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ABOUT ELECTROCHEMICAL STABILITY OF A CoCr ALLOY USED AS STENTS MATERIAL IN MEDICINE

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The aim of the paper is a comparison between the electrochemical behavior of a CoCr commercial alloy in three different bioliquids that simulates the electrolytes in the human body. The variation of potential in time (open circuit potential-OCP), potentiodynamic polarization tests, electrochemical impedance spectroscopy measurements (EIS) and inductively coupled plasma mass spectrometry (ICP-MS) have been used to test the stability of the alloy in the chosen environments. The kinetic parameters have been calculated using two methods. Based on experimental results one can say that the CoCr alloy Diadur show a low corrosion rate in the chosen media due to oxide coating formation on the alloy surface. The small amount of metal ions released in solution is in the range of parts per million.

Keywords: EIS, ICP-MS, electrochemical stability.

1. Introduction

Small and medium sized arteries may be affected by the atherosclerotic lesions formation, which could lead to vessel narrowing and may necessitate revascularization. The most surgical acts consist in stents implantation in order to maintain the blood flow after percutaneous intervention [1].

For many years, due to the excellent mechanical properties and corrosion resistance, 316L stainless steel has been successfully used for cardiovascular stents fabrication. Recent studies reveal that stainless steel is releasing metallic ions into the tissues after long-term contact with blood. Moreover, these alloys more or less contain leachable toxic elements, leading to localized allergic reactions [2].

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In the last years, the most investigated and used biomaterials in medical applications were CoCr [3 - 5] and titanium alloys [6, 7] with and without surface modifications in order to improve their performance [8, 9].

CoCr stents have the following characteristics: a good quality/price ratio, best mechanical and corrosion properties and good radioopacity. Due to these remarkable properties, CoCr alloys are increasingly used in different biomedical fields, as dentistry, orthopedics, and stents applications [10, 11]. The formation of a thin passive layer on the CoCr alloy surface confers it a very good corrosion resistance [12]. The metallic biomaterials, despite the fact that they exhibit a protective layer, are becoming a major cause for concern when implanted into the human body due to their ions release which can cause metal allergies, and can be found in urine, blood and human tissues [13].

Therefore, the present study investigates the stability in specific bioliquids of a CoCr based alloy, in order to assess CoCr alloys thromboresistance.

2. Experimental

For this study, the CoCr alloy Diadur, marketed by the company DSF Germany, was submitted to testing.

The composition of this alloy is given in Table 1.

Table 1.

Chemical composition of the Co-Cr alloys

	Co %	Cr %	Mo %	Mn %	Si %	C %
Diadur	62.5	30	5	1	1.3	0.2

A cylindrical shape having 0.5 cm^2 was preferred as metallic samples because it has a larger surface area and a small number of edges and corners that are more susceptible to corrosion. These samples were exposed to corrosive environments.

A conventional electrochemical cell consists of three electrodes: the working electrode represented by CoCr alloys, the platinum (Pt) electrode with a large area as the counter-electrode and the Ag/AgCl, KCl electrode as reference electrode.

The working electrode was mechanically polished, rinsed with redistilled water and ultrasonicated for 5 minutes in acetone in order to ensure a clean surface before the tests by removing grease and impurities from the electrode surface after polishing.

Several types of electrolyte bioliquid that simulates electrolytes in the human body were used: saline solution (SF), simulated body fluid (SBF) as well as mannitol 20%. The compositions of simulated physiological fluids solutions were: SF - NaCl (9 g/l), SBF - NaCl: 8.367255 g; $NaHCO_3$: 5.534 g; $Na_2HPO_4.2H_2O$: 22.165 g; $MgCl_2.6H_2O$: 0.51359 g; $CaCl_2.2H_2O$: 0.51891 g;

Na_2SO_4: 0.071 g for 1 liter of bidistilled water [14] and mannitol (20% polyalcohol obtained from mannose).

For testing the stability of the alloys the variation of potential in time (open circuit potential-OCP), potentiodynamic polarization tests, electrochemical impedance spectroscopy measurements (EIS) and inductively coupled plasma mass spectrometry (ICP-MS) were performed.

