreznimi nadomestnimi shemami

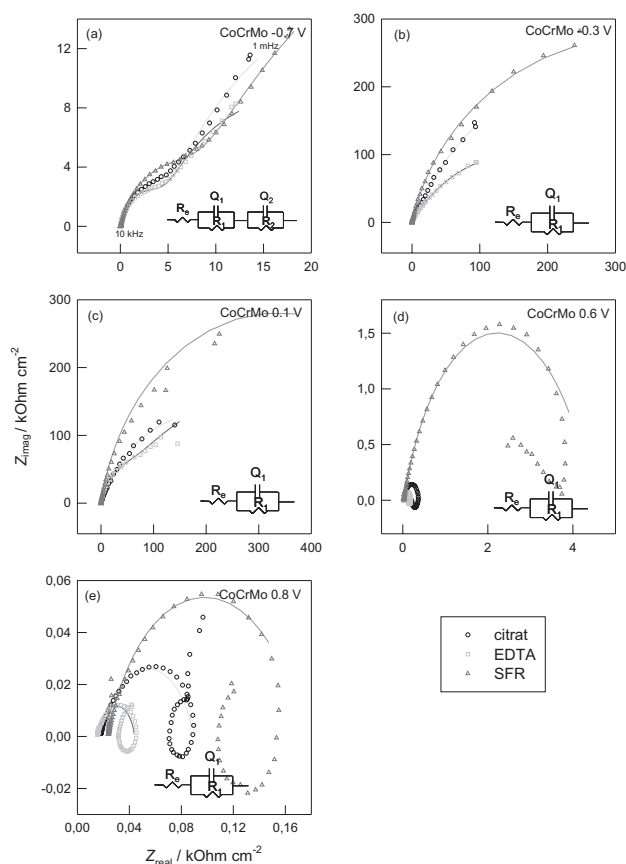
Figure 5: Nyquist plot recorded for Co-Ni-Cr-Mo alloy at (a) $-0,7$ V, (b) $-0,3$ V, (c) $0,1$ V, (d) $0,6$ V in (e) $0,8$ V in SPS and SPS containing 50 mM EDTA or citrate. The equivalent circuit models are inserted in the figure

Pri potencialu $-0,4$ V so vsi trije impedančni odzivi v obliki polkroga (**slika 4b**). Polarizacijske upornosti so višje kot pri $-0,7$ V, kar kaže na rast pasivne plasti, in so 75 $\text{k}\Omega/\text{cm}^2$ v SFR, 60 $\text{k}\Omega/\text{cm}^2$ v citratu in 25 $\text{k}\Omega/\text{cm}^2$ v EDTA (**slika 7**).

Pri potencialu $-0,1$ V molibden prehaja v območje transpasivne oksidacije, kar je razvidno tudi iz impedančnega odziva v obliki polkrogov, kjer so vrednosti polarizacijskih upornosti precej manjše kot v preostalih dveh primerih, in sicer 3750 Ω/cm^2 v SFR, 400 Ω/cm^2 v citratu in 325 Ω/cm^2 v EDTA (**slika 4c**).

Pri zlitini Co-Ni-Cr-Mo je impedančni odziv pri potencialu $-0,7$ V sestavljen iz odseka na abscisi in dveh polkrogov (**slika 5a**). Polkrog pri višjih frekvencah smo pripisali elektrodni reakciji, vrednosti polarizacijske upornosti so reda velikosti 1000 Ω/cm^2 (**slika 8**). Pri nižjih frekvencah se pojavi difuzija, kar je razvidno tudi iz vrednosti difuzijskih koeficientov (n_2) okrog $0,5$, ki so značilne za difuzijski proces, v tem primeru gre verjetno za difuzijo ionov Co^{2+} .

