



## CORROSION BEHAVIOR OF A COBALT ALLOY WITH LESS CHROMIUM AND MOLYBDENUM CONTENT IN LACTIC ACID ENVIRONMENT

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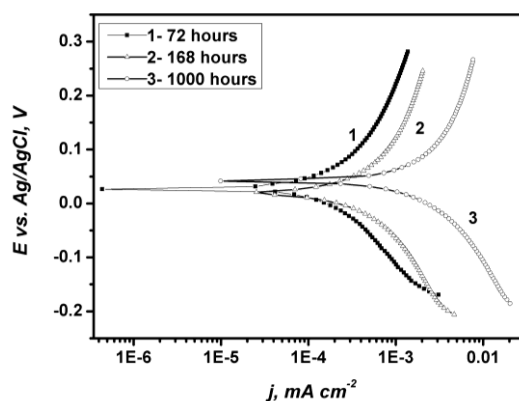
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This study presents the effects of using a lower level of chromium and molybdenum alloying elements on corrosion behavior of Co<sub>24</sub>Cr<sub>3</sub>Mo<sub>8</sub>W alloy regarding its stability in a lactic acid environment. The corrosion parameters, *i.e.* corrosion potential ( $E_{cor}$ ) and corrosion current density ( $i_{cor}$ ), were estimated from potentiodynamic polarization at different period of immersion in 0.1 M lactic acid +0.1 M NaCl solution at 37°C. A small value of  $i_{cor}$  (*i.e.* 0.417  $\mu\text{A cm}^{-2}$ ) after 1000 h of immersion underlines a good corrosion resistance of this alloy in biological environments. This behavior is provided by a thin oxide layer formed on the surface of Co<sub>24</sub>Cr<sub>3</sub>Mo<sub>8</sub>W alloy in the first 100 hours of immersion. Electrochemical investigations highlighted that the Co<sub>24</sub>Cr<sub>4</sub>Mo<sub>8</sub>W alloy, with lower content of chromium and molybdenum, has proven corrosion resistance and ion release comparable to those of Co<sub>28</sub>Cr<sub>8</sub>Mo<sub>6</sub>W alloy and can be a less expensive alternative for medical applications.



### INTRODUCTION

Cobalt-based alloys have dominated the alloy market in many areas of application for aggressive corrosive environments such as high temperatures, high chloride ion solutions, precisely because of their high corrosion resistance,<sup>1,2</sup> most of these containing 28-30% Cr, 6-8% Mo and 5-8% W. Among the applications developed a lot in the last decades, a special place is occupied by the medical ones because, in the human physiological conditions, characterized by high aggressiveness

due to the presence of water, chlorine ions and other organic compounds, the passivity films formed on the surface of surgical implants help to retain them in the human body for a long time.<sup>3-6</sup> It must not neglect the fact that in the conditions of the increase of the prices of the noble metals, the chromium-based alloys represented a viable alternative both from the economic point of view and of the patients' health.<sup>2</sup>

Because of the well-known capacity of molybdenum to increase the passivation behavior of chromium alloyed metals, most CoCr alloys

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used in surgical applications contain molybdenum in the range of 6-8 wt. %. On the other hand, the regular cobalt alloys contain more than 27% of chromium for their corrosion properties improvement.<sup>7,8</sup>

Therefore, the trend in recent decades has been to replace Mo partially or completely with other alloying elements so that the corrosion resistance properties of chromium cobalt alloys do not decrease. Among the most studied alloying elements were nickel and tungsten,<sup>4</sup> and of these two elements W preserves the most chemical stability of CoCr alloys.<sup>9</sup>

The dissolution of the elements with higher atomic radius in the crystalline cells of Co, favors the stability of the  $\epsilon$  phase (hcp) and the increase of the fragility of the alloys. The atomic radius of Mo is 139 pm, higher than that of W (137 pm) and Ni (125 pm), respectively, so its hardening effect of the matrix is higher and the alloys with high molybdenum content are more difficult to process.<sup>10,11</sup> Other studies reported the effect of tungsten alloying on stacking faults density decreases.<sup>12</sup>

The main objective of this paper is to highlight the effect of a lower level of chromium and molybdenum alloying of CoCrMoW alloy on its chemical stability in synthetic biofluidic media. To analyze the biocompatibility of this alloy with lower molybdenum content, an aggressive

environment, 0.1 M lactic acid + 0.1M NaCl solution (pH = 2.5) was taken into account in correlation with the information present in the literature.<sup>13-15</sup> As a standardized method, stationary immersion<sup>16</sup> was used for 168 hours, which was accompanied by electrochemical measurements designed to highlight the tendency of the alloy to passivate or activate. To better understand the corrosion behavior of Co24Cr3Mo8W alloy in an aggressive environment the immersion period was prolonged up to 1000 hours.

