



IMPROVING BIOCOMPATIBILITY OF Co-Cr ALLOY USED IN DENTISTRY BY SURFACE MODIFICATION WITH ELECTROCHEMICAL METHODS – CORROSION OF UNTREATED Co-Cr ALLOY IN SOLUTION WITH DIFFERENT pH

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ABSTRACT

The use of metals and alloys in dentistry has seen remarkable progress due to the deep research on their biocompatibility or the application of advanced technologies to improve surface properties by controlling material/environment interactions occurring in the mouth. The biocompatibility of metals and alloys is a consequence of the presence of the surface oxide layer. The chemical properties and therefore the interface chemical processes are determined precisely by this oxide layer and not the metal itself. The material response to changes in pH, to the application of force or the degrading effects of fluids may impair biocompatibility. Corrosion resistance, an important feature of the biocompatibility, can be verified by studying the electrochemical behaviour of metals and alloys in specific environments. This paper presents some research results on the corrosion behaviour of Co-Cr biomaterial composition in aqueous solutions with different pH (Fusayama - Meyer artificial saliva, Hank's and Ringer's solutions, citric acid) given that many of chemical reactions in the mouth are extremely sensitive to the environmental pH. The electrochemical methods used (free potential, potentiodynamic curves and cyclic polarization) are relevant methods for studying interactions of materials - specific environment of use/exploitation. Research has shown different behaviour of the alloy according to the pH, the chloride content and the oxidizing nature of the environment.

KEYWORDS: Co-Cr dental alloy, pH values, corrosion resistance, simulated saliva, electrochemical methods

1. Introduction

Metallic biomaterials are the most suitable for replacing failed hard tissue up to now. Co-base alloys are generally used in applications which require wear resistance, corrosion resistance and/or thermal resistance.

Cobalt chromium alloys can be basically categorized into two types: one is the castable Co-Cr-Mo alloy, which usually has been used for many decades in dentistry and recently, in making joints, and the other is the wrought Co-Ni-Cr-Mo alloy

which is a relative newcomer now used for making the stems of prostheses for heavily loaded joints such as the knee and hip [1, 2].

Modern alloys based on Co-Cr due to superior mechanical properties and advantageous cost prices have replaced noble alloys of class IV in conventional technology (metal-polymer) and modern (metal and metal-ceramic composite). They are alloys with a high content of cobalt and their main alloying element is chromium.

Co-Cr alloys have an excellent corrosion resistance, which is provided by a thin adherent layer



and passive of chromium-based oxides with additions of Mo on the surface even in chloride environments [3-6]. Ly *et al.* [7] in their study report the identification of different Cr and Co species in the passive films formed under different potentiostatic conditions, which play important roles in alloy passivation. In this work was studied the corrosion behaviour of the Co-Cr alloy, in aqueous solution with different pH values, in particular as metallic biomaterial, because it is well known that in the body all vital processes take place at exact pH values.

2. Materials and methods

Electrochemical tests were performed on Co-Cr biomaterial alloy intended to be used for dentistry having the chemical composition and mechanical properties shown in Table 1.

In order to perform the corrosion tests, to the Co-Cr samples were applied contacts with copper conductors. After that, the samples 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), finally achieving a mirror surface. Polished samples were cleaned with ethanol and then dried with hot air and stored in a desiccator. The active surface of the Co-Cr samples tested for corrosion was 0.5 cm². The electrochemical cell (Fig. 1b) used for corrosion experiments consisted of: biomaterial – Co-Cr alloy which served as the

