Electrochemical behavior of cobalt - chromium alloy as biomaterial in different pH environments

L. Benea(1),*, V. Dumitrascu(1), E. Danaila(1), Iulian Bounegru(1), (2)

(1) Competences Center: Interfaces-Tribocorrosion-Electrochemical Systems, Faculty of Engineering, Dunarea de Jos University of Galati, Domnească Street, 47, Galați, Romania
(2) Faculty of Pharmacy and Medicine, Dunarea de Jos University of Galati.
* Phone Number: +40 744216277, e-mail: Lidia.Benea@ugal.ro

1. Introduction

The ageing population, high expectations for a better quality of life and the changing lifestyle of modern society require improved, more efficient and affordable health care. This poses new challenging problems regarding the increasing number of implants required, new diseases to be treated (e.g., Parkinson’s and Alzheimer’s) and organ shortage problems. On the other hand, some medical devices ideally should survive without experiencing any failures for the patent’s lifetime [1].

Co–Cr alloys are used for medical prosthetic implant devices, components in the power generation, marine, aerospace, and oil and gas industries due to their good wear, corrosion and fatigue resistance along with biocompatibility [2].

Co-Cr alloys have been used as orthopedic implant materials for more than 70 years due to their biocompatibility and beneficial combination of high strength and fatigue resistance, low creep, low to moderate elastic modulus, and high resistance to wear and corrosion [3]. Optimum mechanical properties and corrosion resistance of these alloys are usually obtained in the presence of 10–30% chromium [4].

Co-Cr alloys have an excellent corrosion resistance, which is provided by a thin adherent layer and passive of chromium-based oxides wit additions of Mo on the surface even in chloride environments [5]. Ly et al [6] in their study report that the identification of different Cr and Cp species in the passive films formed under different potentiostatic conditions, which play important roles in alloy passivation. In this paper was studied the corrosion behavior of the Co-Cr alloy in aqueous solution with different pH values, in particular as metallic biomaterial, because it’s well known that in the human body all vital processes take place at exact pH values.

2. Materials and methods

Electrochemical tests were performed on Co-Cr biomaterial alloy intended for dentistry containing 63%Co, 29.4%Cr, 5.95%Mo, 0.6%Mn, 0.29%C, 0.05%Fe and 0.7% Si. The samples with active area of 0.5 cm² were connected with a copper wire and after were polished successively with waterproof abrasive paper with grain size from 320-4000 mm, with diamond paste of dimensions 3-1 μm and a suspension of SiO₂ (particle size 0.04 μm) to achieve a mirror surface. Polished samples were cleaned with ethanol and dried with hot air and stored in a desiccator.

The electrochemical cell has the following structure: as working electrode (WE) is used Co-Cr sample with active area of 0.5 cm², an Ag/AgCl electrode (saturated solution of KCl, E=200 mV vs. Standard Hydrogen Electrode) as reference electrode (RE) and a Pt-Rh grid as the counter electrode (CE).

Three types of simulated body fluids were selected, namely Hank’s solution (pH=7.4 and the following composition: 8.8g/L NaCl, 0.4g/L KCl, 0.4g/L CaCl₂, 0.35g/L NaHCO₃, 1g/L C₆H₅O₆, 0.2g/L MgSO₄x7H₂O, 0.1g/L KH₂PO₄xH₂O and 0.06g/L Na₂HPO₄x7H₂O), Ringer’s solution (pH=6.6 and the following composition: 8.4g/L NaCl, 0.3g/L KCl and 0.29g/L CaCl₂) and Fusayama Meyer artificial saliva (pH=5 and the following composition: 0.4g/L NaCl, 0.4g/L KCl, 0.8g/L CaCl₂, 0.79g/L NaH₂PO₄ and 1g/L Uree) in order to study the corrosion behavior of Co-Cr alloy as metallic biomaterial. It is selected and another type of environment, citric acid (pH=1.8) because this medium is a powerful oxidant and has a lower pH and that could influence the state of the oxide layer on the surface of the sample.

Citic acid was also selected for corrosion study of Co-Cr alloy because it is found in citrus juice, apples, tobacco leaf, wine, etc. and can affect the composition and change the pH of the mouth cavity. For the investigation of corrosion processes was selected the following electrochemical techniques: open circuit potential of the electrode (OCP), potentiodynamic polarization curves (PD), electrochemical
impedance spectroscopy (EIS) and cyclic polarization.

3. Results and discussions

3.1. Open circuit potential
The corrosion investigation of Co-Cr sample began with monitoring the open circuit potential after immersion into the testing solution during 30 minutes and it is shown in Fig. 1. This method indicates the oxidation tendency of a material in a corrosive environment. The potential can vary with time, as changes occur at the electrode surface (formation of the passive layer, etc.).

![Fig 1. OCP time plots for Co-Cr alloy in (1) Citric Acid, (2) Hank’s solution and (3) Ringer’s solution, (4) Fusayama-Mayer saliva, during 30 min. immersion time](image)

From Fig. 1 can be seen a shift of the potentials to electropositive values, which confirm the formation of a protective oxide film on the surface of Co-Cr alloy for all studied environments. Even if the pH of solution is reduced, citric acid solution is a strong oxidant, which leads to a shift of the Co-Cr electrode potential to more noble values.