All electrochemical measurements have been done using AutoLab PGSTAT 12 Eco Chemie potentiostat/galvanostat. In order to apply potentiodynamic polarization method, a potential sweep starting from cathodic region, with very low speed of 2 mV/s to allow the corrosion process to proceed, was carried out [11].

From the polarization curves, the kinetic parameters (especially the corrosion current density) were calculated and then they were compared with the parameters obtained for solutions of different concentrations, with addition of different anions [15, 16].

The results obtained from electrochemical impedance spectroscopy (EIS) procedure made in a 10^5 Hz to 10^{-1} Hz frequency range, with an **AC** voltage amplitude of 10mV, were represented as Nyquist and Bode diagrams.

A mass spectrometer with inductively coupled plasma (***ICP-MS***), Elan DRC-e model from Perkin Elmer Company was used for ion release analysis. For the calibration of the apparatus, multielement standard from Perkin Elmer with the concentration of 10 µg/mL was used.

3. Results and Discussion

The study of electrochemical behavior of CoCr based alloy in different artificial fluids, in order to use it in the stents manufacture, was the primary objective of this paper.

3.1. Open circuit potential determination

In Fig. 1 open circuit potential variation in time is presented. OCP value registration was made during one hour testing time. As one can see, for all studied electrolytes, in the first minutes of immersion the potentials value shift rapidly towards electropositive values. A second phase follows in which a potential increase (moving towards electropositive values) is slower. The shifting potentials towards electropositive values suggest a continuous increase of the superficial passive film with the immersion time. At the end a plateau is observed at higher immersion time. This plateau is reached easier if CoCr is immersed in SBF or mannitol. As one can see in Fig. 1, the potential values reaches stable values after 1 h of immersion in all studied media, being an indication of the stable chemical nature of the passive film.

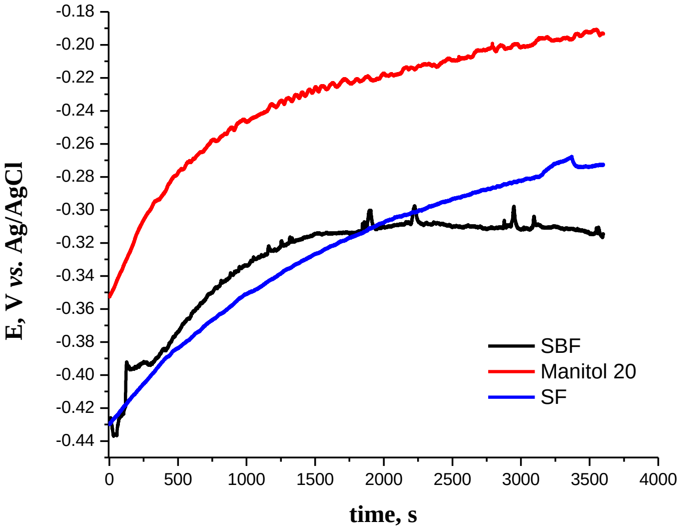

Fig.1. OCP variation in time for Diadur alloy at 37°C in SF, SBF and mannitol

3.2. Potentiodynamic polarization study

Firstly, the electrochemical behavior of Diadur alloy in the physiological saline solution (SF) at different immersion periods was studied.

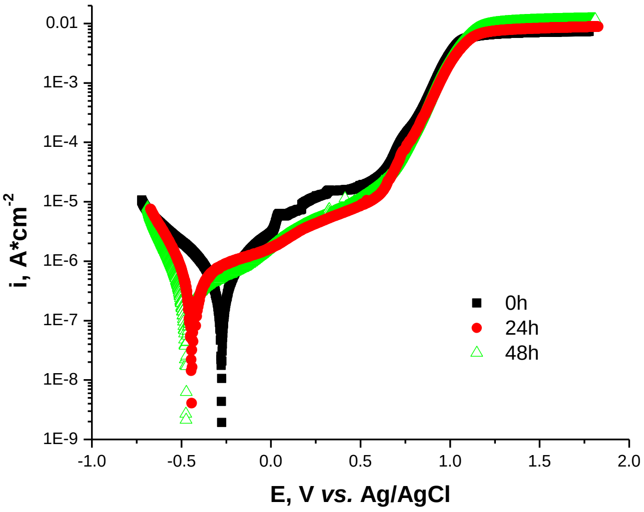

Fig. 2. Polarisation curves for Diadur in SF at different immersion periods.

