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Corrosion behavior of CoCrMoW cast alloy in lactic acid environment for surgical applications



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KEYWORDS

Corrosion; Biomaterials; CoCrMoW alloy; Electrochemical impedance spectroscopy; X-ray photoelectron spectroscopy; AFM **Abstract** The corrosion behavior of CoCrMoW alloy in lactic acid environment during 168 h of immersion at 37 °C has been studied and assessed by means of electrochemical techniques (open circuit potential (OCP), potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS)). Further, the oxide film thickness formed after immersion and the quantity of ions released have been evaluated by X-ray photoelectron spectroscopy (XPS) and inductively coupled plasma optical spectroscopy (ICP-OES). A good correlation between the results, related to the oxide film thickness, obtained from these experimental techniques was achieved. The research has also shown that the tendency of growing of oxide film becomes slower as the time of immersion is longer. The higher corrosion resistance of CoCrMoW alloy in lactic acid environment is due to the formation of the oxide film highly enriched in Cr(III) on the alloy surface. With a small corrosion rate, e.g. 45 nm year⁻¹, this alloy is characterized as "Perfect Stable" according to ISO 8044/2000. Overall, the present study provides additional evidences with respect to the benefic influence of tungsten on passivity, explained by a higher resistance to pitting corrosion of the CoCr-MoW alloy in lactic acid with sodium chloride.

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1. Introduction

Medical sector demands for materials with corrosion resistance and superior biocompatibility are increasingly higher in the last decades. The most important characteristic of a material used in reconstructive surgery or replacement of diseased or damaged bone tissue is undoubtedly carcinogenic effect or adverse tissue reactions of ions released in human body fluids as a result of corrosion (Dahlstrand et al., 2009; Mareci et al., 2012; Milosev and Strehblow, 2003; Mitsuo, 2002;

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Ocazaki and Gotoh, 2005; Reclaru et al., 2016; Sargeant and Goswami, 2007; Vasilescu et al., 2015). It is obvious that the noble metals and titanium are the most recommended materials but their costs are prohibitive for a large number of potential beneficiaries. Therefore, in last decades, were developed a series of metal materials to meet these requirements. Among the materials that were used heavily, those based on cobalt chromium alloys are on first places because of their corrosion and wear resistance. The main applications of these materials are dental and orthopedic implants (pins, plates, and hip).

It is indubitably established that the most powerful passivating element for metallic alloys is chromium and the alloying with chromium is the method to increase the localized corrosion resistance of metals, in halide environments as body fluids. In addition to chromium, also for improvement of resistance to localized corrosion attacks, molybdenum is used on a large scale. In the last decades of the 20th century, they have been reported some studies (Walke et al., 2006; Drob et al., 2015) for replacing the molybdenum, in stainless steels and cobalt alloys, with different elements such as copper and tungsten. Because tungsten belongs to the same group as molybdenum in the periodic table, it has a similar atomic structure and chemical properties. The mechanical properties of tungsten are similar to those of molybdenum. Thus, replacement of the molybdenum with other alloying elements (W, Cu), depends on of their availability and of synergetic effects in base alloys. In this connection, was reported that substituting tungsten for the element molybdenum in high chromium stainless steels would give even better local corrosion resistance and also higher structural stability of alloys (Ocazaki and Gotoh, 2005; Paital and Dahotre, 2009). The corrosion resistance of Co-W co-deposited alloys increased with tungsten content up to 21.5 wt.% and then decreased according to recent researches (Bodaghi and Hosseini, 2012). Other studies reported the effect of tungsten alloying on stacking faults density decreases (Karaali et al., 2005). On the other hand, some studies (Jonsson and Wegrelius, 2001) have reported that substitution of 2% of molybdenum with tungsten in the high alloyed austenitic stainless steels has low resistance to localized corrosion in the halide solution.

In recent years begin to impose on the medical devices market the manufacturing technologies which use CoCrMoW alloy and taking into consideration the rather contradictory literature reported data, concerning the influence of tungsten on corrosion behavior of CoCrMo alloy, it was considered appropriate the study of corrosion behavior of CoCrMoW alloy in lactic acid and NaCl solution.

2. Materials and methods

2.1. Materials

Alloy

The obtaining cobalt base dental alloy CoCrMoW (Remanium 2000 type) was made by pouring in cold crucible levitation melting furnace Five Cells type, under argon controlled atmosphere. Several specimens were cut from obtained ingots, whose chemical composition is given in Table 1.

2.2. Preparation of specimens

Base

All specimens used as working electrodes (of about 1 cm² as aria) were mechanically polished with silicon carbide paper

Table 1 (Chemical	composition	(%	weight)	of	CoCrMoW
alloy cast sp	pecimens.					
	Со	Cr	Μ	0	W	Si

7.84

5.74

1.74

27.95

of grade from 700 up to 1200, followed by a final finish with the water suspension of micrometric diamond powder and ultrasonically rinsed with ethanol and distilled water.

For preparing specimens a Cast'nVac Buehler vacuum machine was used to embed the CoCrMoW plates in organic resin. Specimens were further polished with Forcimat Digipret machine.