## RESULTS AND DISCUSSION

The microstructure of the Co24Cr3Mo8W alloy illustrated in Figure 1 shows a typical casting structure. The intermetallic phase varies in size and distribution, and it is presented by the gray area in the figure bordered with small amounts of carbides. Carbide precipitates can be seen as dark grey points of different sizes and shapes in the intermetallic phase. These phases are due both to the structure and as a result of the increase of the dislocation density, by increasing the mismatch of the atomic radii of the alloying elements.<sup>4,17</sup>

The right up corner of Figure 1 presents the average chemical composition of studied alloy performed by EDX analysis.

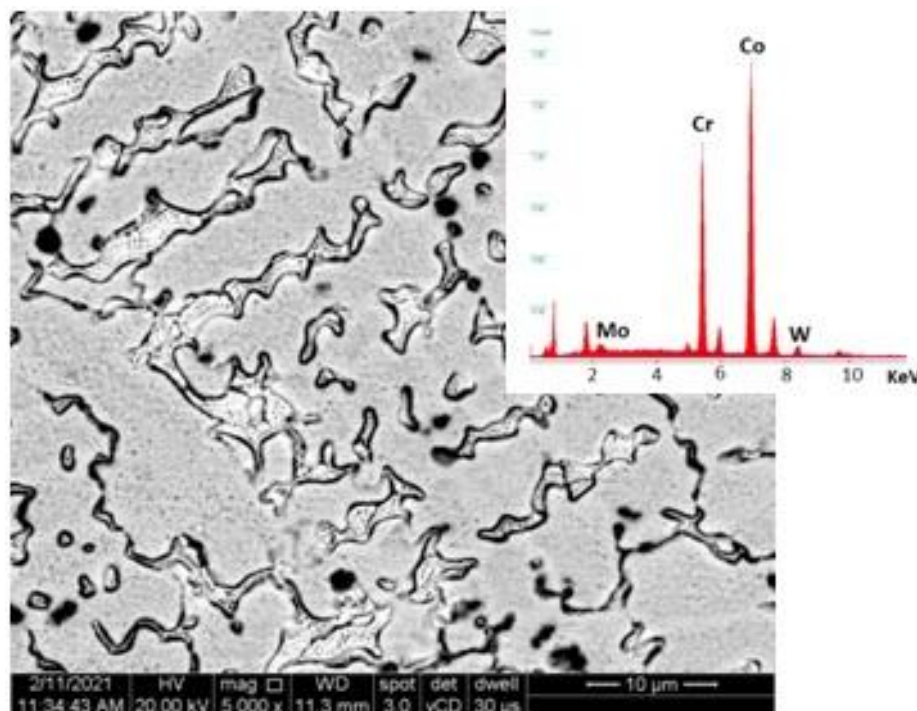


Fig. 1 – SEM micrograph of the Co24Cr3Mo8W alloy before immersion; in set: EDAX result of chemical analysis of the Co24Cr3Mo8W alloy.