In order to observed the behavior of Diadur alloy in SF, the polarization curves were recorded after different immersion periods in the electrolyte, held at a constant temperature of 37°C and shown in Fig. 2. One may see a decrease of the corrosion density values when increasing the immersion time. These can be explained by the formation of a protective film on the alloy surface, which leads to slower corrosion processes. A shift of the corrosion potential towards electronegative values with increase of immersion time can be also observed from Fig. 1.

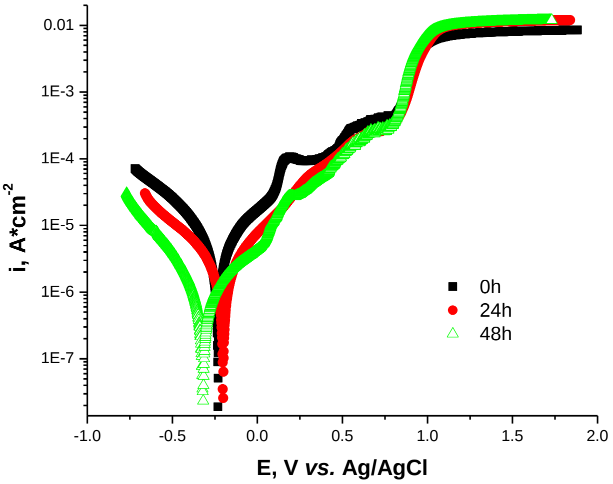

Fig. 3. Polarisation curves for Diadur in SBF at different immersion periods.

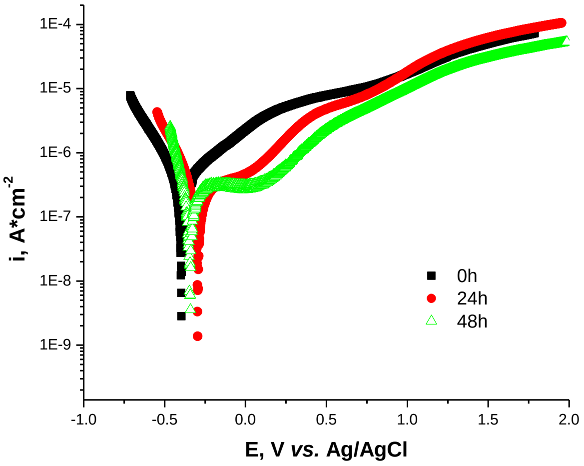

Fig. 4. Polarisation curves for Diadur in mannitol at different immersion periods.

As for the two other electrolytes, the polarization curves are presented in Fig. 3 (for SBF) and Fig. 4 (for mannitol). Similarly to the Diadur immersion in SF, the corrosion density current value decrease with immersion time for these two latter media. From Fig. 4 one can observe a passive region in the cathodic domain, which widens when increasing the immersion time of the CoCr alloy in mannitol solution.

The kinetic parameters obtained from these polarization curves (Figs. 2-4) were computed using two methods: the Tafel slopes method and the polarization resistance method. The values obtained for the corrosion potential (E_{corr}), the corrosion current density (i_{corr}), the corrosion rate in mil/year (R_{mpy}), the gravimetric index (Kg), the penetration index (P), the polarization resistance (R_P) are shown in Table 2.