As regards with the three simulated body fluids (Hank’s, Ringer’s and Fusayama-Mayer saliva) due to different pH values and different chloride content there are three levels with different lower values of potential stabilization compared with the potential of citric acid solution. Lower values of the potential for the three simulated body fluids can be explained by the presence of chloride ions that can generate in long-term localized corrosion on passive alloys.

3.2. Potentiodynamic polarization curves
Fig. 2 presents the polarization curves for the Co-Cr alloy studied immersed in the four different solutions. Potentiodynamic polarization curves were measured in the potential range between -1500 mV to +1200 mV vs. Ag/AgCl at a scan rate of 5 mV/s.

![Fig. 2. Potentiodynamic polarization curves obtained for Co-Cr alloy in (1) 0.5 M Citric Acid, (2) Hank’s solution, (3) Ringer’s solution and (4) Fusayama-Mayer saliva](image)
From Fig. 2 (Tafel curves), Co-Cr biomaterial immersed in all environments are observed extended passive domains but different corresponding to SBF environments, compared to citric acid solution. The higher pH values of solution lead to the rapid formation of oxide layer on the alloy surface resulting in surface passivation and immunity to corrosion.

3.3. Cyclic polarization curves

The cyclic voltammograms of Co-Cr alloy in four solution with different pH were recorded in the potential range of -1500 mV vs. Ag/AgCl to +1200 mV vs. Ag/AgCl at a scan rate of 5 mV/s and are presented in Fig. 3(a). Highlighting the localized corrosion susceptibility in the presence of chloride ions in the solution can be seen very well due to the specific hysteresis aspect (Fig. 3(b)) which presents the anodic transpassivation part of the curves from Fig. 3(a).

In Fig. 3(b) we can observe the specific hysteresis of Co-Cr alloy in Hank’s solution which reveals the pitting corrosion susceptibility behavior. This behavior can be explained by the presence of chloride ions in a higher concentration, which can generate in long term localized corrosion on passive alloys. The sizes of hysteresis domain are inversely proportional to the pH values and directly proportional to chloride content of solutions. The electrochemical behavior of cobalt alloys are very sensitive to the solution composition.

3.4. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) measurements were obtained at free potential in a frequency range of 100 KHz to 10 MHz with 10 points per decade using 10 mV peak-to-peak sinusoidal potential amplitude and are presented in Bode format in Fig. 4(a) and (b) and Nyquist plots in Fig. 5.

At seen in Fig 4 (a) and (b) the wide peak with a maximum near 90° suggest the presence of a compact
film on the surface acting as an efficient barrier to corrosion, which increases the resistance of charge transfer at the interface. Also from Fig. 4 (a) and (b) can be seen that no significant changes in the impedance and phase shift of the Co-Cr alloy occurred over the frequency range during the test suggesting the formation of a stable passive film at the interface for all studied solutions. The Nyquist plots of impedance diagrams for all four solutions exhibit capacitive behavior over a relatively wide frequency, which is typical for passive alloy systems. The semicircle diameters corresponding to Hank and Ringer solutions are lower than the semicircle of Fusayama-Meyer solution. This behavior can be explain by the presence of a larger quantity chloride ion in solution and confirms the results obtain from cyclic voltammetry measurements.

![Nyquist plots of EIS data for Co-Cr in (1) 0.5 M Citric Acid, (2) Hank’s solution, (3) Ringer’s solution and (4) Fusayama-Meyer saliva recorded at their open circuit potentials](image)

**Fig. 5. Nyquist plots of EIS data for Co-Cr in (1) 0.5 M Citric Acid, (2) Hank’s solution, (3) Ringer’s solution and (4) Fusayama-Meyer saliva recorded at their open circuit potentials**

**4. Conclusion**

This paper presents the corrosion behavior of Co-Cr alloy in different simulating saliva fluids environments. Interpretation of results according to open circuit potential and polarization curves for the Co-Cr alloy immersed in four aqueous media reveals that there are different levels of stabilization of the potential and different current densities depending on the pH value.

The Co-Cr biomaterial showed a different behavior of corrosion tests in solutions with different pH, different content of chlorides and different oxidizing character.

This biomaterial is very sensitive to localized corrosion (pitting) in Hank solution, being visible on the cyclic polarization curves and localized corrosion after the first hours of immersion.

**Acknowledgements**

UEFISCDI - Ministry of Education and Research is acknowledged for the financial support to Competences Centre Interfaces - Tribocorrosion and Electrochemical Systems (CC-ITES) - Dunarea de Jos University of Galati - Research Project: HyBioElect, contract 10 /30-08-2013 (2013 - 2016) in the frame of National Research Programme Romania - PN II PCE. Eliza Dănăilă acknowledge also POSDRU Project/159/1.5/S/13896 - PERFORM.

**5. References**