2.3. Microstructure, composition and surface morphology analysis

The structural analysis was done using scanning electron microscopy (SEM) with a microscope FEI Inspect F50, field emission and equipped with energy dispersive spectroscopy (EDS). The chemical analysis and the thickness of passive layer were studied using the X-ray Photoelectron Spectroscopy technique (Quantera SXM with AlK α radiation and overall resolution of 0.65 eV) by the full width at half-maximum (FWHM) of the Au4f7/2. The thickness of the surface film was assessed from layer by layer depth profiling experiments using Ar⁺ ion beam. The thickness was calculated using the relative sputter rate reported by (Baer et al., 2010) under similar experimental conditions (Ar⁺ beam kinetic energy, current density on the target, rastered area and incident angle).

The surface roughness was examined with atomic force microscopy (AFM). These measurements have been performed in noncontact mode, using the XE-100 microscope from Park Systems. All AFM images have been recorded with sharp NCHR (NanosensorsTM) tips, with less than 8 nm radius tip, app. 125 μ m length, 30 μ m width, spring constant 42 N/m, and 330 kHz resonance frequency. The AFM images have been processed with XEI program (v 1.8.0 – Park Systems) for displaying purpose root mean square roughness (RMS).

2.4. Corrosion characterization (evaluation)

In order to evaluate the corrosion behavior, the electrochemical measurements were performed using a Gamry Reference 600 potentiostat/galvanostat in a conventional three electrodes electrochemical system with: saturated Ag/AgCl electrode as a reference electrode, Pt electrode as an auxiliary electrode and a 1 cm² working electrode with a shape according with standard requirements for each test.

A solution of 0.1 M lactic acid and 0.1 M NaCl was used as corrosion environment according to ISO 10271/2001 standard. To evaluate the corrosion and biocompatibility behavior of CoCrMoW alloys performed the following tests according to ISO 10271/2001:

• The static immersion test during 168 h of immersion followed by ions released evaluation. The chemical analysis of electrolyte after immersion was done using an inductively coupled plasma optical emission spectrometer with axial and radial viewing plasma configuration (ICP-OES, Optima 2100 DV Perkin Elmer) operating at a 40 MHz free-running ratio-frequency. For each extraction environment, two blank samples are measured as a reference. The immersion period of specimens was prolonged up to 390 h in order to evaluate the protection performance of the passive film.

- The monitoring of open circuit potential (OCP) in time, during 390 h, and EIS response at different time periods as initial (0 min), 72 h, 168 h and 390 h of immersion. EIS measurements were performed at open circuit potential with 10 mV dc of perturbation potential, between 100 kHz and 0.01 Hz of frequency.
- The anodic polarization curves between $\pm 250 \text{ mV}$ around OCP, with the rate of potential scan of 0.05 mV s⁻¹ in order to evaluate the corrosion rate using Tafel analysis. The Tafel curves were acquired after EIS measurements, were done to evaluate the time evolution of corrosion rates.
- At the end of immersion time was done an anodic polarization curve from the cathodic zone (-50 mV) to anodic up to +1000 mV with a potential scan rate of 1 mV s⁻¹.

All reagents were of analytical quality. Each measurement was performed using three specimens in sterile containers with 50 mL of the incubation solution, at 37 $^{\circ}$ C.

3. Results and discussions

(a)

3.1. Microstructure and surface morphology

Fig. 1a displays the microstructure of cold cast CoCrMoW alloy with a specific cast dendritic microstructure which attests a relatively homogenous surface. Fig. 1b shows the chemical average composition revealed by EDS. The main alloying elements Co, Cr, Mo and W are detected.

The surface topography roughness of CoCrMoW alloy was estimated by AFM after mechanical polished of specimens and

40.0K Co (b) Cr 32.0K 24.0K 16.0K 8.0K Мо Co Co Cr Mo W w 0.0K 20 40 6.0 8.0 10.0 12.0 keV 00

Figure 1 SEM micrograph (a) and EDS elemental analysis (b), of CoCrMoW alloy.

the roughness surface parameters are presented in Table 2 and Fig. 2. The values of roughness surface parameters Rz, Rpv, Ra and the profile Z - corrugation suggest a porous and a rough surface of CoCrMoW alloy. It seems that the pores in the polished surface, which are the remnants of the sintering, result in the formation of such rough surface.

Keeping in mind that an implant with a rough and porous surface could improve the bioactivity and bone bonding ability, (Kheimehsari et al., 2015) it is expected that this surface might provide a good cells adhesion property. Furthermore, literature data (Andrei et al., 2016; Jakubowicz et al., 2012), show that a porous and rough structure assists with the supply of oxygen and blood, as well as bone in growth and anchoring at the interface. Thus, this surface might be proper for surgical applications as well.

3.2. Static immersion and ions release analysis

The static immersion test was conducted during 168 h for ions release evaluation according to ISO 10271/2001 at body temperature of 37 °C. Simultaneously, were performed the electrochemical and corrosion evaluation, by the open circuit potential-time monitoring coupled with the electrochemical impedance spectroscopy (EIS) and linear polarization curves. At the end of immersion time, according to the standard requirement (168 h), the ions release concentration was measured using the ICP method.

The amount of ions released during 168 h exposure of CoCrMoW compared with CoCrMo alloys in 0.1 N lactic acid +0.1 N NaCl aerated solution at 37 °C is displayed in Fig. 3. The ICP measured values are significantly higher for W-alloyed material (up to 20 times for cobalt ions release and 300 times for chromium) that confirms the slightly negative effect of tungsten on stainless steels reported by (Jonsson and Wegrelius, 2001). Calculating the percentage of each type of ion lost from total quantity it has been obtained the same percentages as in alloy which means that the material was uniformly dissolved (Fig. 3 in set).