Table 2

Corrosion kinetic parameters for the CoCr alloy at different immersion times in all three studied media

Electrolyte	Time, h	Tafel slope method					Polarization resistance method	
		E_{corr}, mV	i_{corr}, µA/cm^2	R_{mpy}	K_g, g/m^{2}h	P, mm/year	R_p, Ω	i_{corr}, µA/cm^2
SF	0	-278	0.8355	0.3788	0.0092	0.00961	58780	0.5297
	24	-442	0.5048	0.2289	0.0055	0.00581	112640	0.3252
	48	-474	0.3061	0.1388	0.0033	0.00352	153690	0.1549
SBF	0	-220	3.1108	1.4101	0.0340	0.0358	18846	1.7619
	24	-190	1.2681	0.5749	0.0139	0.0146	69225	0.5124
	48	-315	0.4632	0.2099	0.0051	0.0053	124700	0.2947
mannitol	0	-396	0.1883	0.0852	0.0021	0.0021	195430	0.1860
	24	-295	0.1108	0.0498	0.0012	0.0013	273620	0.1079
	48	-346	0.0912	0.0412	0.001	0.0010	294010	0.0743

It should be noted that using both methods similar values were obtained for the corrosion current density. The values are different compared to corrosion current density in the same media from literature [17] due to the fact that Diadur has a different composition compared to other previously used CoCr alloys. The polarization resistance values increase with the immersion time in the solution, indicating a decrease in the corrosion rate of the Diadur biomaterial in all studied media. Thus, as we can see from the polarization curves, when increasing the immersion time in the corrosive media, the values of the kinetic parameters decrease, proving the decrease of the corrosion rate of the biomaterial. If one compare the three electrolytes, one can say that Diadur performs best when immersed in mannitol, i.e. has the lowest corrosion rate.

3.3. Electrochemical impedance spectroscopy tests

Electrochemical impedance spectroscopy (EIS) tests for Diadur in SF have led to the recording of the spectra presented in the Nyquist and Bode diagrams (Fig. 5).

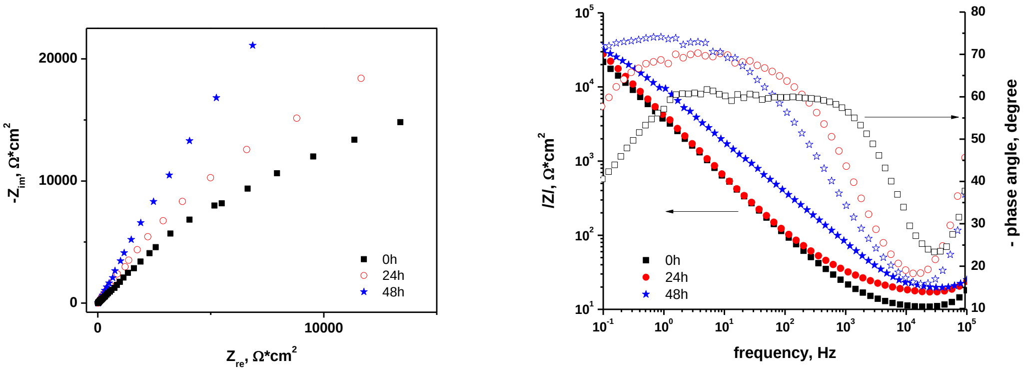

Fig 5. Nyquist (a) and Bode (b) diagrams for Diadur after 30 min of immersion at OCP in SF

From Fig. 5 showing Nyquist diagrams, the presence of a single open capacitive semicircle whose diameter increases as the immersion time of the alloy increases, can be observed. This indicates an increase in polarization resistance, which leads to a decrease of the corrosion rate as the immersion time increases, thus confirming the data obtained from the polarization curves. The Bode diagram reveals the presence of a single time constant corresponding to a single semicircle on the Nyquist diagrams. The maximum phase angle moves to lower frequencies and increases slightly once the immersion time in the physiological serum increase. The increase of the maximum phase angle values from -60 to -78°, indicates the formation of a passive oxide film on the surface of the alloy, which results in an almost capacitance response of the interface.

