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Development of Ti–Mo alloys for biomedical applications: Microstructure and electrochemical characterization

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Abstract

Ti–Mo alloys from 4 to 20 Mo wt.% were arc-melted. Their compositions and surfaces were analyzed by EDX, XRF and SEM. The Mo mapping shows a homogeneous distribution for all alloys. The XRD analysis showed that the crystal structure of the alloys is sensitive to the Mo concentration; a mixture of the hexagonal α′ and orthorhombic α″ phases was observed for the Ti–4Mo alloy, and the α″ phase is observed almost exclusively when the concentration of Mo added to the Ti reaches 6%. A significant retention of the β phase is observed for the alloy containing 10% Mo, while at higher Mo concentrations (15% and 20%), retention of phase β is only verified. Preliminary electrochemical studies have indicated a valve-metal behavior and good corrosion resistance in aerated Ringer solution for all alloys.

Keywords: Ti–Mo alloys; Biocompatible alloys; Biomedical titanium alloys; Corrosion; Microstructure

1. Introduction

The necessity to substitute hard tissue devices such as artificial hip joints for functionally disordered hard tissues like bone and teeth is growing, whereas the population over 65 years of age and the number of bedridden old persons is increasing [1]. Growing interest has been observed recently in the development of a new generation of biocompatible, corrosion- and wear-resistant materials [2]. In order to expand their applications as biomaterials, new alloys with local and systemic biocompatibility [3], appropriate mechanical properties, and resistance to corrosion [4] must be developed and studied. Osseointegration, i.e., a direct contact between viable bone and the implant without a soft-tissue layer [4], must be enhanced.

Titanium and its alloys still attract much attention for their application as biomedical metallic materials. Their superior qualities, such as low specific gravity, high corrosion resistance, low elasticity modulus, and good biocompatibility are desirable for biomedical materials [5,6]. Most biomedical uses of Ti alloys are in orthopedic surgery, e.g., artificial joints or bone plates; stainless steel and cobalt–chromium alloys are still used for these devices, but the number of cases where Ti or Ti alloys are used is increasing [6]. The high corrosion resistance of titanium and its alloys is partly due to a protective titanium dioxide passive film spontaneously formed on the titanium surface. The physicochemical and electrochemical properties of the oxide film and its long-term stability in biological environments play a decisive role for the biocompatibility of Ti implants [7]; in addition, the film improves the osseointegration process [8].

Titanium undergoes an allotropic transformation from a Hcp (α phase) into a Bcc structure (β phase) at 882 °C [9]. As a result of this structural change, titanium alloys fall into three classes: α alloys, α + β alloys, and β alloys, but these metallographic transformations can be improved by additions of selected α or β alloying stabilizers [9].

Most research on titanium biomaterials is done by focusing on β titanium alloys because processing variables can be controlled to produce selected results. Enhanced properties such as lower elasticity modulus, increased corrosion resistance, and improved tissue response are possible when compared with α + β type alloys [10]. Therefore, β titanium alloys composed of non-toxic elements such as Nb, Ta, Zr, Mo, and Sn showing lower elasticity modulus and greater strength should be developed [1].

In recent years, Ti–Mo alloys employed as biomaterials have been studied with emphasis on their microstructure and mechanical properties. Ho et al. [5], Sugano et al. [11], Guo and Enomoto

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[12], Sukedai et al. [13], and Liu et al. [14], for example, have conducted different studies on phase transformations, stress release, and mechanical properties of different Ti–Mo alloys.

Zhang et al. [15] studied the formation of stress-induced α martensite in a metastable β Ti–Mo-based alloy using X-ray diffraction and transmission electron microscopy. In a second paper, Zhang et al. [16] used high-resolution transmission electron microscopy and *in situ* X-ray diffraction analyses to elucidate the compositional sensitivity of the deformation behavior in two Ti–Mo-based alloys. The alloy with 8% Mo exhibited conventional elastic/plastic behavior in tension which corresponds to the irreversible formation of stress-induced orthorhombic martensite. The alloy containing 10% Mo exhibited a pronounced pseudoelastic response with recovery of 80% of the imposed tensile strain.

Considering that there are only a few studies dealing with Ti–Mo alloys and their potential use as biomaterials, the goal of this work was to obtain Ti–Mo alloys with different Mo concentrations from 4 to 20 Mo wt.%, and carry out their chemical, morphological, structural, and electrochemical characterizations in as-cast conditions.

