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Electrochemical characterization and passivation behaviour of new beta-titanium alloys (Ti35Nb10Ta-xFe)

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ABSTRACT

Passivation kinetics is a crucial factor in the electrochemical behavior of passive metals and alloys when subjected to operating conditions in real systems such as biomedical devices or aeronautical applications. The aim of this work is to describe the passivation behavior of new beta-titanium alloys (Ti35Nb10Ta-xFe with x = 1.5, 3 and 4.5 where numbers indicate the %wt in the alloying elements) obtained by powder metallurgy using different electrochemical techniques and existing theoretical models for oxide film growth (High Field Model, HFM, and Interface Models, IFM). Influence of Fe content in the alloy and prevailing electrochemical conditions (i.e. applied potential) on the kinetic parameters were analyzed. The oxide film growth can be described by a HFM approach considering that the film thickness is related to the current flowing through the system, thus constant values for passive film formation were considered. The electric field in the film and the thickness of the oxide layer were quantified. Iron content in the alloy does not significantly modifies the passive film properties of the obtained materials but decreases the passive film growth of the resulting alloy. The applied potential reduces the electric field in the oxide layer while increasing its thickness.

1. Introduction

Titanium and titanium alloys are widely used as prosthetic materials in the biomedical field due to their physico-chemical properties and high biocompatibility. However, the limited mechanical properties and the toxicity of certain alloying elements make necessary the continuous development of new titanium-based alloys [1–3]. Beta-titanium alloys are therefore a promising alternative to the classical alpha-beta ones, such as Ti-6Al-4V, because they reduce the elastic modulus of the resulting material, thus decreasing the probability of stress shielding in the interface between the bone and the implant. Those beta-alloys also contain less toxic alloying elements (i.e. iron) which constitute a good substitute to Aluminium or Vanadium.

Powder metallurgy as a fabrication process is a versatile alternative to obtain a great variety of titanium alloys although it also presents associated problems such as the lack of diffusion of refractory elements, grain growth and alpha phase transformation in the grain boundaries due to the thermal process [4]. Indeed, stabilization of the beta-phase in the titanium alloys can be achieved by simply melting blending elements of alloying elements to the titanium powder such as niobium, tantalum or iron, among others [5]. However, the addition of those elements is known to cause some additional problems in the manufacturing process due to their refractory properties and also may change the mechanical and electrochemical properties of the surface, thus the biocompatibility of the resulting material [6–9].

Titanium, as a valve metal, spontaneously forms an oxide film on its surface which determines its corrosion mechanism, passivity and passive dissolution [10]. From scientific and technological reasons, the passivation of titanium alloys is of great interest especially in the biomedical field. Indeed, the passive dissolution rate and the film growth determine the stability of the titanium surface, thus their biocompatibility, because they govern the metal ion release from a titanium implant in the human body.

Typically, the titanium oxide films formed at room temperature have a thickness in between 2–5 nm [11] and it increases around 2–3 nm/V during anodization [12–15]. Two main rate-limiting

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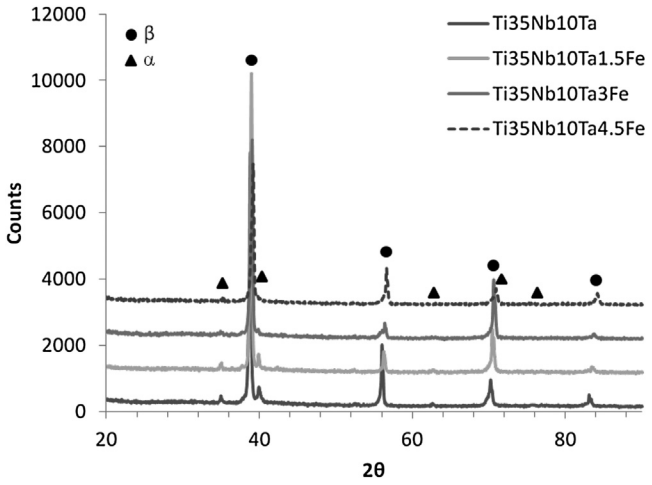

Fig. 1. XRD diffractograms for the Ti35Nb10Ta, Ti35Nb10Ta1.5Fe, Ti35Nb10Ta3Fe and Ti35Nb10Ta4.5Fe alloys sintered at 1250 °C.

processes can be considered for describing the passive film growth mechanism [16,17]: the ionic transport through the film (High Field Model, HFM) or the growth/dissolution reactions at the film/solution interface (Interface Model, IFM). When the film growth is limited by the high field ion conductivity across the passive film, the ionic current flowing through the growing film, $i(t)$, can be expressed as a nonlinear relationship between current and the electric field, $E(t)$, across the charge space as:

$$i(t) = k'_B \exp(B\,E(t)) \quad (1)$$

where the constant k'_B ($A\,cm^{-2}$) is related to the concentration of mobile charge carriers inside the film and the activation energy for the charge jump and the constant B ($nm\,V^{-1}$) is related to the symmetry of the energy barrier and the distance between two jump equilibrium positions.

