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Electrochemical behavior of near-beta titanium biomedical alloys in phosphate buffer saline solution

A. Dalmau [a,*], V. Guiñón Pina [a], F. Devesa [b], V. Amigó [b], A. Igual Muñoz [a]

[a] *Institute for Industrial, Radiophysical and Environmental Safety Universidad Politécnica de Valencia, P.O. BOX 22012, E-46071 Valencia, Spain*
[b] *Institute of Materials Technology, Universidad Politécnica de Valencia, P.O. BOX 22012, E-46071 Valencia, Spain*

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ABSTRACT

The electrochemical behavior of three different near-β titanium alloys (composed by Ti, Nb and Sn) obtained by powder metallurgy for biomedical applications has been investigated. Different electrochemical and microscopy techniques were used to study the influence of the chemical composition (Sn content) and the applied potential on the microstructure and the corrosion mechanisms of those titanium alloys. The addition of Sn below 4 wt.% to the titanium powder improves the microstructural homogeneity and generates an alloy with high corrosion resistance with low elastic modulus, being more suitable as a biomaterial. When the Sn content is above 4%, the corrosion resistance considerably decreases by increasing the passive dissolution rate; this effect is enhanced with the applied potential.

1. Introduction

The use of titanium and its alloys in the biomedical field has increased considerably due to their excellent properties: low density, high hardness, good corrosion resistance, inactivity with the biological environment, low elastic modulus and high capacity to attach to tissue and bone, making titanium a good choice as a biomaterial [1,2]. Pure titanium is an allotropic element, which can form more than one crystal structure. At low temperatures, the titanium forms an α phase with hexagonal closed-packed (HCP) structure. Above 882.5 °C it is transformed into a β phase with body center cubic (BCC) structure. The α to β phase transformation temperature (β transus) can be raised or lowered depending on the alloying elements and their content. Some elements, aluminium or oxygen, stabilize the α phase and raise the β transus temperature, while other elements, vanadium, molybdenum or niobium, stabilize the β structure and lower the β transus [3]. Some other elements, tin and zirconium, behave neutrally at low and moderate concentrations. According to the concentration of the alloying elements and the phases present at room temperature, titanium alloys are classified as α, α + β and β alloys. Commercially pure titanium (α alloy) and the Ti6Al4V alloy (α + β alloy) were found to be the most employed alloys for dental implants during years, although they exhibit prolonged use limitations: high elastic modulus compared to the bone, and low wear resistance [4,6]. Ti6Al4V was also found to be toxic due to the release of aluminium and vanadium ions [6]. Recent effort has been focused on developing new titanium alloys specifically for biomedical applications [7] such as the β alloys. The β microstructure has good specific properties, because of their low density, excellent corrosion resistance [8] and low elastic modulus compared with α and α + β titanium alloys.

The corrosion behavior of titanium alloys depends on an oxide film formation mainly composed of TiO_2, which spontaneously covers the titanium surface and its alloys in the presence of oxygen [6]. The chemical properties of the oxide layer play an important role in the biocompatibility of titanium implants and the surrounding tissues. The corrosion behavior of β Ti alloys is governed by the β stabilizing elements. These Ti alloys form a single compact layer that contains TiO_2 and traces of other oxides. The presence of niobium in the alloy enhances its passivation by decreasing the concentration of the anion vacancies in the TiO_2 film [6]. Therefore, TiNb alloys show superior corrosion resistance when compared to the traditional Ti6Al4V [9]. TiNbSn alloys have a uniform surface corrosion which provides a passive film which can be formed by Ti_2O_3, TiO_2, Nb_2O_5 and SnO_2 [10-13]. Several studies have demonstrated that TiNbSn alloys have lower Young's modulus than the Ti alloys which reduces the stress shielding phenomena [3,4,14]. Kuroda et al. compared TiNbTaSn alloys [5], showing that the alloy containing 2 wt.%. of Sn (Ti29Nb13Ta2Sn) had the lowest Young's modulus, compared to the same alloy containing 4.6 and 6% of Sn. It has also been observed that the tensile strength of the TiNbSn alloy is higher than that of the Ti6Al4V [12].

In order to meet the demands of longer human life and implantation in younger patients, the development of novel metallic alloys for biomedical applications is a requirement nowadays. The most promising

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* Corresponding author.
E-mail address: aldalbor@posgrado.upv.es (A. Dalmau).

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alloys for implant application are β-type titanium alloys composed of non-toxic elements. Many β-type alloys composed by Nb, Ta, Zr, Mo, Hf, Au, Pd, Pt, Ag, Ga, Ge, Sc and Sn were developed in the last two decades [13]. One recently developed promising biomedical alloy, Ti3Zr2Sn3Mo25Nb shows significant improvement of the corrosion resistance and biocompatibility compared to previous generation of Ti alloys such as CP Ti and Ti6Al4V [14]. Liu and Zheng [15] studied the in vitro effects of some alloying elements, including the Sn on pure iron and they obtained that there was not significant cytotoxicity to ECV304 cells, except for the FeMn alloy. Wan et al. also studied the biocompatibility of Ti35Nb2.5Sn and Ti35Nb1.4Sn alloys [16], revealing that osteoblasts cells have good growing and spreading ability on the surface of Ti35NbxSn and that cell viability for the Ti35Nb2.5Sn is 0.4 times higher than for CP Ti.