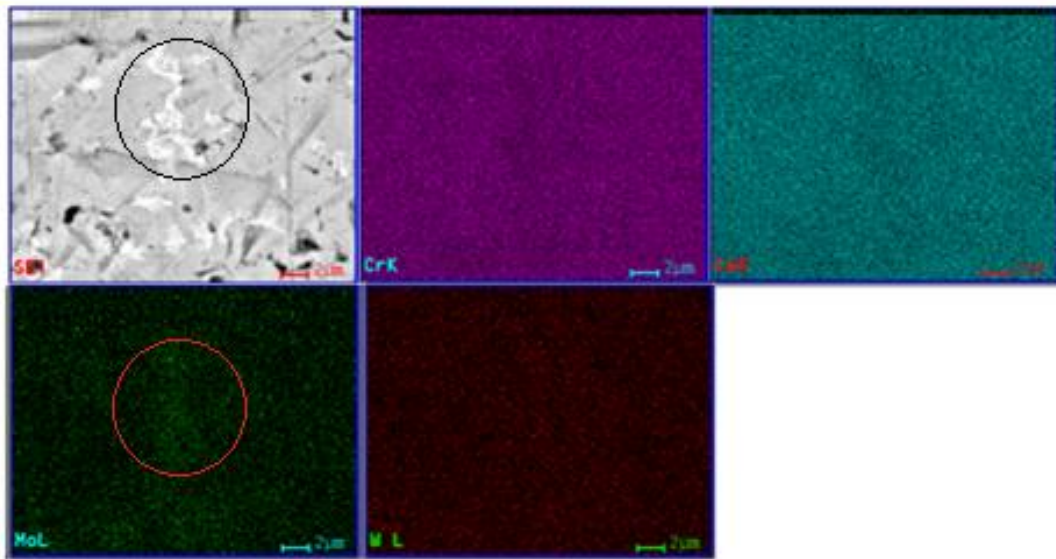


Fig. 2 – The elemental maps distribution of main alloying elements for Co24Cr3Mo8W alloy.

The distribution maps of the elements made by EDX, illustrated in Figure 2, show a homogeneous distribution of the elements in the solid solution. However, the small, brighter areas are richer in molybdenum, Figure 2.

### Open Circuit Potential evolution

It is well known that the open circuit potential of passive alloys, including chromium alloys, depends on the pH of the solution they come into contact with,<sup>18, 19</sup> as the stability of spontaneously formed passive films on their surface is influenced by the presence in the solution of different ion species such as  $H^+$ ,  $Cl^-$ . Figure 3 shows the

evolution, in 1000 hours of immersion, of stationary potentials of the cobalt studied alloy.

Regarding this studied environment (0.1 M Lactic Acid +0.1M NaCl), it is characterized by several aspects related to its aggressiveness on metal alloys. The first aspect is the acidic pH of the environment with the depassivating action of  $H^+$  ions. The second aspect is the presence of the organic radical (lactate), known for its ability to bind with metal ions and to form complex compounds thus contributing to the dissolution of oxide films at low pH values.<sup>20-22</sup> Another aspect is the presence of chlorine ions in solution, depassivating ions that generate, especially in acidic environments, localized corrosion forms as it can be seen in the Figure 4.

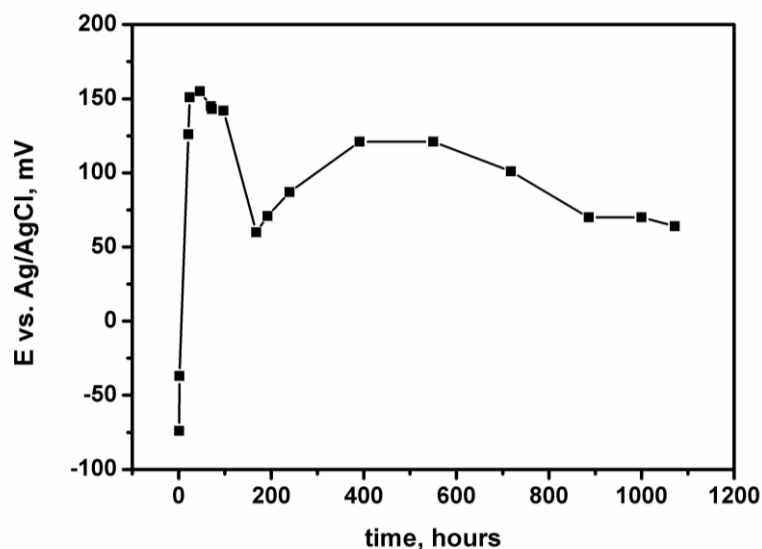


Fig. 3 – The OCP-time evolution of Co24Cr3Mo8W alloy in 0.1M Lactic Acid +0.1M NaCl solution.