3.3. XPS analysis

The XPS surveys (wide scans) spectra shown in Fig. 4 exhibit the main elements found on the outermost surface layer: Cr, Co, Mo.

It is well known that in the initial state, an oxide layer is formed in the air on the CoCrMoW surface alloy. The thickness of native oxide layer estimated from XPS depth profiling experiments using the relative sputter rates is of about 3 nm in good agreement with literature data (Milosev and Strehblow, 2003).

After 168 h of immersion the oxide film becomes thicker, i.e. of about 12 nm. In order to evaluate the tendency of growth rate of the oxide film, the specimens were maintained in solution up to 720 h taking into account that 390 h of immersion did not reveal significant differences compared with 168 h. As can be observed in Fig. 4 and Table 3, the spectrum of CoCrMoW surface alloy immersed for 720 h shows the largest amount of oxygen suggesting that the oxide thickness is the largest, i.e. 20 nm. The results revealed that the thickness of oxide is four times higher after 168 h of immersion, whereas after 720 h the thickness of oxide film is six times higher as

Table 2	Roughness	surface	parameters	of	CoCrMoW	alloy	taken	from	two	surface	areas	4 μm².	•
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Surface area	R_{pv} (nm)	$R_q (\mathrm{nm})$	R_a (nm)	R_z (nm)
$2 \times 2 \mu m$	127.032	17.628	13.823	125.201

 R_{pv} -maximum valley depth (nm); R_{q} -(R_{RMS})—root means squared (nm); R_{a} -arithmetical means roughness (nm); R_{z} -ten point mean roughness (nm).



Figure 2 Optical profiler surface scan (a) and X-profiles (b) of the CoCrMoW alloy ($2 \times 2 \mu m$ as scale).

shown in Fig. 4 and Table 3. It appears that the tendency of growing of oxide film becomes slower as the time of immersion is longer. We can conclude that the growth rate is controlled by oxygen and chrome diffusion through the film, in accordance with EIS results.

By comparing the CoCrMoW alloy immersed for different periods of time (Fig. 4 and Table 3) one can notice higher relative concentrations of oxygen and chromium accompanied by a significant decrease in cobalt content on the CoCrMoW surface alloy immersed 720 h. Therefore, the CoCrMoW surface alloy after immersion of 720 h appears enriched in chromium and depleted in cobalt. These results are in accordance with



Figure 3 Ions release after 168 h of immersion in aerated 0.1 M lactic acid + NaCl solution at 37 °C. Amount of released ions expressed in μ gcm⁻²: 1- CoCrMoW; 2- CoCrMo. In set: Percentage (w%) of total metal ions for each element from CoCrMoW alloy.



Figure 4 XPS superimposed wide scan (surveys) spectra for the CoCrMoW alloy: 1- native film; 2- after 168 h of immersion; 3- after 720 h of immersion (0.5 min Ar ion sputtering).

the ions release analysis. During immersion, the oxide film is formed mostly of chromium oxide, whereas the oxidized cobalt species are dissolved.

The deconvoluted Cr-2p spectrum of CoCrMoW alloy is shown in Fig. 5. The spectrum was well fitted with one doublet. We considered the spin orbit splitting for doublet of 9.7 eV and the Cr 2p3/2/Cr 2p1/2 ratio of 2. Since the major peak Cr-2p 3/2 of the doublet is located at 576.7 \pm 0.2 eV this doublet corresponds to the Cr(III) oxide species, (Moulder et al., 1995; NIST X-Ray, 2008).

Table 3 XPS data: element relative concentrations (at.%)obtained after different periods of immersion in lactic acidsolution of CoCrMoW alloy.

Specimens (0.5 min sputt.)	C1s	Ols	Cr2p	Co2p	Mo3d
1-native film ^a	24.2	27.7	11.8	25.8	2.5
2-after 168 h of immersion	38.7	36.0	16.3	7.6	1.4
3-after 720 h of immersion	28.2	49.9	17.6	3.5	0.8

^a The specimen 1 shows 8 (at.%) contribution from Cu2p doublet due to surface contaminating with Cu during sample handling. We emphasize that this element does not disturb the surface chemistry of specimen.

It is important to point out that in the formed surface oxide only Cr(III) species were assigned, without carcinogenic impact (Ocazaki and Gotoh, 2005; Milosev and Strehblow, 2003). Therefore the CoCrMoW alloy might show appropriate features for further surgical applications.

3.4. Electrochemical evaluation of CoCrMoW cast alloy

The electrochemical evaluation was carried out through the analysis of the open circuit potential variation with time and electrochemical impedance spectroscopy (EIS) tests. In order to analyze the corrosion behavior of the CoCrMoW dental alloy as well as to study the modifications of the properties of the passive film during immersion in lactic acid + Na Cl solution, EIS measurements were performed along with open circuit potential monitoring.