Pri potencialu $-0,3$ V in $0,1$ V je zlitina Co-Ni-Cr-Mo v pasivnem območju, impedančni odziv je



Slika 6: Nyquistovi diagrami za zlitino Co-Cr-Mo pri (a) $-0,7$ V, (b) $-0,3$ V, (c) $0,1$ V, (d) $0,6$ V in (e) $0,8$ V v SFR in v prisotnosti 50 mM EDTA ali 50 mM citrata z ustreznimi nadomestnimi shemami

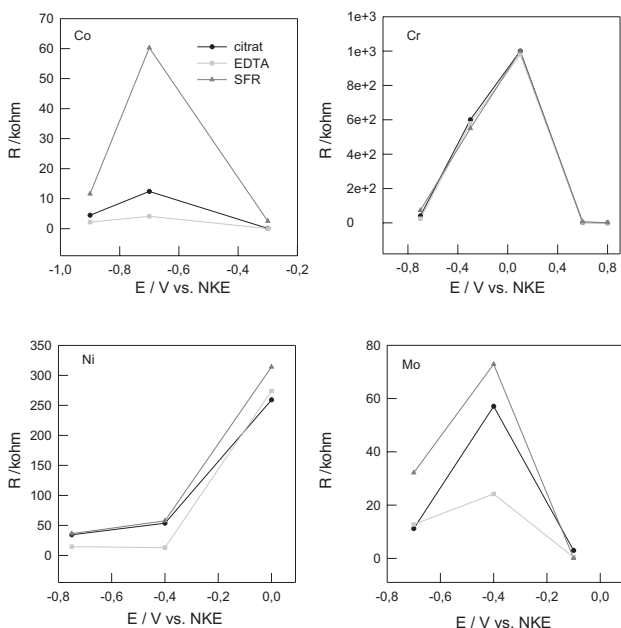
Figure 6: Nyquist plot recorded for Co-Cr-Mo alloy at (a) $-0,7$ V, (b) $-0,3$ V, (c) $0,1$ V, (d) $0,6$ V in (e) $0,8$ V in SPS and SPS containing 50 mM EDTA or citrate. The equivalent circuit models are inserted in the figure

EDTA, i.e., $17,5$ in the citrate and $5,5$ kW/cm^2 in the EDTA (**Figure 7**). In the presence of the complexing agent, complexation of the released Ni^{2+} ions from the oxidation of Ni occurs, and consequently a thinner passive layer is formed.

At a potential of 0 V the Ni is in the passive region, the impedance response is combined from a high-frequency intercept and a low-frequency arc (**Figure 3c**). The values of the polarization resistance are around 10^5 W/cm^2 ; they are higher than at the other two potentials and, accordingly, a thicker passive layer is formed.

In the case of Mo at a potential of $-0,7$ V the impedance response consisted of a high-frequency intercept and a low-frequency arc in the SPS and in the citrate (**Figure 4a**). In the presence of the EDTA the diffusion occurs at low frequencies. The polarization resistance values were 40 kW/cm^2 in the SPS, 35 kW/cm^2 in the citrate and 20 kW/cm^2 in the EDTA (**Figure 7**).

The impedance response for Mo at a potential of $-0,4$ V consisted of a high-frequency intercept and a low-frequency arc in all three solutions (**Figure 4b**). The



Slika 7: Vrednosti polarizacijskih upornosti v odvisnosti od potenciala polarizacije za kovine Co, Cr, Ni in Mo v SFR in v prisotnosti 50 mM EDTA ali 50 mM citrata

Figure 7: Evolution with the potential of polarization resistance values obtained for Co, Cr, Ni and Mo in SPS and SPS containing 50 mM EDTA or citrate

sestavljeno iz odseka na abscisi in enega polkroga (**slika 5b, 5c**). Vrednosti polarizacijske upornosti so visoke, reda velikosti $10^5 \Omega/\text{cm}^2$, kar potrjuje prisotnost izredno stabilne pasivne plasti, zato je tudi vpliv kompleksantov na impedančni odziv zanemarljiv.

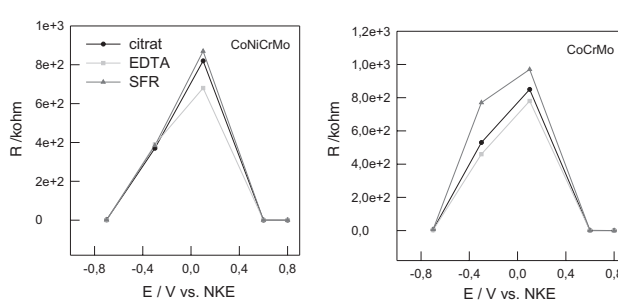
Pri potencialu 0,6 V preide zlitina Co-Ni-Cr-Mo v območje transpasivne oksidacije, kjer pride do raztapljanja pasivne plasti (**slika 5d**). Impedančni odziv je značilen za korozijske procese in ima obliko polža. Polarizacijske upornosti se zmanjšajo za 4-krat (**slika 8**), kar potrjuje rezultate anodne polarizacije, kjer gostota toka močno naraste pri potencialih, večjih od 0,4 V.