By conventional powder metallurgy elemental powders are mixed and good final properties of the alloy, such tensile stresses, specific strength and a good combination of toughness and fatigue resistance are obtained despite of the inherent porosity of the process [15,16]. It avoids the remelting of the material and subsequent heat treatments performed in the fusion process [17-19]. Nowadays porous titanium has become a popular surgical implant material since it increases the roughness and the porosity of the material, thus increasing the integration of the material device to the bone [18–20]. As the roughness increases the osseointegration is greater, but the active surface is also higher promoting the corrosion and the formation of oxides on the titanium surface [16,21,22]. An homogeneous microstructure is achieved even though all the diffusion process is conducted in solid state [9]. On the contrary, Sn helps to the titanium–niobium diffusion spread as it has a relatively low melting point and form a liquid phase in the

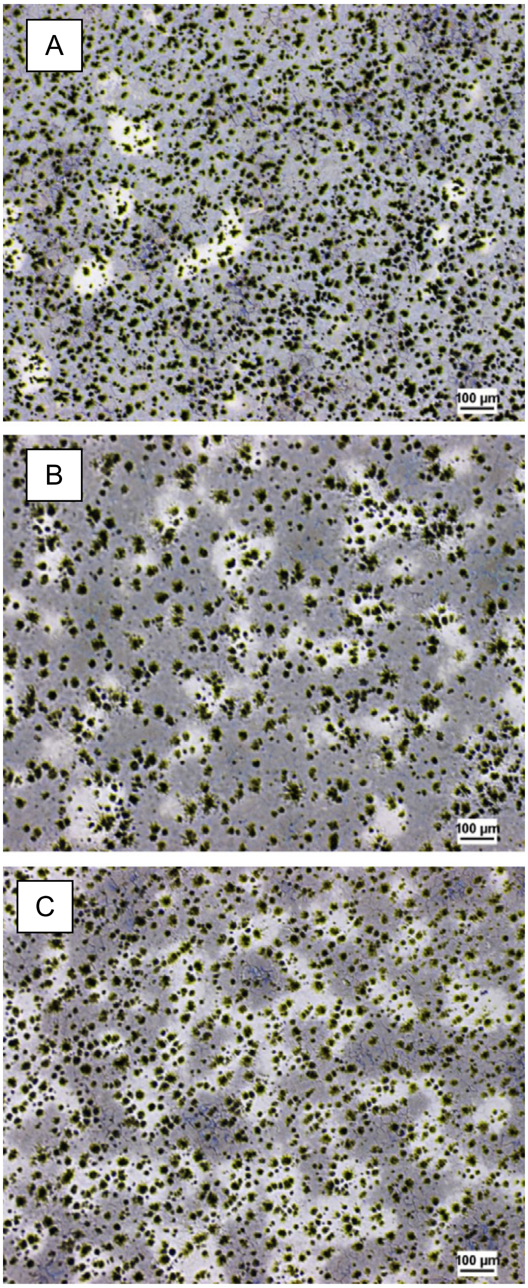

Fig. 1. Optical images of etched A) Ti30Nb, B) Ti30Nb2Sn and C) Ti30Nb4Sn alloys, ×50.

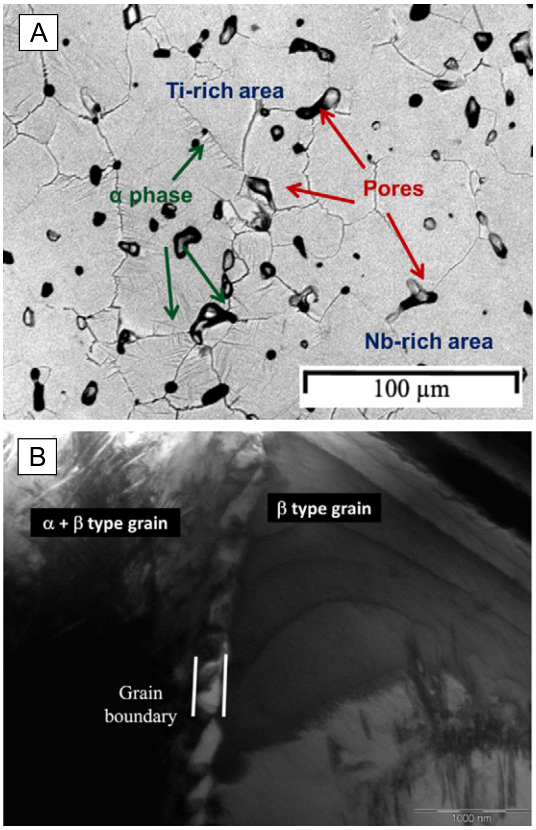

Fig. 2. A) SEM and B) TEM micrographs of the etched Ti30Nb at ×500 and ×5200, respectively.

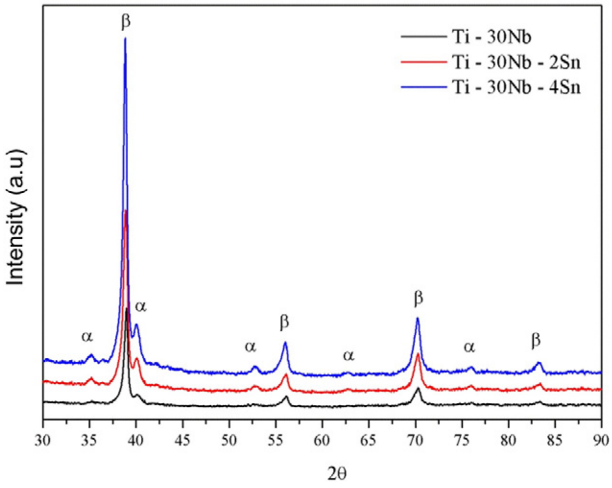

Fig. 3. X-ray diffraction patterns of the surface of the different Ti30NbxSn studied alloys.