3.4.1. Open circuit potential (OCP) and EIS analysis

The open circuit potential (or rest potential) is an important irreversible parameter which characterizes the specimen's surface tendency to passivate or not by its movement to the electropositive or electronegative values. The passivation mechanism of a chromium alloy was described by (Banu et al., 2004) based on (Stiansy and Grimm, 1928) oxolation and hydro oxolation reactions of this element in aqueous environments. According to (Rollinson, 1966), the "olated compounds are complexes in which metal atoms are linked through bridging OH groups" and these groups are distinct

 $1.8 \times 10^{4} Cr2p$ $1.6 Cr^{3+}$ $1.2 \times 10^{4} Cr^{3+}$

Figure 5 The XPS Cr 2p spectrum for CoCrMoW alloy after 168 h of immersion in 0.1 M lactic acid + NaCl solution.

5 580 5 Binding Energy (eV)

585

575

570

0.4

590

from hydroxo groups from which they are derivated, as results of olation process.

The OCP-time evolution (Fig. 6) can be described as follow: during the first 50 h (zone z1) the initial potential of -117 mVmoved to the electropositive values at an approximative rate of 4 mV h^{-1} up to +100 mV (the OCP measured at 72 h was +103 mV). The Bode plot (Fig. 7a) acquired at the initial state of surface revealed a quasi-capacitive state. In the middle range of frequencies the phase angle is about -80° to -85° and decreases slowly at the low frequencies, characteristic of a passive state, so the surface is covered by a nonconsolidate native film confirmed by XPS analyze, too. During the next 340 h of immersion (Fig. 5 zone z2), the OCP remains approximatively constant at about $+100 \text{ mV} \pm 10 \text{ mV}$. Overlay the values of rest potential over anodic polarization curve (Fig. 10 inset) can be seen that it places at the beginning of passivation potential range, 2-3 mV. This has a correspondence in EIS diagram (Fig. 7b) where the phase angle tends to remain constant in the middle-low range of frequencies.

As can be observed, after 168 h of immersion the phase angle remains practically constant, close to -82 degrees, at medium and low frequencies and reached their maximum values (-85 degrees) at frequency range of 1–0.01 Hz, even though the initial trend was to drop to -75 degrees in the low frequency range. These high values of phase angle suggest the passive state of the surface (Zuo et al., 2008) and highlight a good corrosion resistance of the CoCrMoW alloy. In addition, the passive behavior of the CoCrMoW surface was observed at these frequency ranges because the phase angle values were independent of frequency while the absolute impedance values were increasing. At high frequency range the phase angle showed a resistive behavior corresponding to the solution resistance between the working and the reference electrode.

The Nyquist diagrams (Fig. 7c) show that the data are distributed along a large semicircle which is related to a passive film formed on the surface of the alloy. After 168 h of immersion, the high values of impedance in the low frequency range were observed and together with a capacitive behavior indicate that the passive film formed on CoCrMoW alloy becomes more protective. This sums up the impedance of surface passive film and the impedance of metal's charge transfer reaction. According to (Mansfeld, 1993) the oxide film can block the



Figure 6 OCP in 0.1 M lactic acid + NaCl solution (pH = 2.2) for CoCrMoW cast alloy.



Figure 7 Bode (a) and (b), and Nyquist (c) diagrams of CoCrMoW alloy after immersion in 0.1 M lactic acid + NaCl solution: initial time, t = 0; after 168 h of immersion.

access of electrochemically active species to the electrode surface, restricting ion diffusion to the surface, and thus reducing the overall corrosion rate.

This behavior is significantly changed as compared to dental cobalt alloy, without tungsten and with lower molybdenum content, studied and reported earlier (Banu et al., 2008). In the initial state, the EIS diagrams of CoCrMo alloy show a reactive behavior, with a total Rp about 50 k Ω , compared with the current value of 1 M Ω . This is explained by increasing molybdenum content from 4% to 8% despite slightly negative effect induced by tungsten and is correlated with the other reported data (Metikos-Hukovic et al., 2006). While, in principle, there are two- time constant for both alloys (related to passive film and charge transfer processes), the increase in molybdenum content from 4% to 8% changed the shape of angle plot. As shown in Fig. 7 for CoCrMoW alloy, both time constants overlap together as a quasi-horizontal region, and a highly capacitive behavior manifested as a linear display on Bode curve is clearly seen, suggesting a passive state due to the presence of the formed oxide film (Banu et al., 2006; Moisel et al., 2008). According to this behavior the electrical equivalent circuit, EEC, used to model the electrolyte - surface specimen interface is presented in Fig. 8 and Table 4 after data fitting.

The EIS results are good fitted with the EEC proposed in Fig. 8 consisting of two R-C groups disposed in series. The physical meaning of the EEC proposed is attributed to the resistance oxide (R_2)/capacitance (CPE₂) in parallel combination across the oxide and to the charge transfer resistance (R_1 -)/double layer capacitance (CPE₁) parallel combination.

These two times constant can be attributed at high frequencies to the electrical double layer and at middle –low frequencies to the passive layer on the surface. The numerical fitting values show the increase of passive film resistance from $5.9 \times 10^6 \Omega$ to $1.23 \times 10^7 \Omega$ (at about 10 times) during 168 of immersion hours in lactic acid and NaCl solution and tend to continuously increase. The passive film resistance increasing is confirmed by film thickening as results of calculations made with data from EIS curves (Table 4) and XPS measurements. Furthermore, the film thickness could be calculated according to the known expression of capacitance (Bommersbach et al., 2005; Preda et al., 2013; Valero Vidal and Igual Munoz, 2010)

$$C = \varepsilon \varepsilon_o \frac{A}{d} \tag{1}$$

where ε is the relative dielectric constant of the oxide, ε_o is the vacuum permittivity (8.85 × 10⁻¹⁴ F cm⁻¹), A is work surface area (cm²) and d is the film thickness.