working electrode (WE), an Ag/AgCl electrode (saturated solution of KCl, E=200 mV/NHE) as reference electrode (RE) and a Pt-Rh grid as the counter electrode (CE). The composition of the tested solutions used in the corrosion experiments is presented in Table 2. Three types of simulated body fluids (SBF) were selected, namely Fusayama Meyer artificial saliva (pH = 5), Hank's solution (pH = 7.4) and Ringer's solution (pH = 6.6) in order to study the corrosion behaviour of the Co-Cr alloy as metallic biomaterial. The reason of using another type of environment (other than SBF), such as citric acid is that this medium is a powerful oxidant and has a lower pH value (pH = 1.8). This acid environment can influence the state (the formation, growth) of the oxide layer on the surface of the sample. Citric acid was also selected to study the corrosion of the alloy with biomedical destinations as it is found in citrus juice, apples, pears, cherries, raspberries, currants, in conifers, fungi, leaf tobacco, wine and even in milk, and can affect the composition change and the pH of the mouth cavity. For the investigation of the corrosion processes there have been used different analysis techniques such as: open circuit potential of the electrode (OCP), potentiodynamic polarization curves (PD) and cyclic polarization curves (CV). These testing techniques of corrosion were applied with a potentiostat/galvanostat VoltaLab PGZ 100, with interface to computer - soft VoltaMaster 4 (Fig. 1a).

Table 1. Chemical composition and mechanical properties of the Co-Cr alloy

Chemical composition, [%]								
Standard EN 10204 -3.1B	Co	Cr	Mo	Mn	C	Fe	Si	Sonstige
Max. [%]	63	29.4	5.95	0.6	0.29	0.05	0.7	0.1
Phisico-mechanical Properties								
Density [g/cm ³]		Hardness, HV10			Modulus of elasticity, (E) [MPa]			
8.3		420			230			

Table 2. The chemical composition of the electrolyte used in the corrosion tests

Components	Hank s solution	Ringer s solution	Saliva Fusayama Meyer (SFM)	Citric acid
NaCl	8.8 g/L	8.4 g/L	0.4 g/L	-
KCl	0.4 g/L	0.3 g/L	0.4 g/L	-
CaCl ₂	0.14 g/L	0.29 g/L	0.8 g/L	-
NaHCO ₃	0.35 g/L		-	-
C ₆ H ₆ O ₆ (glucose)	1 g/L		-	-
MgSO ₄ x 7H ₂ O	0.2 g/L		-	-
KH ₂ PO ₄ x H ₂ O	0.1 g/L		-	-
Na ₂ HPO ₄ x 7H ₂ O	0.06 g/L		-	-
NaH ₂ PO ₄	-		0.79 g/L	-
Urea	-		1 g/L	-
C ₆ H ₈ O ₇	-		-	0.5 M
pH	7.4	6.6	5.0	1.81

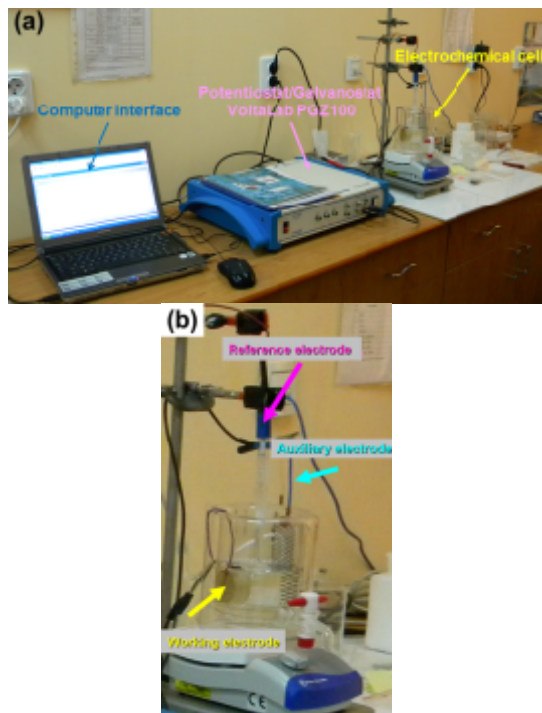


Fig. 1. (a) Set-up used at the investigation of corrosion with the potentiostat/galvanostat VoltaLab PGZ 100 and (b) Electrochemical cell used during corrosion experiments

3. Results and discussions

3.1. Evolution of open circuit potential during immersion

One of the ways to study the corrosion behaviour of the untreated Co-Cr alloy is to check the open circuit potential (OCP) as a function of time. This method indicates the oxidation tendency of a material to a corrosive environment. The potential can vary with time, as changes occur at the electrode surface (oxidation, formation of the passive layer or immunity). The potential-time measurements of the Co-Cr alloy in Hank's solution, Ringer's solution, Fusayama – Mayer saliva and citric acid, during 30 min. immersion time are shown in Fig. 2.