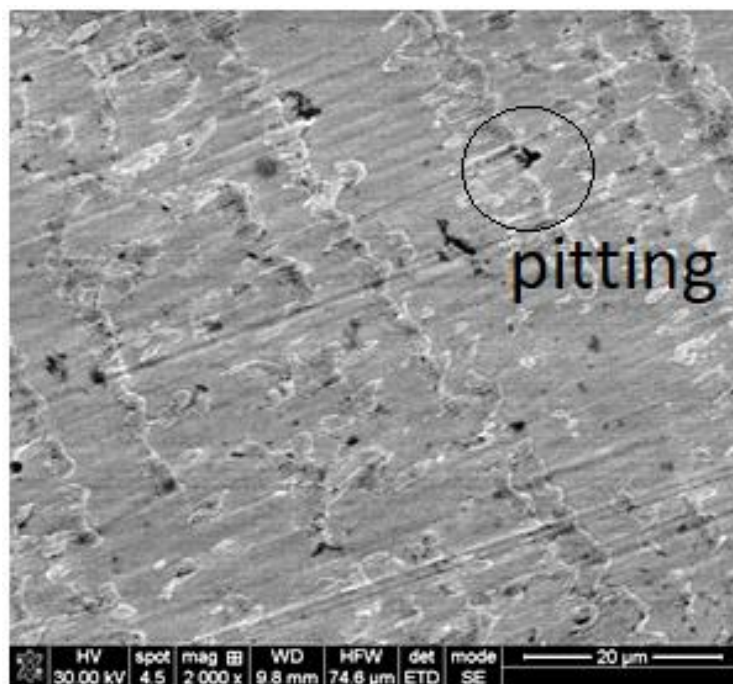


Fig. 4 – SEM surface aspect of Co24Cr3Mo8W alloy after 1000 ore immersion in 0.1M LA+0.1M NaCl.

In our previous paper,<sup>21</sup> the influence of chlorine ions in the lactic acid solution on the evolution of OCP of a CoCrMo alloy was shown. The tendency to depassivation of the oxide layer by penetration of Cl<sup>-</sup> ions in the passive layer that causes a local activation of the surface followed by its repassivation by the restoration of the passive layer was noticed. This behavior translates into oscillations of OCP with 10 mV around of the average value. Compared with the previously reported results<sup>21</sup> for the Co29Cr6Mo8W alloy the Co24Cr3Mo6W studied alloy shows different evolution of OCP. The higher chromium and molybdenum content stabilized OCP after 100 hours of immersion at values of +100 mV vs. Ag/AgCl with oscillations of ±10 mV,<sup>18</sup> while the OCP of the alloy with 24% Cr and 3% Mo shows a steep increase up to +150 mV vs. Ag/AgCl of potential in the first 50 hours of immersion, followed by a decrease of the potential up to +70 mV vs. Ag/AgCl in the next 100 hours, and then a relative stability (±20 mV) at values of about +100 mV for almost 800 hours. Therefore, the decrease in the content of the passivating elements, Cr and Mo, could cause the dissolution of the native film on the surface after 50 hours of immersion, and the formation over time of a new thin passive film. These results are supported by the SEM image of the alloy surface performed after 1000 hours of immersion (Figure 3) where the oxide film presented on the surface covers both, the cobalt matrix and the interdendritic

segregated hard phases. Based on literature reports<sup>7, 22</sup> and our results on may assert that the decrease of the concentration of Cr and Mo and increasing the concentration of W slightly decreases the ability of the cobalt alloy to form thick oxide films on the surface.

A consequence of the formation of the oxide film and the corrosion products on the surface of the specimen consists in the modification of its hygroscopicity, an aspect analyzed by the contact angle method. The contact angle measurements of Co24Cr3Mo8W alloy, before and after immersion in 0.1M lactic acid and 0.1M NaCl solution were carried out and the results are presented in Table 1. Compared with the bare specimen the contact angle of Co24Cr3Mo8W alloy surface diminished after immersion with about 18 degrees, from 96.3±1.5 dgr. to 68.5±1.5 dgr. (Table 1). It appears that the hydrophilic character of the Co24Cr3Mo8W surface in contact with 0.1M Lactic Acid +0.1M NaCl solution has increased.

From water contact angle (WCA) values, by using equation 1, the thermodynamic work of adhesion,  $W_a$  was estimated as well. This parameter also brings out information about the surface of the material in terms of wettability.

$$W_a = \gamma_L (1 + \cos\theta) \quad (1)$$

where,  $\gamma_L$  is the liquid surface tension and  $\theta$  is the measured contact angle. For distilled water  $\gamma_L = 72.86 \text{ mNm}^{-1}$  at 20°C<sup>1,23</sup>

Table 1

The contact angle values, and calculated energies performed after 1000 hours of immersion in 0.1 M lactic acid and 0.1M NaCl solution, at 37°C

	Contact angle, dgr	Work of adhesion, mN m <sup>-1</sup>
Before immersion	96.3±1.5	64.85
After immersion	68.5±1.5	99.53

Adhesion of the solid/water contact interface is reduced, in the case of hydrophobic surface, because of the lowered surface tension of the solid. This can be expressed quantitatively in terms of changes in the interfacial area and thus of interfacial free energy. It is basically the energy release in the process of wetting.

As it can be seen in Table 1 the adhesion strength parameter,  $W_a$ , of Co24Cr3Mo8W alloy significantly enhances, *i.e.* 31%, after immersion.