In order to use the Eq. (1), the CPE from the EEC has been converted in a pure capacitance *C*, with the following equation (Cosman et al., 2005):

$$CPE = R^{n-1} \times C^n \tag{2}$$

where *R* corresponds to R_2 when calculating capacitance values of the inner layer of the passive film C_2 .

To calculate the film thickness from EIS data with Eq. (1), was used the dielectric constant of Cr_2O_3 ($\epsilon \sim 12$ from Scherer et al., 1999). The results are shown in Table 4 and are in good agreement with those obtained by XPS depth-profiles.

The excellent fitting between values resulting from EIS data and XPS measurements related to film thickness (*d*), suggests that the film formed during immersion on CoCrMoW surface alloy is composed predominately of Cr_2O_3 tacking into



Figure 8 Equivalent electrical circuit used to fit the impedance data. Rs –solution resistance; R_1 -charge transfer resistance; CPE_1 -double layer capacitance; R_2 -oxide film resistance; CPE_2 -oxide film capacitance.

Table 4	Impedance parameters	obtained by data	fitting with the electric	al equivalent circuit an	d calculation using Eq. (1) .
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Immersion time, h	$R_s, \Omega\mathrm{cm}^{-2}$	CPE_1 , $S cm^{-2} s^n$	n_1	$R_1, \Omega\mathrm{cm}^{-2}$	CPE_2 , S cm ⁻² s ⁿ	C_2 , $F \text{ cm}^{-2}$	n_2	$R_2, \Omega\mathrm{cm}^{-2}$	d, nm
0	32.4	0.31e-4	0.75	7.92e6	2.28e-6	3.10e-6	0.92	5.9e6	3
168	35.9	3.25e-5	0.77	2.27e7	7.29e-5	7.29e-6	0.96	1.23e7	11
Chi-squared value $\gamma^2 = 1.3 \times 10^{-4}$.									

account the theoretical reported value of $\varepsilon = 12$ used, is the electrical permittivity of Cr₂O₃.

3.5. Corrosion evaluation

3.5.1. General corrosion

General corrosion or uniform corrosion is "corrosion that proceeds at about the same rate over a metal surface" as defined by the ASTM Standard G 15. The corrosion rate can be calculated by weight (mass) loss accordingly to Guidelines for mass loss corrosion rate determination given in the ASTM Standard G 31 and G1. For these experiments, general corrosion rate ($gm^{-2} h^{-1}$) was calculated using two ways: by mass loss, weighting each specimen at the beginning and after 168 h, and with Tafel slops method.

3.5.2. Corrosion rates from Tafel plots

Electrochemically, the general corrosion evaluation of CoCr-MoW alloy was done from corrosion current densities i_{corr} . The i_{corr} values were calculated with Tafel method which consists in counting the corrosion rates from polarization resistance (R_p) and slopes of anodic and cathodic branches of polarization curves using Stern-Geary equation (ASTM G 102 -1999):

$$i_{corr} = \frac{\frac{b_a b_c}{2.303(b_a + b_c)}}{R_p}$$
(3)

where b_a and b_c are anodic and cathodic slopes respectively; R_p is polarization resistance.

Fig. 9 shows the polarization curves, acquired in 0.1 M NaCl + 0.1 M lactic acid, after different periods of immersion and Table 5 displays the main electrochemical parameters extract from curves. From the polarization curves very low current densities were obtained, indicating a passive behavior for CoCrMoW alloy argued in the previously presented results.

After 72 of immersion hours, the corrosion rate is very small, at about 6 nm per year, and tends to increase up to ten times in 15 days up to 60 nm per year. Despite that, all corrosion rates values remain very small and the alloy is included in the corrosion resistance group in conventional stability scale "Perfect Stable" according to ISO 8044/2000 ($v_{corr} < 1 - \times 10^{-3}$ mm year⁻¹). These obtained values are in agreement with those reported by the other authors (Andrei et al., 2016) adding that the solutions are different in terms of corrosiveness.

Based on Faraday equation the conversion relationship between current density and general corrosion rates express in $\text{gm}^{-2} \text{ h}^{-1}$, is as follows:

$$v_{corr} = 0.89 \times i_{corr} \tag{4}$$

where i_{corr} is the current corrosion density, $A \text{ cm}^{-2}$. Corrosion rate calculated with Eq. (3) after 168 h of immersion is $1.54 \times 10^{-5} \text{ gm}^{-2} \text{ h}^{-1}$ and by mass loss is $1.6 \times 10^{-5} \text{ gm}^{-2} \text{ -} \text{ h}^{-1}$, practically the same value.

On the other hand, all steady state potential values (Fig. 6) are around +100 mV/Ag/AgCl more positive compared with the corrosion values from Tafel measurements (Table 5), so the CoCrMoW surface alloy is passivated, the anodic polarization curve acquired after 390 h of immersion exhibits a diffusion limited current density at about 200 nA cm⁻².