In Fig. 2 it can be seen a shift of the Co-Cr electrode potential towards electropositive values, which confirms the formation on the surface of a protective oxide film, for all studied environments. Also it is observed that in the case of citric acid solution, due to its composition without chlorides, even if the pH of the solution is reduced, this environment is a strong oxidant which leads to a shift of the Co-Cr electrode potential to more electropositive (more noble) values. As regards the three simulated body fluids (Hank's, Ringer's and SFM) due to different pH values and different

chloride content, there are three levels with different values of potential stabilization. These values are inversely proportional to the pH values and directly proportional to the chloride content of solutions.

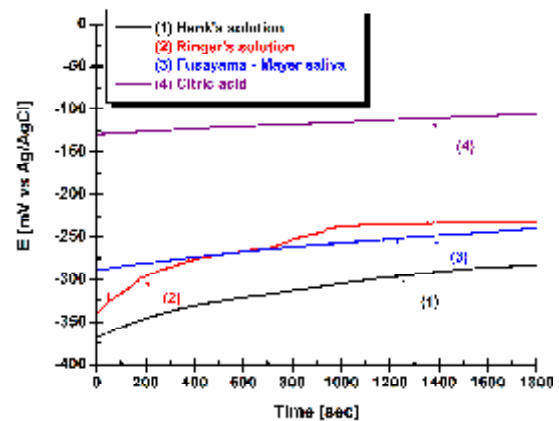


Fig. 2. OCP time plots obtained for Co-Cr alloy in: (1) Hank's solution, (2) Ringer's solution, (3) Fusayama – Mayer saliva and (4) citric acid, during 30 min. immersion time

Lower values of the OCP in Hank's solution, Ringer's solution and Fusayama – Mayer saliva can be explained by the presence of chloride ions that can be generated in long-term localized corrosion on passive alloys.

3.2. Potentiodynamic polarization curves

In order to assess the kinetics of the corrosion processes for the studied material, potentiodynamic polarization (PD) curves were measured at a scan rate of 5 mV/s, in the potential range between -1500 mV to +1200 mV vs. Ag/AgCl. Fig. 3 presents the polarization curves, current - potential ($i - E$) for the Co-Cr biomaterial studied immersed in the four solutions tested.

From this representation (Fig. 3) the Co-Cr alloy immersed in all four aqueous environments presents extended passive domains but between different potential domains corresponding to SBF environments, compared to citric acid solution. This behaviour of the Co-Cr alloy in SBF environments indicates immunity to corrosion from the electrochemical point of view.

This type of diagrams (intensity-potential curves) recorded in a wide range of potential, from cathodic to anodic potential with a constant scan rate allow us to make some predictions on the material and testing environment. In these diagrams can be distinguished four domains, namely:

- cathodic domain, where the passive film is destroyed by hydrogen evolution;

- critical domain, where the passive film is formed in competition with the dissolution of the metal, being an instability domain;
- passive domain, where the passive film is formed and is characterized by a passive current density;
- transpassive domain, where dissolution of material takes place through the passive film.

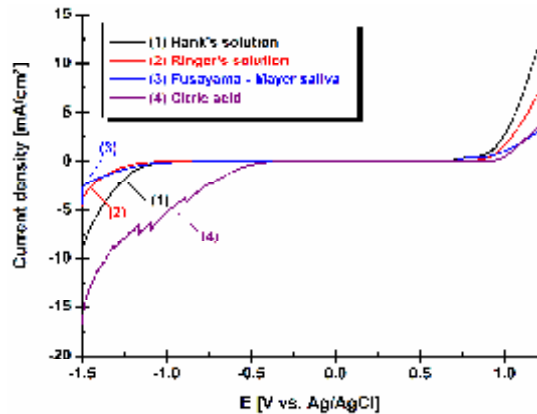


Fig. 3. PD (current - potential) curves obtained for Co-Cr alloy in: (1) Hank's solution, (2) Ringer's solution, (3) Fusayama – Mayer saliva and (4) citric acid

Usually the passive state is studied with respect to corrosion protection. If the passive state covers a higher potential domain and the passivation current value is smaller, then the metal or alloy shows a high corrosion resistance [8].

