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Effect of physico-chemical properties of simulated body fluids on the electrochemical behaviour of CoCrMo alloy

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The behaviour of the CoCrMo alloy was studied under different experimental conditions of solution pH, chemical composition (phosphate buffer solution with and without addition of bovine serum albumin) and aeration (presence and absence of oxygen in the solution). With this purpose, electrochemical techniques such as open circuit measurements (OCP), potentiodynamic curves, potentiostatic tests and electrochemical impedance spectroscopy (EIS) were employed.

The results show that the general corrosion behaviour of CoCrMo alloy depends on the solution pH. Thus, the effect of BSA and the aeration conditions are related to the solution pH. At pH 3 no influence of BSA was observed in deoxygenated solutions which imply that BSA acts over the oxygen reduction reaction in acidic media. On the contrary, a noticeable influence of BSA addition was observed at pH 7.4 (independently on the gas content). Finally, at pH 10, the influence of BSA was only significant in oxygenated solution. It was found that $H_2PO_4^-$ favours the formation of passivating compounds which improves the resistance of the CoCrMo alloy to passive dissolution. Therefore, when the concentration of the $H_2PO_4^-$ increases (when pH decreases) the polarization resistance of the alloy also increases. On the other hand, the oxygen (aerated conditions) decreases the polarization resistance of the alloy in all the studied conditions.

1. Introduction

CoCrMo alloys are widely used as biomaterial for manufacture of prosthetic devices due to their good corrosion resistance and biocompatibility [1,2]. Their used is based on the well-established high resistance to corrosion in physiological media, imparted by a passive oxide film that forms spontaneously on the alloy surface and to their excellent mechanical properties (wear and hardness) [3]. The composition of this layer is predominantly Cr_2O_3 oxide with some minor contribution of other oxides (Co- and Mo- oxides, especially if the film is air formed) [4,5]. The physico-chemical properties of the passive film control the material's corrosion behaviour, the interaction with tissues and the surrounding part replaced into the body and thus the grade of the material's biocompatibility.

Biocorrosion has been considered one problem for the long durability of implants into human bodies and release of metal ions can cause adverse physiological effects, toxicity, carcinogenicity and metal allergy [6–11]. Although the definitive effects of these metal ions have not been determined, toxicity and metal allergy are the most significant concerns. For example, it has been demonstrated that Cr^{3+} and Co^{+2} have a toxicity effect on osteoblasy and induced cell mortality [12]. Tkaczyk et al. [13] found a chelating ability of the Cr(III) specie to form complexes with PO_4^{3-} groups, amino acids and calcium. Thus, the lower toxicity of the Cr(III), in comparison with other ions released from the alloy, may be related to the formation of these chemical complexes. Some studies support the chromium complex formation after observing the presence of $CrPO_4$ compounds in tissues surrounding orthopaedic implants [14].

The pH in biological systems is modulated mainly by phosphate buffering and it is kept around 7.4 under normal conditions. Nevertheless, pH may be modified by several factors such as wound-healing process after surgery (reaching values from 5.5 to 9 with infection) or haematomas and corrosion in some local sites where the pH may drop to approximately pH 1 or even lower [15,16]. Furthermore, pH also plays a role in the formation and modification of different metal-complexes generated into the body. Moulton et al. [17] observed different behaviour on the protein adsorption depending on the solution pH. Attending to these situations, electrochemical studies on CoCrMo biomedical alloys have not been found in the literature in biological solutions at different pH value.

Another parameter that can alter the stability of the passive layer is the presence of proteins due to their adsorption onto the

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Table 1
CoCrMo alloy composition.

Element	CoCrMo alloy (wt.%)
C	0.259
Si	0.9
Mn	0.38
P	0.05
S	0.005
Al	0.016
B	0.002
Co	Balance
Cr	28.45
Fe	0.22
Mo	5.39
Ni	0.29
Ti	0.02
W	<0.05
N	74.9 ppm
O	10.6 ppm

surface of the biomaterials [18–25]. These organic molecules could limit the diffusion of oxygen to certain regions of the metallic surface, causing preferential corrosion of the oxygen-deficient regions and leading to the breakdown of the passive layer. Igual Muñoz and Mischler [26] studied the effect of the interactions between phosphate and bovine serum albumin (BSA) in model-simulated body fluids on the CoCrMo passive behaviour. Thus, phosphate ions and albumin molecules present competitive adsorption on the CoCrMo implant alloy and they influence the electrochemical behaviour of the alloy. The isoelectric point in water at 25 °C for the BSA is 4.7–4.9 [27,28] changing the global charge with the pH (negative charge for values of pH above the isoelectric point and positive charge for more acidic pH). Furthermore, its conformational structure also changes with the pH [29]. Ithurbide et al. [24] studied the influence of pH in passivated chromium surfaces. They demonstrated that the pH has not strong effect on the total amount of BSA adsorbed on the Cr surfaces. Furthermore, this study showed that electrostatic forces do not govern the interactions protein-passivated surface of Cr. However, the influence of pH on the BSA adsorption on CoCrMo alloy has not been carried out.