3.5.3. Anodic linear polarization curve

Fig. 10 displays the linear polarization curve acquired by potential scanning between -50 mV and 1000 mV at rate of 0.1 mV s^{-1} . It can be seen that in all anodic potential range the alloy surface is passive, there is a diffusion limited density current of 200 nA cm⁻².

The current density increasing, at about +800 mV vs Ag/AgCl, is far from the transpassive dissolution of Cr⁺³ to Cr⁺⁶, according to Pourbaix (Pourbaix, 1974) diagrams and following reaction:

$$Cr_2O_3 + 5H_2O \leftrightarrow 2HCrO_4^- + 8H^+ + 6e^-$$

(*E*₀ = 1.108 V vs Ag/AgCl, pH = 2.2) (5)

$$Cr_2O_3 + 4H_2O \leftrightarrow 2Cr_2O_7^{-2} + 8H^+ + 6e^-$$

($E_0 = 1.188 V \text{ vs } Ag/AgCl, pH = 2.2$) (6)

$$Cr_2O_3 + 5H_2O \leftrightarrow CrO_4^{-2} + 10H^+ + 6e^-$$

($E_0 = 1.215 V \text{ vs } Ag/AgCl, pH = 2.2$) (7)



Figure 9 Polarization curves acquired in 0.1 M lactic acid + NaCl, after different immersion periods (72, 168 and 390 h, respectively), at 37 °C.

Table 5 The main electrochemical parameters obtained frompolarization curves after different periods of immersion in0.1 M lactic acid + NaCl solution at 37 °C.

Time, h	E_{corr} , m V	i_{corr} , nA cm ⁻²	v_{corr} , $\mu m y^{-1}$
72	7.9	0.25	0.006
168	33	1.74	0.045
390	26	2.4	0.06

The electrochemical behavior of CoCrMo alloy at very electropositive potentials might be attributed to the oxygen evolution (Bettini et al., 2013).

$$2H_2O \leftrightarrow O_2 + 4H^+ + 4e^- \quad (E_0$$

= 0.84 V vs Ag/AgCl, pH = 2.2) (8)

A supplementary argument of water oxidation at this value of electrode potential is electro catalytic activity of cobalt species for oxygen overpotential decreasing that was described by (Nikoloski and Nikol, 2010).

Thus, the alloy is not sensitive to localized corrosion during immersion in lactic acid and sodium chloride, the length of passivation potential range is same with those acquired in solution without chloride ions (Banu et al., 2008). It seems then possible to conclude that the CoCrMoW alloy exhibits a stable passive behavior.

According to (Jonsson and Wegrelius, 2001), quantifying the contribution to pitting corrosion resistance of stainless steels, as PREN number, is given by the coefficients of 3.3 for Mo and 1.65 for W.

$$PREN = Cr + 3.3Mo + 1.65W + 30N$$
(9)

For studied alloy was calculated the contributions only of Mo and W, and are obtained the PREN $_{CoCrMoW} = 35.343$. This is over two times bigger compared with regular CoCrMo alloy (Stelite type) calculated for an average chemical composition, PREN $_{CoCrMoW} = 16.269$.

This explains the much higher resistance to pitting corrosion in the lactic acid with sodium chloride solution of CoCr-MoW alloy and the benefic influence of tungsten on passivity.



Figure 10 Anodic polarization curve of CoCrMoW alloy in aerated 0.1 M lactic acid and NaCl solution at 37 °C. Scan rate 1 mV s^{-1} . In set: OCP on first 10 min.

4. Conclusions

Electrochemical techniques (OCP, potentiodynamic measurements, EIS) and X-ray photoelectron spectroscopy were employed to characterize the corrosion behavior of CoCrMoW cast alloy in lactic acid environment. From the obtained results, the following conclusions are reached:

- 1. In the initial state, an oxide layer is formed spontaneously in the air on the CoCrMoW surface alloy. Its thickness was calculated, of about 3 nm, from XPS depth profiling experiments. After 168 h of immersion the oxide film becomes thicker, i.e. of about 12 nm, whereas after 720 h the thickness of oxide film is of about 20 nm. It appears that the tendency of growing of oxide film becomes slower as the time of immersion is longer. We can conclude that the rate of growing is controlled by oxygen and chrome diffusion through the film, in accordance with polarization curve.
- 2. The Bode plot acquired at the initial state of surface revealed a quasi-capacitive state. In the middle range of frequencies the phase angle is about -80° to -85° and decreases slowly at the low frequencies characteristic of a passive state, so the surface is covered by a non-consolidate native film confirmed by XPS analyze, 3 nm.
- 3. There are two- time constant that overlap together as a quasihorizontal region, and a highly capacitive behavior manifested as a linear display on Bode curve, suggesting a passive state due to the presence of the formed oxide film.
- 4. Was calculated the film thickness from EIS data. The excellent fitting between values resulting from EIS data and XPS measurements related to film thickness, suggests that the film formed during immersion on CoCrMoW alloy is composed predominately of Cr₂O₃ tacking into account the theoretical reported value of $\varepsilon = 12$ used, is the electrical permittivity of Cr₂O₃.
- 5. Corrosion rate calculated with Eq. (3) after 168 h of immersion is $1.54 \times 10^{-5} \text{ gm}^{-2} \text{ h}^{-1}$ and it is consistent with the corrosion rate calculated from mass loss, e.g. $1.6 \times 10^{-5} \text{ gm}^{-2} \text{ h}^{-1}$.
- 6. Since the length of passivation potential range is the same with that one acquired in solution without chloride ions the CoCrMoW alloy is not sensitive to localized corrosion during immersion in lactic acid solution and sodium chloride. These results suggest the benefic influence of tungsten on passivity and a better resistance to pitting corrosion in lactic acid solution with sodium chloride.
- 7. The ICP measured values for ions released are significantly higher for W-alloyed material (up to 20 times for cobalt ions release and 300 times for chromium) that confirms the slightly negative effect of tungsten.
- 8. One of the more significant findings to emerge from this study is that in the formed surface oxide only Cr(III) species were assigned, without carcinogenic impact. Therefore the CoCrMoW alloy might show appropriate features for further surgical applications.