2. Experimental

The Ti–Mo alloys with different compositions (4, 6, 8, 10, 15, and 20 Mo wt.%), were melted in an arc-melting furnace with a non-consumable W electrode and a water-cooled copper hearth under an ultra-pure argon atmosphere, following a well-known procedure described in the literature [6,17]. Initially, a vacuum of 10^{-3} atm was created and then ultra-pure argon was injected. This procedure was repeated three times and a vacuum of 10^{-3} atm argon was maintained at the end of the process, ensuring the removal of all gaseous oxygen from the system. After this procedure, the different alloys were melted from high-purity chemical elements. Ingots with approximately 60 g were obtained for each alloy. In order to ensure homogeneity, the samples were turned and remelted another 20 times [17].

All Ti–Mo alloys were studied in as-cast conditions, and prior to the XRF, EDX, and XRD analysis the samples were polished with grade 1500 silicon carbide paper and rinsed with distilled and deionized (Milli-Q®) water.

Preliminarly, the chemical composition of the alloys was assessed by X-ray fluorescence spectroscopy (XRF) and energy dispersive X-ray (EDX) analysis. The XRF experiments were conducted using a Shimadzu EDX-800 RayNy X-ray fluorescence spectroscometer, and a model 440 LEO microscope was used for EDX, coupled with a model 760 Si(Li) energy dispersive analyzer with a resolution of 133 eV.

The XRD analysis was conducted using a SIEMENS D5000 diffractometer; Cu Kα radiation was used and the phase was identified by matching the diffractograms with the JCPDS files (Match 1.3 software).

All Ti–Mo alloys were studied by scanning electron microscopy (SEM) and the Mo elemental mapping was done on the same surfaces by using the same equipment used for the EDX analyses. The samples were etched in a HF 7.5 mL, HNO_3 6.7 mL, H_2O 37.5 mL solution, after polishing the surface mechanically with silicon carbide papers (180–1500 grade).

Electrochemical experiments were performed in a standard three-electrode cell with a 0.44 cm^2 area of the working electrode exposed, having a graphite cylinder as a counter electrode and a saturated calomel electrode (SCE) as reference. The working electrolyte consisted of aerated Ringer physiological solution (NaCl 8.61 g/L, $CaCl_2$ 0.49 g/L, KCl 0.30 g/L) held at room temperature, and before any anodic oxide growth, the working electrodes were polished with grade 1500 silicon carbide paper and rinsed with distilled and deionized (Milli-Q®) water.

The voltammetric analyses were started at −1.0 V by scanning at 100 mV/s towards more positive potentials up to 8 V, when the scanning was reversed towards the initial potential. The voltammetric profiles were obtained for all Ti–Mo alloys. Later, experiments were also carried out at different scan rates (1, 25, 50, 100, and 200 mV s^{-1}).

3. Results and discussion

3.1. Chemical analyses

The chemical analyses (EDX and XRF) were performed in many different areas (bulk and surface) and results show that the actual chemical composition of the alloys is close to their nominal values (Table 1) and agree with ASTM F-67. As can be seen, only the Ti–20Mo alloy was slightly different (around 2%) when the experimental and nominal values were compared. The chemical composition of the alloys was homogeneous and no expressive differences between surface and bulk were found.

3.2. XRD analyses

The results obtained in this work showed that the crystal structure of the binary Ti–Mo alloys is sensitive to the molybdenum concentration in the alloy (Fig. 1). By comparing the results obtained for different alloys, it can be seen that a mixture of the hexagonal α′ and orthorhombic α″ phases was observed for the Ti–4Mo alloy, and the α″ phase is observed almost exclusively when the concentration of Mo added to the Ti reaches 6%. A significant retention of the β phase is observed for the alloy containing 10% Mo, while at higher Mo concentrations (15% and 20%), retention of phase β is only verified in the X-ray spectra.

Table 1
EDX and XRF analysis for Ti–Mo alloys

Alloy nominal composition	EDX Mo (at.%)	XRF Mo (at.%)
Ti–4Mo	4.2	4.3
Ti–6Mo	6.5	6.3
Ti–8Mo	7.3	8.1
Ti–10Mo	9.7	10.1
Ti–15Mo	15.1	14.6
Ti–20Mo	17.8	18.2