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Influence of carbides and microstructure of CoCrMo alloys on their metallic dissolution resistance

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ABSTRACT

CoCrMo alloys are passive and biocompatible materials widely used as joint replacements due to their good mechanical properties and corrosion resistance. Electrochemical behaviour of thermal treated CoCrMo alloys with different carbon content in their bulk alloy composition has been analysed. Both the amount of carbides in the CoCrMo alloys and the chemical composition of the simulated body fluid affect the electrochemical properties of these biomedical alloys, thus passive dissolution rate was influenced by the mentioned parameters. Lower percentage of carbon in the chemical composition of the bulk alloy and thermal treatments favour the homogenization of the surface (less amount of carbides), thus increasing the availability of Cr to form the oxide film and improving the corrosion resistance of the alloy.

1. Introduction

Cobalt–chromium–molybdenum alloys are widely used as biomedical materials due to their good mechanical properties (high mechanical resistance and low wear) combined with good corrosion resistance in body fluids. This adequate corrosion behaviour is attributed to the spontaneous formation of an oxide film of few nanometres (mainly composed of chromium oxide) that protects the bulk alloy to the surrounding environment [1–4]. Metal-on-metal (MoM) hip and knee replacements fabricated with CoCrMo have increasingly become the preferred choice for younger and/or more active patients due to their superior mechanical properties, longer service duration and reduced inflammatory osteolysis resulting from such services [5–8]. It is important to highlight that CoCr alloys shows higher fatigue and wear resistance when compared to stainless steel and titanium, and are therefore preferred in total hip and joint joint replacements, in both supportive and articulating locations [1].

For the manufacturing of CoCrMo orthopaedic implants thermal treatments are needed on the base materials in order to improve their physico-chemical and mechanical properties. These treatments modify the microstructure of the alloy and generates high amount of defects (porosity and lack of homogeneity) and consequently the material properties may change. Main metallurgical modifications produced by the high temperatures sintering cycles consist of dissolution of interdendritic carbides, massive precipitation of lamellar carbides eutectic phases at grain boundaries, localized porosity from incipient melting (not completely eliminated by following hot isostatic pressing) and grain boundary in fine-grained materials [9].

It is well known that the microstructure of CoCrMo alloys and the resulting properties strongly depend on the fabrication process (e.g. casting or forging), degree of cold-working and heat treatments. Several authors have reported that those changes in the microstructure of the CoCrMo alloy as a consequence of thermal treatments affect both the mechanical and wear behaviour [10–13]. Cawley et al. [10] determined that the as-cast microstructural condition with the highest carbide volume has the lowest wear and they also found a correlation between carbide volume fraction and wear-rate with the highest carbide volume fraction giving the lowest wear-rate. Clemow and Daniell [14] examined the influence of time and temperature upon the solution treatment on the metallurgical behaviour of CoCrMo alloy and they proposed that a reduction in the carbon content of this alloy would improve its solution treatment behaviour. In addition, the alloy microstructure also plays a crucial role on the general electrochemical behaviour as was demonstrated in previous works [9,15].

The different electrochemical and mechanical behaviour between CoCrMo alloys with different carbon content has been reported by numerous authors [10,16–24]. The alloys with higher carbon content are characterized by the presence of chromium carbides which increase hardness but affect the corrosion stability by depleting the metal matrix in chromium [12,17,25]. However, no general consensus exists on this matter because other authors did not find significant differences in the corrosion or dissolution mechanisms with the presence of carbide inclusions [25]. Therefore, although previous works point out better wear resistance properties of carbon richest CoCrMo alloys, there is not a pure

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electrochemical study focused on this topic. For this reason, the novelty of this work is to present an electrochemical study of the influence of different carbon content in the bulk composition of the CoCrMo alloys subjected to different thermal treatments on their corrosion behaviour in order to get a better understanding of previous tribological studies [15,17–19].

The aim of this work is to study the passive behaviour of CoCrMo alloys combining the synergic effect of carbon content with the thermal treatments (critical factors affecting material properties and clinical lifetime in the metallic implants). The alloys performance in three simulated body fluids was electrochemically evaluated by means of Open Circuit Potential (OCP) measurements, potentiodynamic curves, potentiostatic test and Electrochemical Impedance Spectroscopy (EIS).