### Corrosion behavior characterization

The Tafel curves permit to gain an approach of the corrosion behavior of the Co24Cr3Mo8W alloy in studied environment and to evaluate the corrosion parameters; the corrosion potential  $E_{cor}$ , the corrosion current density  $i_{cor}$  and the corrosion rate,  $r_{cor}$ .

Figure 5 presents the Tafel curves acquired after 72, 168 and 1000 hours of immersion respectively, and Table 2 lists the main corrosion parameters extracted from these curves.

As can be seen in Table 2 the corrosion potential does not change significantly after 1000 hours of immersion, and these small variations are fully

correlated with the changes in OCP during time. After 168 hours of immersion there is a slight activation of the surface by moving the potential with 10 mV to electronegative values (as well as OCP) and after 1000 hours its value is + 41 mV. The corrosion potentials values determined from the Tafel curves are in accordance with those reported<sup>21</sup> for the alloy with higher chromium and molybdenum content. However, the values of the corrosion current densities that express the corrosion rate are higher in this case, which means that the decrease in chromium and molybdenum content is not fully compensated by the higher tungsten content from corrosion rate point of view. It is also worth mentioning that after 1000 hours of immersion in the solution containing 0.1M lactic acid and 0.1M NaCl on the surface of the samples, small corrosion points appeared (Fig. 4). As shown by the anodic polarization curve Fig. 7 these points were re-passivated because the potential did not reach the breakthrough value. An increase in current density, comparable to the value reported for CoCrMo alloy in 0.1 M lactic acid solution without chlorine ions,<sup>19</sup> was observed at a potential value of + 850 mV vs. Ag/AgCl.

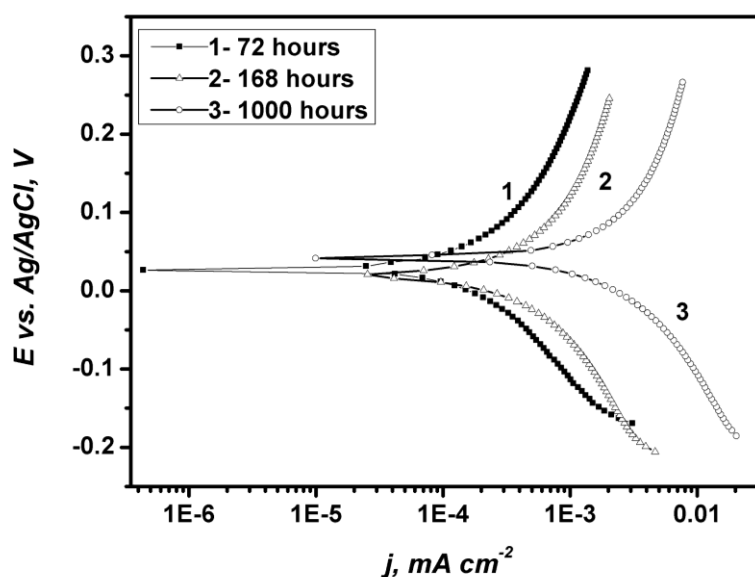


Fig. 5 – Tafel curves obtained on Co24Cr3Mo8W alloy in lactic acid solution (0.1M LA +0.1M NaCl) after different period of immersion 1-72h; 2-168h; 3-1000h.

Table 2

The main corrosion parameters extracted from Tafel curves

Time, h	$E_{cor}$ , mV	$i_{cor}$ , $\mu\text{A cm}^{-2}$	$r_{cor}$ , $\mu\text{m y}^{-1}$
72	27.1	0.02	9.24
168	18.9	0.12	55.04
1000	41.4	0.417	85.6

These results are also confirmed by the EIS data (Bode plots) presented in Figure 6 where a surface activation was observed after 1000 hours of immersion by decreasing the impedance from 100 k $\Omega$  to 40 k $\Omega$  (curve 3). Also, curve 3 obtained after 1000 hours shows by its shape the presence of a reaction constant with a lower resistance of charge transfer compared to the one after short time of immersion. These findings are supported by considerable decrease of film thickness,  $d$ , after 1000 hours of immersion, calculated from EIS data and presented in Table 3. The film thickness was calculated according to literature reports<sup>21, 24, 25</sup> using the expression of capacitance:

$$C = \varepsilon \varepsilon_0 \frac{A}{d} \quad (2)$$

where,  $\varepsilon$  is the relative dielectric constant of the oxide,  $\varepsilon_0$  is the vacuum permittivity ( $8.85 \times 10^{-14}$  Fcm<sup>-1</sup>),  $A$  is work surface area (cm<sup>2</sup>) and  $d$  is the film thickness. To calculate the film thickness from EIS data with equation 2, was used the dielectric constants of Cr<sub>2</sub>O<sub>3</sub> ( $\varepsilon \sim 12$ ).<sup>26</sup>