Authors contributions

Maria Marcu performed electrochemical test, analyzed data and wrote the paper; Alexandra Banu planned the experiments, analyzed the data and wrote the paper; Cristina Juganaru performed OCP measurements; Petre Osiceanu performed XPS measurements; Mihai Anastasescu carried out AFM measurements; Luiza Capra performed ICP-OES analysis of electrolyte after immersion.

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References

- ASTM G 15 (Withdrawn 2010). Standard Terminology Relating to Corrosion and Corrosion Testing.
- ASTM G 31–72, 2004. Standard Practice for Laboratory Immersion Corrosion Testing of Metals.
- ASTM G 1-03, 2011. Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens.
- ASTM G 102, 1999. Standard Practice for Calculation of Corrosion Rates and Related Information from Electrochemical Measurements.
- Andrei, M., Galateanu, B., Hudita, A., Costache, M., Osiceanu, P., Calderon Moreno, J.M., Drob, S.I., Demetrescu, I., 2016. Electrochemical comparison and biological performance of a new CoCrNbMoZr alloy with commercial CoCrMo alloy. Mater. Sci. Eng., C 59, 346–355.
- Baer, D.R., Egelhard, M.H., Lea, A.S., Nachimuthu, P., Drobay, T. C., Kin, J., Lee, B., Mathews, C., Opila, R.L., Saraf, L.V., Stickle, W.F., Walace, R.M., Wright, B.S., 2010. Comparison of the sputter rates of the oxide films relative to the sputter rate of SiO₂. J. Vac. Sci. Technol., A 28, 1060–1072.
- Banu, A., Radovici, O., Marcu, M., Pirvu, C., 2004. Electrochemical behavior of corroding Co-Cr dental alloys in artificial saliva. In: Brillas, E., Cabot, P.L., (Eds.), Trends in Electrochemistry and Corrosion at the Beginning of the 21st Century. Universidad de Barcelona Publish, pp. 613–621.
- Banu, A., Marcu, M., Radovici, O., Pirvu, C., Vasilescu, M., 2006. Electrodissolution studies of three aluminum alloys in acid, neutral and alkaline solutions. Rev. Roum. Chim. 51, 193–198.
- Banu, A., Radovici, O., Marcu, M., 2008. The alloying influence on corrosion behavior of chromium surgical alloys. Rev. Roum. Chim. 53, 947–953.
- Bettini, E., Leygraf, C., Pan, J., 2013. Nature of current increase for CoCrMo alloy: "transpassive" dissolution vs water oxidation. Int. J. Electrochem. Sci. 8, 11791–11804.
- Bodaghi, A., Hosseini, J., 2012. Corrosion behavior of electrodeposited cobalt-tungsten alloy coatings in NaCl aqueous solution. Int. J. Electrochem. Sci. 7, 2584–2595.
- Bommersbach, P., Emany-Dumont, C., Millet, J.P., Normand, B., 2005. Formation and behavior study of an environment friendly corrosion inhibitor by electrochemical methods. Electrochim. Acta 51, 1076–1084.
- Cosman, N.P., Fatih, K., Roscoe, S.G., 2005. Electrochemical impedance spectroscopy study of the adsorption behaviour of α -lactalbumin and β -casein at stainless steel. J. Electroanal. Chem. 574, 261–271.
- Dahlstrand, H., Stark, A., Anissian, L., Hailer, N.P., 2009. Elevated serum concentrations of cobalt, chromium, nickel, and manganese after metal-on-metalalloarthroplasty of the hip: a prospective randomized study. J. Arthroplasty 24, 837–845.
- Drob, S.I., Vasilescu, C., Andrei, M., Calderon Moreno, J.M., Demetrescu, I., Vasilescu, E., 2015. Microstructural, mechanical and anticorrosion characterization of new CoCrNbMoZr alloy. Mater. Corros. 67, 739–747.
- ISO 10271/2001- Dentistry Corrosion test methods for metallic materials.
- ISO 8044/2000. Corrosion of metals and alloys. Basic terms and definitions Status: Revised, Withdrawn Published: April 2000 Replaced By BS EN ISO 8044, 2015.
- Jakubowicz, J., Adamek, G., Jurczyk, M.U., Jurczyk, M., 2012. 3D surface topography study of the biofunctionalised nanocrystalline Ti-6Zr-4Nb/Ca-P. Mater. Charact. 70, 55-62.