In Fig. 4 which shows a zoom of potentiodynamic polarization curves in the passive zone are observed the passive domains corresponding to tested solutions indicated by vertical arrows and their corresponding values. In Fig. 4 it can be seen a broad passivity domain for all three SBF studied, which is greater than 1 V, while the citric acid reveals a passive domain below 1 V. For the citric acid solution, the lower passivity domain around 0.972 V indicates that the Co-Cr alloy is more susceptible to corrosion. The potential values in different domains and solutions are given in Table 3. Also the table provides the passivation current density of the Co-Cr alloy in the tested solutions according to passivation domain.

Table 3. The potential domains and the passivation current density of Co-Cr alloy for tested solutions

Solution	Potential Domain, E [mV vs Ag/AgCl]				
	Cathodic domain	Critical Domain	Passive domain		Transpassive domain
			E	i_{pasiv} [$\mu\text{A}/\text{cm}^2$]	
Hank	< -940	-940 to -749	-749 to +394	36	> +394
Ringer	< -1030	-1030 to -533	-533 to +508	42	> +508
Fusayama Meyer saliva	< -764	-764 to -512	-512 to +524	36	> +524
Citric acid	< -344	-344 to -206	-206 to +766	41	> +766

From these last diagrams (Figures 3 and 4) is noted the importance of solution composition and pH values on the passivity domain (immunity) of Co-Cr alloy biomaterial.

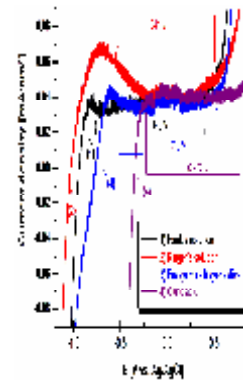


Fig. 4. Identifying the passive domains on the PD curves for the biomaterial Co-Cr alloy immersed in four aqueous environments

For the simple corrosion systems the corrosion reactions are strictly controlled by the charge transfer and the corrosion current density (i_{cor}). I_{cor} can be correlated with the polarization resistance (R_p) by the following relation:

$$i_{\text{cor}} = \frac{B}{R_p}$$

which represents the Stern – Geary equation for the evaluation of the corrosion resistance (in this case the corrosion rate is expressed in A/cm^2) and where B is a constant of the material – medium system given by the relation:

$$B = \frac{b_a |b_c|}{2,303(b_a + b_c)}$$

where, b_a and b_c are the Tafel slopes for the anodic and cathodic corrosion reactions.

Increasing the polarisation resistance means lower corrosion current density and thus a lower rate of corrosion.

Table 4 shows the results obtained for the polarization resistance and corrosion rates in the four solutions used.

Table 4. The values of polarizations resistance and corrosion rates of Co-Cr alloy for tested solutions

Solution	Polarization Resistance R_p [kohms cm ²]	Corrosion potential E [mV vs Ag/AgCl]	Corrosion rate i_{cor}	
			i_{cor} [mA/cm ²]	$\mu\text{m}/\text{year}$
Hank	3.0	-938	17.27	187.0
Ringer	3.08	-1027	36.80	398.8
Fusayama Meyer (SFM)	0.443	-902,6	14.16	153.3
Acid citric	1.69	-345	32.99	357.2

3.3. Cyclic polarization curves

By cyclic polarization method are recorded cyclic voltammograms on a selected potential range (typically starting from a negative value to a positive one) with a constant scan rate. If the reverse branch of the cyclic voltammograms shows lower currents than those of direct branch, then the material studied has a very stable passive behaviour. If the reverse branch shows higher current than those of direct branch at the same potential values it means that the surface is susceptible to pitting corrosion.

On the linear polarization diagrams are shown the different domains, current densities and corresponding potential states of "activity" and "prepassivity", followed by the "passive" (stable) and "transpassive" ones. Potential range for the passive state is between $E_p - E_{tp}$ with the passivation current density I_p . In the transpassive domain, the current density increases, because occurs a transpassive dissolution. In this domain, the passive film loses its protection properties and even disappears at higher potentials. From a practical point of view, the relative width of each domain and associated values depend directly on the material/environment system. The same material behaves differently in solutions with different pH.