Pri potencialu 0,8 V je impedančni odziv v obliki polža še bolj izražen, polarizacijske upornosti so še manjše, kar kaže na nadaljnje raztapljanje pasivne plasti (**slika 5e**).

Rezultati impedančnih meritev za zlitino Co-Cr-Mo so podobni tistim za zlitino Co-Ni-Cr-Mo (**slike 6a–e**). Vrednosti polarizacijskih upornosti so nekoliko višje od tistih za zlitino Co-Ni-Cr-Mo, kar kaže na večjo stabilnost zlitine Co-Cr-Mo (**slika 8**). Obe zlitini sta najbolj stabilni v SFR in najmanj v EDTA, kar potrjujejo znižane vrednosti polarizacijskih upornosti v prisotnosti kompleksantov.

4 DISKUSIJA

Rezultati elektrokemijskih meritev so pokazali, da pri zlitini Co-Cr-Mo v SFR ni klasičnega maksimuma pri prehodu med aktivnim in pasivnim stanjem. Na



Slika 8: Vrednosti polarizacijskih upornosti v odvisnosti od potenciala polarizacije za zlitini Co-Ni-Cr-Mo in Co-Cr-Mo v SFR in v prisotnosti 50 mM EDTA ali 50 mM citrata

Figure 8: Evolution with the potential of polarization resistance values obtained for Co-Ni-Cr-Mo and Co-Cr-Mo alloy in SPS and SPS containing 50 mM EDTA or citrate

polarization resistance values were higher than at -0.7 V, which pointed to the growth of the passive layer, i.e., $75 \text{ kW}/\text{cm}^2$ in the SPS, $60 \text{ kW}/\text{cm}^2$ in the citrate and $25 \text{ kW}/\text{cm}^2$ in the EDTA (**Figure 7**).

At a potential of -0.1 V Mo entered the transpassive region, which was shown from the impedance response in the form of two well-defined arcs (**Figure 4c**). The polarization resistance values were lower than at the other two potentials, i.e., $3750 \text{ W}/\text{cm}^2$ in the SPS, $400 \text{ W}/\text{cm}^2$ in the citrate and $325 \text{ W}/\text{cm}^2$ in the EDTA (**Figure 7**).

The impedance response for the Co-Ni-Cr-Mo alloy at a potential of -0.7 V consisted of a high-frequency and a low-frequency arc (**Figure 5a**). The high-frequency arc was related to the electrochemical reaction, the values of the polarization resistance were around $1000 \text{ W}/\text{cm}^2$ (**Figure 8**). At low frequencies diffusion was present, which is evident from the diffusion coefficients (n) around 0.5 that are characteristic for diffusion processes.

At potentials of -0.3 V and 0.1 V the Co-Ni-Cr-Mo alloy is in the passive region, the impedance response consisted of a high-frequency intercept and a low-frequency arc (**Figures 5b and 5c**). The values of the polarization resistance were around $10^5 \text{ W}/\text{cm}^2$, confirming the formation of an extremely protective passive layer; hence, the influence of the complexing agents was negligible.

At a potential of 0.6 V the Co-Ni-Cr-Mo alloy moved to the region of transpassive oxidation and underwent dissolution of the passive layer (**Figure 5d**). The impedance response was, as is characteristic for corrosion processes, in the form of a spiral. The values of the polarization resistance were reduced four times (**Figure 8**), which confirms the results of the anodic polarization where the current density rapidly increases for potentials higher than 0.4 V⁴.