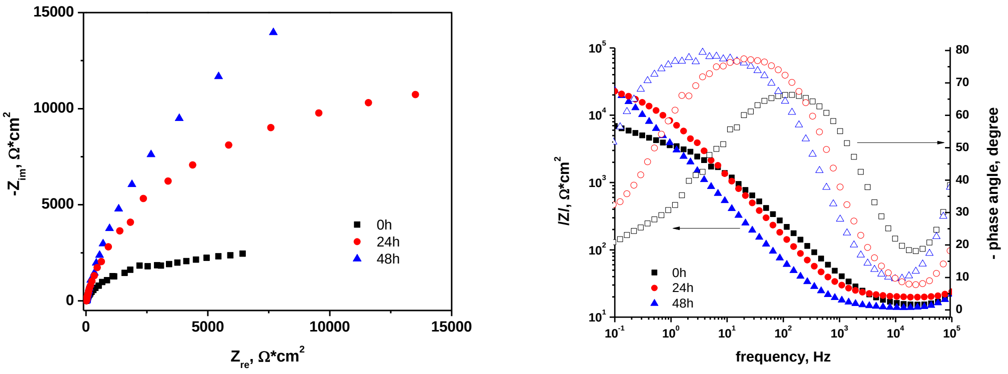

Fig 6. Nyquist (a) and Bode (b) diagrams for Diadur after 30 min of immersion at OCP in SBF

The same behavior was observed for the studied CoCr alloy immersed in SBF solution (Fig. 6). The increase of semicircle diameter values from Nyquist diagrams, as well as the increase of maximum phase angle values from Bode diagrams indicates a passive oxide films formation on the alloy surface.

Fig. 7 shows the diagrams obtained for the CoCr based alloy in mannitol solution at different immersion times. As in the case of the other two electrolytes studied previously, for Diadur immersed in mannitol solution a single semicircle on the Nyquist diagrams appears. The semicircle diameter increases with the immersion time. The resistance of the solution is high, due to the composition of the electrolyte. On the Bode diagram a single time constant can be observed.

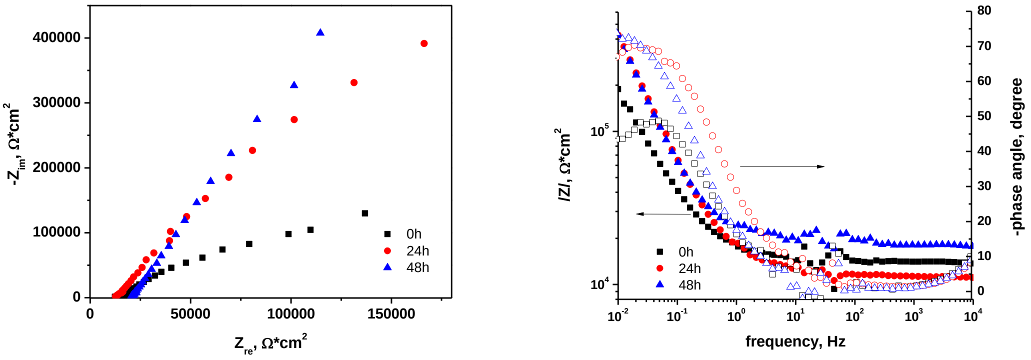

Fig 7. Nyquist (a) and Bode (b) diagrams for Diadur after 30 min of immersion at OCP in mannitol

The maximum phase angle occurs at very low frequency values and moves to even lower values with increasing immersion time in the corrosive environment. The value of -48° for the maximum phase angle value at the initial time indicates the occurrence of a diffusion phenomenon at the alloy surface.

Once the time of immersion increases, the value of the maximum phase angle increases, reaching values of about -70°, which indicates the formation of a passive oxide film on the surface of the alloy.

Table 3

ICP-MS analisys for Diadur in all studied media

Sample	**Concentration (mg/L)**							
	Co	**Cr**	**Mo**	**Mn**	**W**	**Si**	**Fe**	**Ca**
Diadur in SBF 24h	0.152	0.096	0.111	0.065	0.047	0.876	1.087	24.434
Diadur in SBF 48h	0.012	0.028	0.003	0.001	0.001	0.129	0.908	15.846
Diadur in SF 24h	0.004	0.023	0.016	0.001	0.001	0.018	0.337	4.776
Diadur in SF 48h	0.022	0.007	0.001	0.001	0.000	0.013	0.278	3.447
Diadur in mannitol 24h	0.038	0.845	0.001	0.005	0.000	4.489	0.519	4.665
Diadur in mannitol 48h	0.056	0.824	0.002	0.003	0.001	3.881	0.402	5.654

Figs. 8-10 show the ion release concentration for Diadur after 24 and 48 hours in SBF, SF and mannitol.