Another aspect to take into account when simulating the body solution chemistry is the content of dissolved gases [30–32]. The oxygen and carbon dioxide content in the surroundings of a biomaterial can vary depending on the body fluid and physiological conditions. These differences may have effects on the corrosion behaviour of biomaterials in vivo [15].

The main objective of this work is to elucidate the effect of the pH on the electrochemical behaviour of a High-Carbon CoCrMo biomedical alloy in simulated body fluids by means of open-circuit measurements, potentiodynamic polarization, potentiostatic tests and electrochemical impedance spectroscopy (EIS). Phosphate buffered saline solution with and without the addition of bovine serum albumin (BSA) was employed as simulated body fluid to study the effect of the presence of the protein on the electrochemical behaviour. In addition, the aeration conditions were controlled in order to determine the influence of the presence of oxygen on the electrochemical response of the alloy.

2. Experimental

A High-Carbon CoCrMo was tested in form of rods with 9 mm in diameter. The nominal composition of this wrought alloy is shown in Table 1 which corresponded to ISO 5832-12. The thermal treatment applied on the cast alloy consisted on a solution annealing, a porous coating, a hot isostatic pressing and a final solution annealing. The porous coating is a thermal treatment employed in the manufacturing of surface prosthesis that is applied after a solution annealing in order to improve the properties of the as-cast material. Spherical beads are bonded to each other and the solid substrate by sintering at high temperatures (around 1300 °C) to achieve a strong particle–particle and particle–substrate bond [33,34]. Samples were embedded in epoxy mount so that an area of 0.65 cm^2 was exposed to the test solution. Before each experiment, the samples were mechanically polished (1000 and 4000 grit SiC paper), degreased with acetone, washed with pure water and dried with compressed air before use.

The simulated body fluid employed for carrying out the electrochemical experiments was a phosphate buffered solution (PBS) saline with the following composition: 8 g/L NaCl, 0.2 g/L KCl, 1.44 g/L Na_2HPO_4 and 0.25 g/L KH_2PO_4. The electrochemical tests were carried out with and without the addition of bovine serum albumin (BSA). Thus, one aliquot of BSA was added into the electrochemical cell until reaching a concentration of 100 mg/L of BSA. The PBS solution was prepared at pH values of 3, 7.4 and 10. The PBS solutions were adjusted with the addition of diluted HCl and diluted NaOH in order to reach pH values of 3 and 10, respectively before each experiment and before the addition of the BSA. Previously to the electrochemical measurements, a preheating of the solution was realized. The solution was pored into the cell and maintained until the temperature reached 37 °C.

The experimental set-up was a conventional three-electrode electrochemical cell with a platinum wire as a counter electrode and an Ag/AgCl (3 M KCl) as reference electrode. The work electrode (CoCrMo alloy sample) was mounted as a rotating disc electrode (RDE) and the rotation speed was fixed at 1000 rpm. A pH-electrode was introduced into the cell in order to detect any changes in the pH values during the electrochemical test. Furthermore, the nitrogen and oxygen were purged into the cell during the test in order to maintain the aeration (deoxygenated/oxygenated) conditions.

All electrochemical measurements were carried out using a potentiostat Solartron 1286 and a frequency response analyzer Solartron 1250. Open circuit-potential (OCP) was measured for 10 min, followed by a potentiostatic test at cathodic potential of $-1.5\,V_{Ag/AgCl}$ during 5 min. The BSA was added at the end of the potentiostatic measurement. The potentiodynamic polarization tests were performed by scanning the applied potential from $-1.5\,V_{Ag/AgCl}$ and moved in the anodic direction to $1.5\,V_{Ag/AgCl}$ at a scan rate of $1\,mV\,s^{-1}$.

The corrosion potential E_{corr} as well as the corrosion current density i_{corr} were automatically extracted from the polarisation curves by the CorrView Version 3.0 software through Tafel slope extrapolation.

Potentiostatic measurements were carried out at a passive applied potential of $0.05\,V_{Ag/AgCl}$ for 1 h and the current density response was recorded. Previous to this test, for electrochemically pre-conditioning the samples, a cathodic cleaning at $-1.5\,V_{Ag/AgCl}$ during 5 min has been carried out in order to reduce the oxide already formed on the CoCrMo alloy and to assure good reproducibility of the following measurements. EIS measurements were carried out under the same potentiostatic conditions. Impedance measurements were performed for 10 frequency decades from 10 mHz to 10^5 Hz with an amplitude of ±10 mV. The impedance data were analyzed with the *Zview 2.70* software package and fitted to corresponding equivalent circuit.