In order to use the equation 2, the CPE from the EEC has been converted in a pure capacitance  $C$ , with the following equation:<sup>25</sup>

$$CPE = R^{n-1} \times C^n \quad (3)$$

As respect the equivalent circuit that fits the EIS data, it is of the same type as those presented and explained on the other papers,<sup>19,21,27</sup> *i.e.* consisting of two circuits in series with two resistance constant phase elements (CPE), one for the processes that take place in the electric double layer and the second simulates processes in the passive film. As the SEM image of the surface alloy shows (Fig. 4), it appears that after 1000 hours of immersion the surface is not totally covered with a passive film that led to a downward tendency of impedance and a decrease of corrosion resistance as well. Compared to the previously reported data,<sup>21</sup> a much lower impedance value was observed for Co24Cr3Mo8W alloy, *i.e.* 100 K $\Omega$  vs.1M $\Omega$ . This decrease is due to the reduction of chromium and molybdenum content, from about 28% to 24% and from 6% to 3%, respectively.

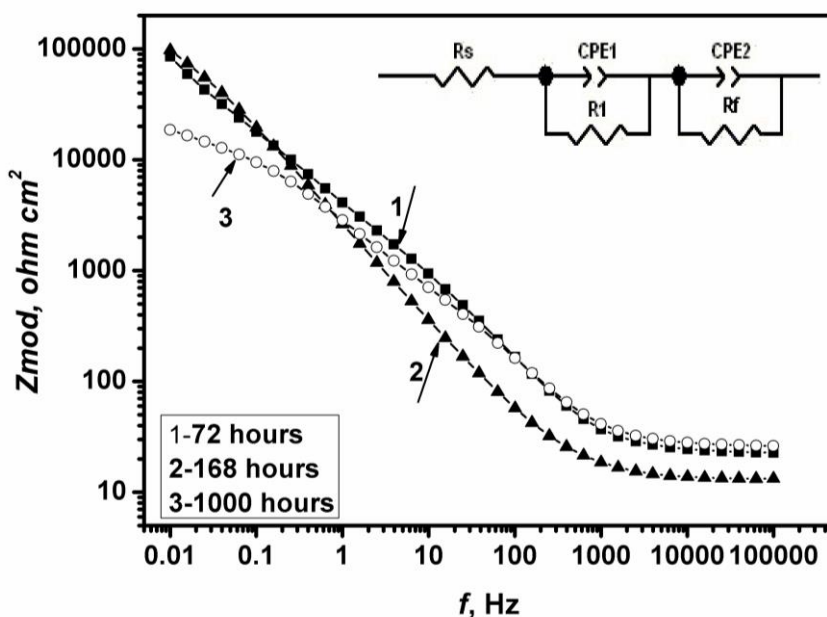


Fig. 6 – EIS results, in the form of Bode curves, obtained on Co24Cr3Mo8W alloy, after different periods of immersion in 0.1M Lactic Acid +0.1M NaCl solution: (1)-72 hours; (2)- 168 hours; (3)- 1000 hours.

Table 3

The fitting EIS parameters of Co24Cr3Mo8W alloy obtained after 72, 168 and 1000 hours of immersion

Time	$R_s$ , ohm $\text{cm}^2$	$CPE_1$	$R_1$ , ohm $\text{cm}^2$	$n_1$	$CPE_2$	$R_r$ , ohm $\text{cm}^2$	$n_2$	$d$ nm
72	17.45	7.90e-5	743	0.91	9.91e-5	99318	0.76	10
168	16.77	8.01e-5	632	0.91	9.45e-5	66522	0.75	10
1000	18.54	6.91e-5	125	0.97	12.53e-5	14305	0.71	2