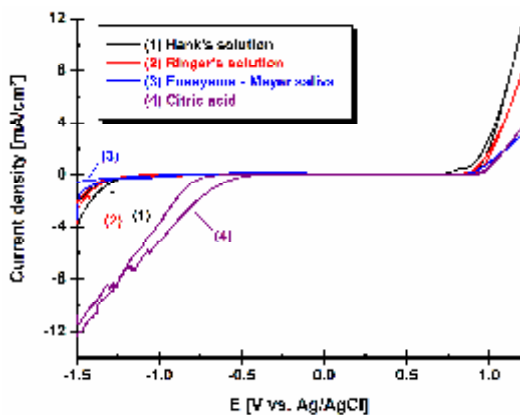


Fig. 5. Cyclic voltammograms of the Co-Cr alloy immersed in four solutions with different pH

Comparative cyclic polarization curves for the four tested solutions with different pH are presented in Fig. 5. Highlighting the localized corrosion susceptibility in the presence of chloride ions in the solutions can be seen very well due to the specific hysteresis aspect (Fig. 6) which presents the anodic transpassivation part of the curves from Fig. 5.

Localized corrosion or pitting corrosion is confined to a point or small hole within the metal. Pitting can initiate at sites where there are small surface defects such as a scratch or a dent, a small change in chemical composition of the alloy or damage to the oxide film. In the pit there is a rapid depletion of oxygen, and the pit behaves as a net anode, undergoing rapid dissolution. This anodic reaction produces electrons that are used further in oxygen reduction reactions at the external surface.

In Fig. 6 it is clearly observed that the Co-Cr alloy biomaterial shows pitting corrosion behaviour in Hank's solution, because of the specific hysteresis aspect. This behaviour 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 domains are inversely proportional to the pH values and directly proportional to chloride content of solutions.

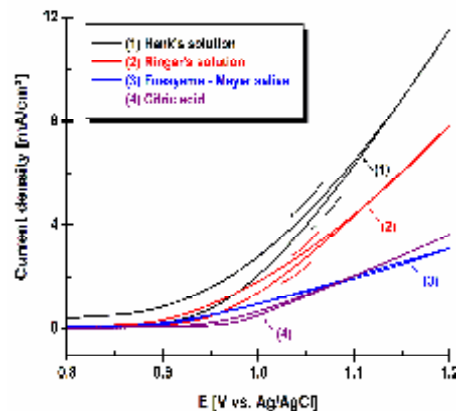


Fig. 6. Cyclic voltammograms of the Co-Cr alloy immersed in four solutions with different pH: Zoom on the anodic part with the transpassive domain



The generation of metal ions in the pit cavity leads to a net positive charge into the pit, resulting in an influx of chloride ions to maintain the charge balance. Hydrolysis of metal cations causes a decrease in pH. These factors promote pit growth, as high concentrations of chloride and hydrogen ions promote metal dissolution.

4. Conclusions

Material corrosion is a very important process to consider when choosing a material that must operate in a specific environment. Electrochemical methods used (open circuit potential, potentiodynamic polarization and cyclic polarization) are relevant methods to the study materials/operating environment interactions.

This paper presents the corrosion behavior in different simulating body fluids environments of Co-Cr alloy, biocompatible metallic material intended for dentistry. The interpretation of results according to open circuit potential and potentiodynamic polarization curves for the Co-Cr alloy biomaterial, 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 alloy biomaterial showed a different behavior of corrosion tests in solutions with different pH, different content of chlorides and different oxidizing character.

The Co-Cr alloy biomaterial is very sensitive to localized corrosion (pitting) in Hank's solution, the localized corrosion being visible on the cyclic polarization curves even after the first hours of immersion.

Future work

The development of a new composite biomaterial suitable for bone implants by controlled anodic oxidation followed by electrodeposition of

chitosan/hydroxyapatite. The anodisation of Co-Cr alloy leads to formation of a nanoporous oxide layer. By electrodeposition of chitosan/hydroxyapatite can be improved the capability of the interface for osseointegration, having simultaneously the protective properties of anodic growth oxide layer.

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