- Jonsson, J.Y., Wegrelius, L., 2001. A comparison between two high molybdenum superaustenitic stainless steel grades. Avesta Polarit, Corros. Manage. Appl. Eng. 1, 2–8.
- Karaali, A., Mirouh, K., Hamamda, S., Guiraldenq, P., 2005. Microstructural study of tungsten influence on CoCr Alloys. Mater. Sci. Eng., A 390, 255–259.
- Kheimehsari, H., Izman, S., Shirdar, M.R., 2015. Effects of HAcoating on the surface morphology and corrosion behavior of a Co-Cr-based implant in different conditions. JMEPEG 24, 2294–2302.
- Mansfeld, F., 1993. Analysis and Interpretation of EIS Data for Metals and Alloys, Technical Report 26. Solartron-Schlumberger, Farnborough, Ch, p. 4.
- Mareci, D., Chelariu, R., Iacoban, S., Munteanu, C., Bolat, G., Sutiman, D., 2012. The estimation of localized corrosion behavior of Ni-based dental alloys using electrochemical techniques. JMEPEG 21, 1431–1439.
- Metikos-Hukovic, M., Pilic, Z., Babic, R., Omanovic, D., 2006. Influence of alloying elements on the corrosion stability of CoCrMo implant alloy in Hank'S solution. Acta Biomater. 2, 693–700.
- Milosev, I., Strehblow, H.-H., 2003. The composition of the surface passive film formed on CoCrMo alloy in simulated physiological solution. Electrochim. Acta 48, 2767–2774.
- Mitsuo, N., 2002. Recent Metallic Materials for Biomedical Applications. Metall. and Mat. Trans.A, 33, 477.
- Moisel, M., de Mele, M.A.F.L., Muler, W.-D., 2008. Biomaterial interface investigated by electrochemical impedance spectroscopy. Adv. Eng. Mater. 10, B33–B45.
- Moulder, J.F., StickleW, F., Sobol, P.E., Bomben, K.D., 1995. Handbook of X-ray Photoeletron Spectroscopy. Physical Electronics, Eden Prairie, MN.
- Nikoloski, A.N., Nikol, M.J., 2010. Addition of cobalt to lead anodes used for oxygen evolution—a literature review. Min. Process. Extractive Metall Rev. 31, 30–40.
- NIST X-Ray, 2008. Photoelectron Spectroscopy Database, Version 4.0. National Institute of Standards and Technology, Gaithersburg.
- Ocazaki, Y., Gotoh, E., 2005. Comparison of metal release from various metallic biomaterials in vitro. Biomaterials 26, 11–21.
- Paital, S.R., Dahotre, N.B., 2009. Calcium phosphate coatings for bioimplant applications: materials, performance factors, and methodologies. Mater. Sci. Eng. 66, 1–70.
- Pourbaix, M., 1974. Atlas of Electrochemical Equilibria in Aqueous Solutions. National Association of Corrosion Engineers, Houston, Texas, p. 260.
- Preda, L., Negrila, C., Lazarescu, M., Enache, M., Anastasescu, M., Toader, a., Ionescu, S., Lazarescu, V., 2013. Ga and As competition for thiole formation at p-GaAs(111) surfaces. Electrochim. Acta 104, 1–11.
- Reclaru, L., Unger, R.E., Kirkpatrik, C.J., Susz, C., Eschler, P.Y., Zuercher, M.H., 2016. Ni-Cr based dental alloys; Ni release, corrosion and biological evaluation. Mater. Sci. Eng., C 59, 346– 355.
- Rollinson, C.L., 1966. Olation and related chemical processes. In: Bailar, J.C. (Ed.), The Chemistry of the Coordination Compounds. Reinhold Pbl., New York, pp. 448–452.
- Sargeant, A., Goswami, T., 2007. Hip implants-Paper VI-Ion concentrations. Mater. Des. 28, 155–171.
- Scherer, H., Weimann, Th., Hinze, P., Samwer, B.W., Zorin, A.B., Niemeyer, J., 1999. Characterization of all-chromium tunnel junctions and single-electron tunneling devices fabricated by direct-writing multilayer technique. J. Appl. Phys. 86, 6956–6964.Stiansy, E., Grimm, O., Collegium 694, 1928.
- Stiansy, E., Grinnin, O., Conegiuni 094, 1926
- Valero Vidal, C., Igual Munoz, A., 2010. Study of the adsorption process of bovine serum albumin on passivated surface of CoCrMo biomedical alloy. Electrochim. Acta 55, 8445–8452.

- Vasilescu, C., Drob, S.I., Calderon Moreno, J.M., Osiceanu, P., Popa, M., Vasilescu, E., Marcu, M., Drob, P., 2015. Long-term corrosion resistance of new Ti–Ta–Zr alloy in simulated physiological fluids by electrochemical and surface analysis methods. Corros. Sci. 93, 310–323.
- Walke, W., Paszenda, Z., Tyrlik-Held, J., 2006. Corrosion resistance and chemical composition investigations of passive layer on the

implant surface of CoCrWNi alloy. J. Achievements Mater. Manuf. Eng. 18, 74–79.

Zuo, Y., Pang, R., Li, W., Xiong, J.P., Tang, Y.M., 2008. The evaluation of coating performance by the variations of phase angles in middle and high frequency domains of EIS. Corrosion Sci. 50, 3322–3328.