The impedance response at a potential of 0.8 V was in the form of a spiral, the values of the polarization resistance were lower, which confirms a further dissolution of the passive layer (**Figure 5e**).

potencialih, nižjih od potenciala pasivacije ($-0,3$ V), zlitina še ni pasivna, kar je razvidno iz meritev elektrokemijske impedančne spektroskopije, kjer so vrednosti polarizacijske upornosti nizke in je prisoten difuzijski proces. Prehod v pasivno območje je povezan s povečanjem polarizacijske upornosti in pojavom polkroga na Nyquistovih diagramih, gostota toka se ne spreminja več s povečanjem potenciala. Vzpostavitev pasivne plasti je posledica povečanja debeline plasti Cr_2O_3 . V notranjem delu pasivne plasti pa postane izrazita tudi tvorba CoO in MoO_3 ⁴. Pasivno območje je stabilno do $0,4$ V, ko začne gostota toka intenzivno naraščati, istočasno se zmanjša tudi polarizacijska upornost.

Vpliv kompleksantov na elektrokemijsko vedenje čistih kovin Co, Ni in Mo je zelo izražen. Stopnja vpliva kompleksantov na posamezne kovinske ione je odvisna od konstant stabilnosti kovinskih kompleksov⁷. Nikelj in kobalt tvorita močne komplekse z EDTA, zato opazimo naraščanje gostote toka. Istočasno se zmanjšujejo vrednosti polarizacijskih upornosti. Premik korozijskega potenciala lahko razložimo z vplivom dodatka kompleksanta na ravnotežni potencial oz. koncentracijo raztopljenih kovinskih zvrsti. To potrjujejo tudi povečane koncentracije kovinskih ionov v raztopini v prisotnosti kompleksantov⁸. Slabšo korozijsko odpornost Co, Ni in Mo v prisotnosti kompleksantov potrjujejo tudi impedančne meritve, kjer so vrednosti R_p pri vseh polarizacijskih potencialih manjše kot v SFR.

Kompleksanti vplivajo na obe zlitini. V pasivnem območju je ta vpliv zanemarljiv zaradi tvorbe izredno stabilne pasivne plasti Cr_2O_3 . Dobro korozijsko odpornost kroma potrjujejo tudi nizke koncentracije kromovih ionov v raztopini, izmerjene s polarografijo⁸. EDTA tvori zelo močne komplekse tudi z ioni Cr^{3+} ⁹, vendar zaradi zelo počasnega raztapljanja močno zaščitne plasti Cr_2O_3 je koncentracija Cr(III) zvrsti, ki je na voljo za kompleksacijo, izredno majhna⁸. Pri drugih potencialih sta obe zlitini korozijsko manj stabilni v prisotnosti kompleksantov, kar je razvidno iz nižjih vrednosti R_p , ker prihaja do tvorbe kompleksov Co^{2+} , Ni^{2+} in Mo^{6+} z EDTA ali citratom in posledično do slabše pasivacije.

5 SKLEPI

Iz dobljenih rezultatov lahko sklenemo, da se obe zlitini vedeta precej podobno v simulirani fiziološki raztopini, vendar pa je zlitina Co-Ni-Cr-Mo kljub vsemu nekoliko manj korozijsko odporna, predvsem v bolj agresivnem okolju v prisotnosti kompleksantov, kar se kaže v nekoliko tanjši pasivni plasti in večjem vplivu kompleksantov na elektrokemijske karakteristike te zlitine. Rezultati so tako potrdili naše domneve, da je zlitina brez niklja in z večjim deležem kroma bolj korozijsko stabilna.

The results of the impedance measurements for the Co-Cr-Mo alloy were similar to those for the Co-Ni-Cr-Mo alloy (**Figures 6a–e**). The values of the polarization resistance were somewhat higher than in the case of the Co-Ni-Cr-Mo alloy, which indicates a better corrosion resistance of the Co-Cr-Mo alloy (**Figure 8**). Both alloys were the most stable in the SPS and the least stable in the EDTA, which is confirmed by the reduced values of the polarization resistance in the presence of the complexing agents.

4 DISCUSSION

The results of the electrochemical measurements show that for the Co-Cr-Mo alloy there is no classical maximum at the crossing between the active and the passive states. At potentials lower than the passivation potential, i.e., $-0,3$ V, the alloy is not yet in the passive state, which is evident from the impedance response, where values of the polarization resistance are low and the diffusion process is present. Transfer to the passive region is related to the increase of the polarization resistance and to the formation of the arc in the Nyquist plots. The current density no longer alters with increasing potential. The formation of the passive layer is a result of the thickening of the passive layer of Cr_2O_3 . In the inner part of the passive layer CoO and MoO_3 are also present⁴. The passive region is stable up to a potential of $0,4$ V, where the current density starts to increase abruptly, and simultaneously the polarization resistance decreases.