On the other hand, when the passive film growth is limited by the reactions taking place at the oxide/electrolyte interface, Vetter and Gorn [18,19] assumed that the film growth is limited by the following reaction:

$$H_2O(aq) \leftrightarrow O^{2-}(ox) + 2H^+(aq)$$

And that the current can be expressed as:

$$i(t) = i_0^{IFM} \exp[(\alpha_1^+ F/RT)(\Delta U(t) - \rho i(t) - E_0 \Delta\lambda(t))] \quad (2)$$

where i_0^{IFM} is a constant, α_1^+ a transfer coefficient, F the Faraday constant, R the gas constant, T the temperature, $\Delta U(t)$ the difference in the applied potential, ρ the solution resistance, E_0 the electric field in the film before the potential step and $\Delta\lambda(t)$ the variation of the oxide film thickness. Typically, the exponential constant term is grouped and defined as:

$$g^+ = \alpha_1^+ F/RT \quad (3)$$

thus the current is expressed according to the following expression:

$$i(t) = i_0^{IFM} \exp[(g^+(\Delta U(t) - \rho i(t))]\ \exp[(g^+ E_0 \Delta\lambda(t))] - E_0 \Delta\lambda(t)) \quad (4)$$

Typically, the growth of the anodic films on titanium takes place under a high field strength of 10^6–$10^7\,V\,cm^{-1}$ and the electric field is assumed to increase with change in potential, thus the current density can be described by the high field formalism [20].

The aim of this work is to characterize the interface biomaterial/environment, the passivation kinetics and the passive film growth parameters of new beta-titanium alloys (Ti35Nb10Ta-xFe, x = 1.5, 3 and 4, where numbers represent %wt) with different iron contents obtained by powder metallurgy.

2. Experimental

2.1. Materials and electrolyte

New beta titanium alloys have been studied (Ti35Nb10Ta-xFe, x = 1.5, 3 and 4, where numbers represent %wt) with different iron contents obtained by via powder metallurgy. Ti cp. and Ti6Al4V were also studied as reference materials. These alloys were obtained by conventional powder metallurgy technique using blending elemental powders. The titanium powders obtained by hydride – dehydride (HDH) process (higher purity of 99.7%, particle size <48 μm), niobium (higher purity of 99.8%, particle size <20 μm) and tantalum (higher purity of 99.8%, particle size <8 μm) were provided by Atlantic Equipment Engineers and the iron powders by Höganäs (higher purity of 99.9%, particle size <34 μm). The compaction of the samples was carried out in an automatic press applying uniaxial pressure of 600 MPa and sintered at 1250 °C for 3 hours under vacuum conditions (<10^{-4} mbars). Cylindrical floating die of 20 mm in diameter were used for obtaining round samples of 6 mm on thick.

The electrolyte employed was a 1 M H_2SO_4 solution.

2.2. Metallographic study

Specimens were wet-grinded with 220 to 4000 grit silicon carbide (SiC) paper and further polished with MD-Chem polishing clothes using the OP-S colloidal silica suspension (Struers) to a mirror like finishing (R_a = 0.1 μm). Porosity and equivalent diameter of the pores were obtained using an optical microscopy NIKON

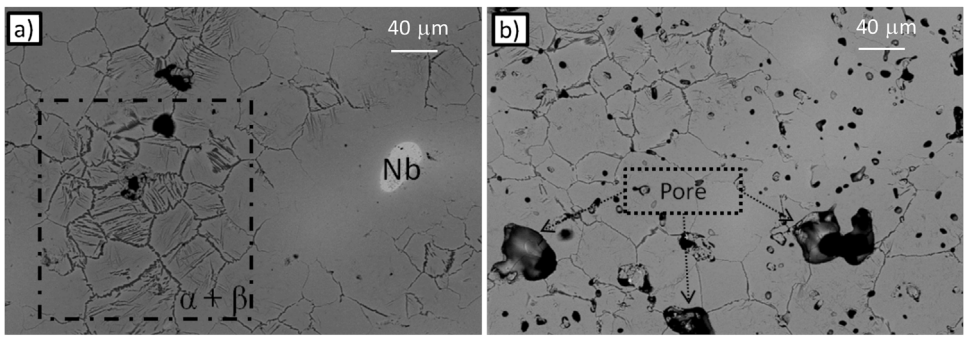

Fig. 2. FE-SEM images in BSE signal of Ti35Nb10Ta1.5Fe (a), Ti35Nb10Ta3Fe (b) sintered at 1250 °C.