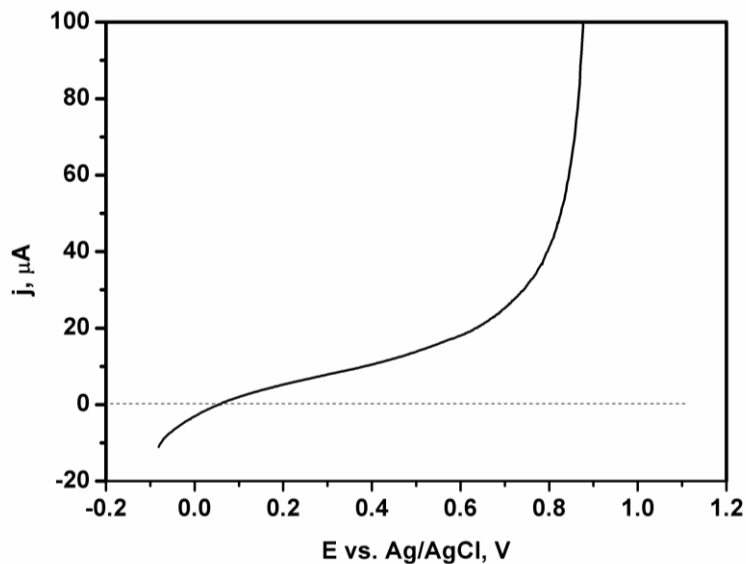


Fig. 7 – Polarization curve acquired on Co24Cr3Mo8W specimen after 1000 hours of immersion in 0.1M Lactic acid + 0.1M NaCl solution.

Table 4

Ions released after 168 hours of immersion in acid lactic + NaCl solution according to the standard ISO 10271/2001

Sample	Ion	Quantity of metal released ( $\mu\text{g cm}^{-2}$ )
Co24Cr3Mo8W alloy	Co	1.07
	Cr	3.15
	Mo	0.001
	W	undetectable

According to literature reports,<sup>7,21,28</sup> the passive film formed on the Co-Cr-Mo alloy surface in the acidic solution was mainly composed of  $\text{Cr}_2\text{O}_3$ , with minor constituents of Mo. Any changes in the chemical composition of the CoCrMo alloy could lead to the modification of the relative levels of Cr and O at the surfaces of alloys that could amend the resulting oxide structures and corrosion resistances of the alloy. A significant decrease of  $R_f$  value noticed after 1000 hours of immersion of Co24Cr3Mo8W alloy could be the result of a modification of the relative levels of Cr and O at the surface of this alloy.

These results correlate with those discussed above and emphasize once again the beneficial effect of chromium and molybdenum on the passivity of the alloy.

Figure 7 illustrates the anodic polarization curve of Co24Cr3Mo8W alloy after 1000 hours of immersion in 0.1M Lactic Acid +0.1M NaCl solution. It is a typical curve to passivating alloys without active dissolution range even if the current density increases continuously and no clear diffusion limit current appears. As can be seen in Figure 7 the current density value remains below of  $10 \mu\text{A cm}^{-2}$ , over the entire potential range of 400 mV. This is a characteristic of the passive state of many other alloys.

According to literature report,<sup>29</sup> the presence of lactic acid in the solution could allow that the lactate to solubilize with  $\text{Cr}^{3+}$  because of relatively small complexation constant of lactic acid ( $k=3.3$ ). As a result of the weak complexation between the lactates and  $\text{Cr}^{3+}$  and their easier dissociation, the

oxide film grown on the surface of the alloy is deteriorated over time.

The quantity of metals ions released by the CoCrMo alloy into the biofluid is the most important aspect in terms of biocompatibility, as it can be responsible for different diseases or allergic reactions. According to the ISO standard,<sup>16</sup> the release of metallic ions over 168 hours of immersion must be below  $200 \mu\text{g cm}^{-2}$  of the tested sample under prescribed conditions.

Comparing the results of the immersion test of Co24Cr3Mo8W alloy, presented in Table 4, with those required by ISO, it can be observed that the quantity of Co, Cr and Mo ions are extremely reduced. Furthermore, the slightly high amount of dissolved Cr could be indicating that overall process of metal dissolution in acidic environment (0.1M Lactic Acid +0.1M NaCl) is controlled by the oxide film of Cr. These results are in line with those reported by other research<sup>7, 21</sup> and clearly point out that Co24Cr3Mo8W alloy fulfills of the standard requirements which make it suited for medical applications.

## EXPERIMENTAL

### Materials

The subject of the study is a cobalt-based alloy with chromium, tungsten, and molybdenum according to Table 5, in casted state.

Table 5

Chemical composition of Co24Cr3Mo8W alloy, weigh % of the main components

Cr	W	Mo	Co
24	8	3	Bal

The corroding solution consists of lactic acid (LA) and NaCl (0.1M LA + 0.1M NaCl, prepared from analytical purity (p.a.) reagents (Sigma- Aldrich) and double-distilled water.