The electrochemical characteristics of pure metals, i.e., Co, Ni and Mo, are significantly affected by the addition of the complexing agents. The level of influence on the particular metal ions depends on the stability constants of the metal complexes⁷. Nickel and cobalt form strong complexes with the EDTA, consequently an increase of the current density simultaneously with a decrease of the polarization resistance is observed. The shift of the corrosion potential is explained by the influence of the complexing agent on the equilibrium potential or on the concentration of the dissolved metal species, which is confirmed by the increased concentration of metal ions in the solution in the presence of the complexing agents⁸. The inferior corrosion resistance of Co, Ni and Mo in the presence of the complexing agents is confirmed by the EIS, where the R_p values in the presence of the EDTA and the citrate are lower than in the SPS at all polarization potentials.

Both alloys are influenced by the addition of the complexing agents. In the passive region the influence is negligible due to the formation of an extremely protective layer of Cr_2O_3 . The excellent corrosion resistance of chromium is confirmed by low concentrations of Cr ions in the solution, measured by polarography⁸. The EDTA forms very strong complexes with Cr^{3+} ions⁹; however, due to an extremely slow dissolution of the highly protective layer of Cr_2O_3 , the

6 LITERATURA/REFERENCES

- ¹ K. Merrit, S. A. Brown, N. A. Sharkey, The binding of metal-salts and corrosion products to cells and proteins in vitro, *J. Biomed. Mater. Res.* 18 (1984), 991–1004
- ² N. J. Hallab, C. Vermes, C. Messina, K. A. Roebuck, T. T. Glant, J. J. Jacobs, Concentration- and composition-dependent effects of metal ions on human MG-63 osteoblasts, *J. Biomed. Mater. Res.* 60 (2002), 420–433
- ³ D. Raistrick, J. R. Macdonald, D. R. Franceschetti v: Impedance Spectroscopy Emphasizing Solid Materials and Systems, John Wiley & Sons, New York 1987, 2
- ⁴ A. Kocijan, I. Milošev, B. Pihlar, Cobalt-based alloys for orthopaedic applications studied by electrochemical and XPS analysis, *J. Mater. Sci., Mater. Med.*, 15 (2004), 643–650
- ⁵ A. Kocijan, I. Milošev, Electrochemical and XPS studies of cobalt-based alloys in a simulated physiological solution, *Mater. tehnol.* 38 (2004) 6, 339–343
- ⁶ N. Bonanos, B. C. H. Steele, W. B. Johnson, W. L. Worell, D. D. Macdonald, M. C.H. McKurbe v Impedance Spectroscopy Emphasizing Solid Materials and Systems, John Wiley & Sons, New York, 1987, 4
- ⁷ I. Milošev, Effect of complexing agents on the electrochemical behaviour of orthopaedic stainless steel in physiological solution, *J. Appl. Electrochem.* 32 (2002), 311–320
- ⁸ A. Kocijan, I. Milošev, B. Pihlar, The influence of the complexing agent and proteins on the corrosion of stainless steels and their metal components, *J. Mater. Sci., Mater. Med.*, 14 (2003), 69–77
- ⁹ Critical Stability Constants, Plenum Press, New York, London, 1977, 3

concentration of Cr(III) species, in option for complexation, is very small⁸. Both alloys are less corrosion resistant in the presence of complexing agents at other polarisation potentials, which is evident from lower R_p values due to the formation of the complexes Co^{2+} , Ni^{2+} and Mo^{6+} with the EDTA or citrate, and therefore the passivation is inhibited.

5 CONCLUSIONS

An electrochemical study of Co-Ni-Cr-Mo and Co-Cr-Mo alloys showed that both alloys act rather similarly in simulated physiological solutions; however, in spite of this, Co-Ni-Cr-Mo alloy is somewhat less corrosion resistant, especially in the more aggressive environment of complexing agents. This results in a thinner passive layer and the pronounced influence of complexing agents on the electrochemical characteristics of the alloy mentioned above. The results thus confirmed our predictions that the alloy without nickel and with a larger chromium content displays superior electrochemical characteristics.