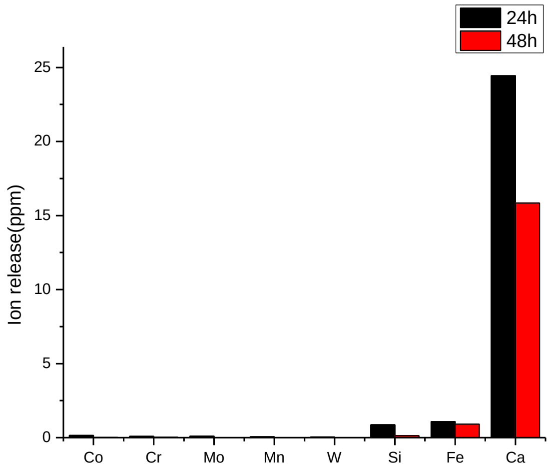

Fig 8. Metallic ion release after 24 and 48 hours in SBF.

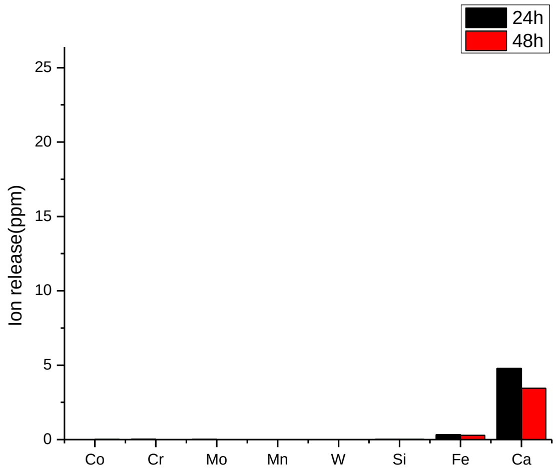

Fig 9. Metallic ion release after 24 and 48 hours in SF.

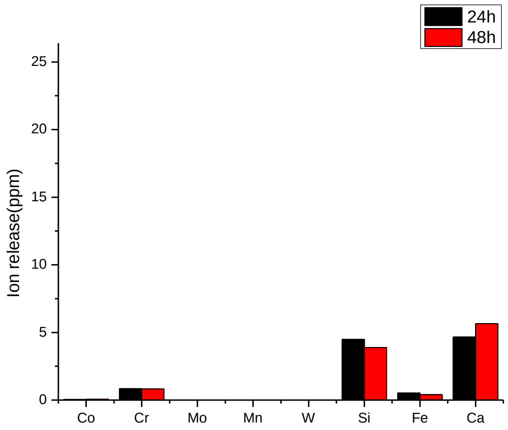

Fig 10. Metallic ion release after 24 and 48 hours in mannitol.

When immersing in SBF, after 24 hours the quantity of ions increases in the range of ppm. After another 24 hours the ions release decrease, due to the oxide layer formation on the Diadur surface. The smallest amount of ions is found in SF. After 48 hours the quantity of ion release is decreasing.

As for the mannitol, after 24 hours of immersion small amounts of metals are present. After 48 hours the quantity of ion release decreases due to the formation of a passive oxide layer on the surface of Diadur.

4. Conclusions

The Diadur alloy exhibit a low corrosion rate in all considered electrolytes. Increasing the immersion time led to lower corrosion current density values; this indicates the formation on the alloy surface of a protective passive film that continuously increases with immersion time. The best behavior of the CoCr based alloy has been obtained in mannitol solution. EIS tests have confirmed the results obtained from the potentiodynamic polarization method. The Nyquist diagrams have shown the presence of a single open capacitive semicircle whose diameter increases as the immersion time increases. Accordingly, on the Bode diagrams was observed the presence of a single time constant, whose value increases with the immersion time. This indicates an increase in polarization resistance, due to oxide layer formation on the alloy surface, which leads to a decrease of the corrosion rate as the immersion time increases, being a clear advantage of preventing the release of ions in the three studied environments. The presence of oxide coating lowers the amount of ions in solution. The small amount of metal ions released is in the range of parts per million concentrations.

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