2. Experimental. Methods and materials

2.1. Samples and electrolytes

The CoCrMo alloy samples were supplied by LAFITT (Valencia) in form of rods of 9 mm (Alloy 1 and Alloy 3) and 12 mm (Alloy 2) in diameter. The composition of the used alloys is shown in Table 1. According to the carbon content in the bulk alloy composition, all the supplied alloys are commercial High Carbon CoCrMo alloys (with > 0.15% weight in C [17]) however, Alloy 2 and Alloy 3 have lower carbon content in comparison with Alloy 1. The as-cast CoCrMo alloys were processed with three different heat treatments: T1 (solution annealing, SA), T2 (solution annealing, hot isostatic pressing and final solution annealing, SA + HIP + SA) and T3 (solution annealing, porous coating, hot isostatic pressing and final solution annealing, SA + PC + HIP + SA). Alloy 1 was treated with the three commented thermal treatments commented; Alloy 2 was treated with T1 and T2; and Alloy 3 only with T3 (as it is reported in Table 1 caption). HIP consist in a thermal process applying high temperature at the issostatic pressure of a gas which is applied in order to decrease the porosity and to improve the fatigue properties of the processed as-cast alloy. On the other hand, it is important to note that the porous coating procedure (PC) is a thermal treatment employed in the manufacturing of surface prostheses. Spherical beads are bonded to each other and the solid substrate by sintering at high temperatures (around 1300 °C) to achieve strong particle–particle and particle–substrate bonds [9,11]. The metallic cylinders were embedded into non-conductive resin, leaving cross-sectional available areas of 0.64 cm^2 and 1.13 cm^2 (Alloy 2). These areas correspond to the specimen surfaces of the CoCrMo alloy which will be in contact with the different electrolytes.

Three simulated body fluids were employed for carrying out the electrochemical experiments. Two solutions were prepared in a 0.14 M NaCl base with and without protein. The albumin containing solution (NaCl + BSA) was prepared with 500 mg L^{-1} of Bovine Serum Albumin fraction V (BSA). The pH of both solutions was adjusted to 7.4 (human conditions). The third simulated body fluid consists of a commercial bovine serum (BS) solution provided by SIGMA which contains 30 wt.% of protein. Temperature of the solution was kept at 37 °C (body temperature).

2.2. Sample preparation for metallographic study

Two different etchings were employed for the metallographic study in order to determine the grain size and the carbide content respectively. *Beraha III reagent* (base composition: 5 g de NH_4HF_2, 60 ml of distilled water and 40 ml of concentrated HCl; with reagent composition of 1 g of $K_2S_2O_5$ for this base solution) was used to reveal the microstructures of the CoCrMo alloys after the different thermal treatments. Thus, this etching allows one to determine the grain size of the CoCrMo alloy. The samples were immersed in the *Beraha III reagent* for 30 s, cleaned and rinsed with distilled water, immersed in ethanol and finally dried with compressed air. The carbide content of the alloys was quantified by using the etching procedure proposed by Cawley et al. [10]. This etching consists of immersing the samples for 5 s in the solution with base composition of 100 mL H_2O, 4 g $KMnO_4$ and 4 g NaOH. The sample were then analysed by optical microscopy and scanning electron microscope (SEM).

2.3. Microhardness measurements

Microhardness testing was performed on the samples with a Vickers microhardness tester Struers Duramin using a load of 500 g according to the ASTM E-384-11e1 [26]. Nine measurements were performed in order to obtain an average value and a standard deviation of the microhardness statistically acceptable. Furthermore, the microidentation procedure has been carried out in specific sites of the material (within of the cobalt matrix) so as to compare the measurement results for the different thermal treatments and alloys. Table 2 shows the values of microhardness measurements for all alloys and thermal treatments.

2.4. Electrochemical equipment and experiments

A conventional three electrode cell configuration (volume 50 mL) was employed with a platinum wire as counter electrode and an Ag/AgCl 3 M KCl as reference electrode. All experiments were accomplished under aerated conditions. Prior to electrochemical measurements, a preheating of the solution at 37 °C was carried out. This temperature was maintaining during the electrochemical tests by means of a heating circuit. Before each experiment, the samples were mechanically polished (1000 and

Table 1
CoCrMo alloys composition in wt.%.

CoCrMo	Alloy 1	Alloy 2	Alloy 3
Element	SA SA + HIP + SA SA + PC + HIP + SA	SA SA + HIP + SA	SA + PC + HIP + SA
C	0.259	0.221	0.19
Si	0.9	0.83	0.73
Mn	0.38	0.56	0.43
P	0.05	0.003	0.003
S	0.005	0.003	0.004
Al	0.016	0.003	<0.01
B	0.002	<0.003	0.002
Co	Balance	Balance	63.14
Cr	28.45	27.83	28.16
Fe	0.22	0.25	0.86
Mo	5.39	5.35	5.82
Ni	0.29	0.49	0.39
Ti	0.02	0.09	0.03
W	<0.05	<0.05	<0.10
N	74.9 ppm	100 ppm	1159 ppm
O	10.6 ppm	0 ppm	83 ppm

Table 2
Micro-hardness values of the CoCrMo alloys.

Treatment	HV_{500g}
Alloy 1T1	421 ± 26
Alloy 1T2	326 ± 17
Alloy 1T3	476 ± 2
Alloy 2T1	325 ± 11
Alloy 2T2	322 ± 16
Alloy 3T3	410 ± 7