The selection of lactic acid, as an aggressive environment for alloy stability checking, was made based on information from the literature; it has been identified in the tissues involved in inflammatory processes, as well as released by bacterial in the oral cavity.<sup>13-15</sup>

### Methods

#### Electrochemical measurements

The open-circuit potential was monitored during approximately 1000 hours of immersion, at 37°C in natural aerated solutions, and the corrosion potential values are related to 3M Ag/AgCl as a reference electrode.

The surface of the immersed samples, of 4 cm<sup>2</sup>, was mechanically prepared by grinding with abrasive paper and suspensions of micrometric alumina powder, up to the

metallographic quality, then washed with distilled water, double distilled water, and ethanol.

Three parallel samples of 4 cm<sup>2</sup>, were used, each immersed in a 60 mL of solution in Berzelius beaker by suspension with a plastic wire; the beakers were tightly closed with a lid in which two holes were made for the reference electrode and the platinum counter electrode. During the immersion, the holes were clogged with rubber plugs to prevent water from evaporating. At predetermined time intervals the stationary potentials were measured in open circuit (OCP).

After different periods of immersion (72, 168 and 1000 hours) the Tafel curves were acquired to evaluate the evolution of corrosion rate and EIS, as Nyquist and Bode curves, for the corrosion tendency of alloy. Tafel curves were recorded in a potential range of 250 mV around the corrosion potential with a rate of 150 mV min<sup>-1</sup>, and the anodic polarization curves were acquired between -1000 mV and + 1000 mV with a potential sweep speed of 150 mVmin<sup>-1</sup>. The EIS analysis has been acquired potentiostatic at rest potential between 1MHz and 10<sup>-2</sup> Hz with a perturbation of 10 mV.

The electrochemical measurements were performed using the Reference 300 Gamry equipment (potentiostat/galvanostat) in a three-electrode electrochemical cell with a platinum sheet as counter electrode, Ag/AgCl 3M as a reference electrode and the acquired data were processed using the EchemAnalist dedicated software.

#### Surface characterization

At the end of the immersion period, the surface of samples was analyzed to highlight the formed film morphology and chemistry by SEM and XPS techniques. SEM analysis was done using FEI INSPECT F50 microscope field 118 emissions equipped with an energy-dispersive x-ray spectrum (EDXS) and K Alpha spectrometer from ThermoFisher, respectively.

The changes in hydrophobicity of the surface because of corrosion products depositions were highlighted by wetting analysis. The contact angle measurement was done with Drop Shape Analysis System apparatus, 133 DSA1 model (FM40 Easy Drop) from KRÜSS GmbH Germany. The samples were placed on a plane support and drops of deionized water with a volume of 3  $\mu\text{L}$  each were put on the surface with a dispensing micro-syringe. The contact angle values were collected in static regime at room temperature, initially, and at 30 seconds after the drop of water was placed on the sample surface. Static contact angle was recorded using Sessile Drop Fitting method for the angles in between 30 - 90° and Circle Fitting method for those less than 30°. Over 7 measurements were averaged for each sample.

The chemical analysis of electrolyte after 168 hours of immersion was performed 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.

## CONCLUSIONS

The obtained results for characterizing the corrosion behavior of Co24Cr4Mo8W alloy in lactic acid solution and sodium chloride that



simulate an aggressive biochemical environment, specific to either inflammatory situations or the activity of oral bacterial plaque, lead us to formulate some conclusions, thus:

The level of passivation capacity of cobalt alloy in synthetic biological media can be highlighted by analyzing the composition and thickness of the formed passivation film, by the electrochemical properties of the surface as well as by the quantity of ions released in solution.

Decreasing the concentration of chromium from 28-30% to 23-24% and molybdenum from 8% to 4% at the same time as increasing the concentration of W from 5% to 8% slightly decreases the ability of the cobalt alloy to form thick oxide films on the surface; this means that W does not act as a passivating element in the cobalt-based alloy.

The oxide layer formed spontaneously on the surface of Co<sub>24</sub>Cr<sub>3</sub>Mo<sub>8</sub>W alloy is kept constant for the first 168 hours of immersion, after that, a decrease in its thickness is noticed as a result of dissolution processes. The decrease of the oxide layer after long period of immersion could be due to the changes in the chemical composition of the CoCrMo alloy as well.

The most important conclusion of this study is, in our opinion, that the less alloyed Co<sub>24</sub>Cr<sub>4</sub>Mo<sub>8</sub>W alloy, therefore cheaper, has proven corrosion resistance and ion release comparable to those of Co<sub>28</sub>Cr<sub>8</sub>Mo<sub>6</sub>W alloy and can be a less expensive alternative for biomedical applications.

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