Applied Surface Science 307 (2014) 372–381

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

In situ characterization of the effects of Nb and Sn on the anatase–rutile transition in TiO_2 nanotubes using high-temperature X-ray diffraction

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ARTICLE INFO

Article history:
Received 8 January 2014
Received in revised form 4 April 2014
Accepted 6 April 2014
Available online 15 April 2014

Keywords:
Phase transformations
Biomaterials
Titanium alloys
TiO_2 nanotubes

ABSTRACT

New metastable β-type Ti alloys for biomedical applications containing biocompatible alloying elements such as Nb can present remarkable mechanical behavior. Whenever the performance of an implant produced from β-type Ti alloys is considered, it is crucial to take into account their surface properties because they are intimately associated with osseo-integration. The osseo-integration of orthopedic implant devices made from CP–Ti to β-type Ti alloys depends directly on the properties of the oxide layer formed on their surface. The aim of this study was to investigate the formation of self-organized TiO_2 nanotubes by an anodization process on CP–Ti and Ti–35Nb and Ti–35Nb–4Sn alloys (wt.%) and analyze the effects of Nb and Sn additions to CP–Ti on the amorphous–anatase and anatase–rutile phase transformations in TiO_2 nanotubes using glazing-angle high-temperature X-ray diffraction. The results obtained suggest that the crystallization of TiO_2 formed on CP-Ti occurs at 225 °C, whereas the anatase–rutile transition occurs at 400 °C. As Nb was added to Ti, the temperatures at which these phase transformations occur increased. When Sn was added to Ti–35Nb alloy, the kinetics of the phase transformations appeared to decrease.

1. Introduction

An interesting combination of properties, such as enhanced biocompatibility, high corrosion resistance, good processability and, especially, superior mechanical behavior, makes Ti and its alloys widely employed in biomedical applications. Ti alloys represent one of the best classes of metallic materials used in the fabrication of orthopedic implant devices [1,2].

The mechanical behavior of a particular Ti alloy depends directly on its microstructure. By adding specific alloying elements and applying proper heat treatments, it becomes possible to achieve a suitable combination of types, volume fractions and morphologies of phases and hence mechanical properties for a given application [3]. The manufacture of implant devices for hard tissue repair requires materials with specific properties, including high corrosion resistance, enhanced biocompatibility, high mechanical strength and low elastic modulus. Although the needs related to biocompatibility, corrosion resistance and mechanical strength are well known, the requirement of materials with a low elastic modulus arises from the ability to allow for the elastic deformation of the bone tissue surrounding implant devices [1]. When submitted to mechanical stress, bone tissues suffer changes in their internal architecture and their external shape. The absence or even the reduction of mechanical loading might induce bone loss or degeneration [4]. This phenomenon suggests that biomaterials to be employed in hard tissue repair need to present a low Young's modulus [1].

With respect to biomaterials designed for implants devices, in the past few years, most efforts associated with the development of metallic materials to be used in hard tissue repair have focused on metastable β-type titanium alloys, prepared by the addition of biocompatible alloying elements, particularly alloys containing Nb [5,6]. Depending on the composition and processing routes employed, alloys of the Ti–Nb–Sn system can exhibit remarkable mechanical behavior [7].

In addition to the intrinsic bulk material characteristics, the performance of an implant device designed for hard tissue repair depends strongly on the surface features of the device material,

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http://dx.doi.org/10.1016/j.apsusc.2014.04.040
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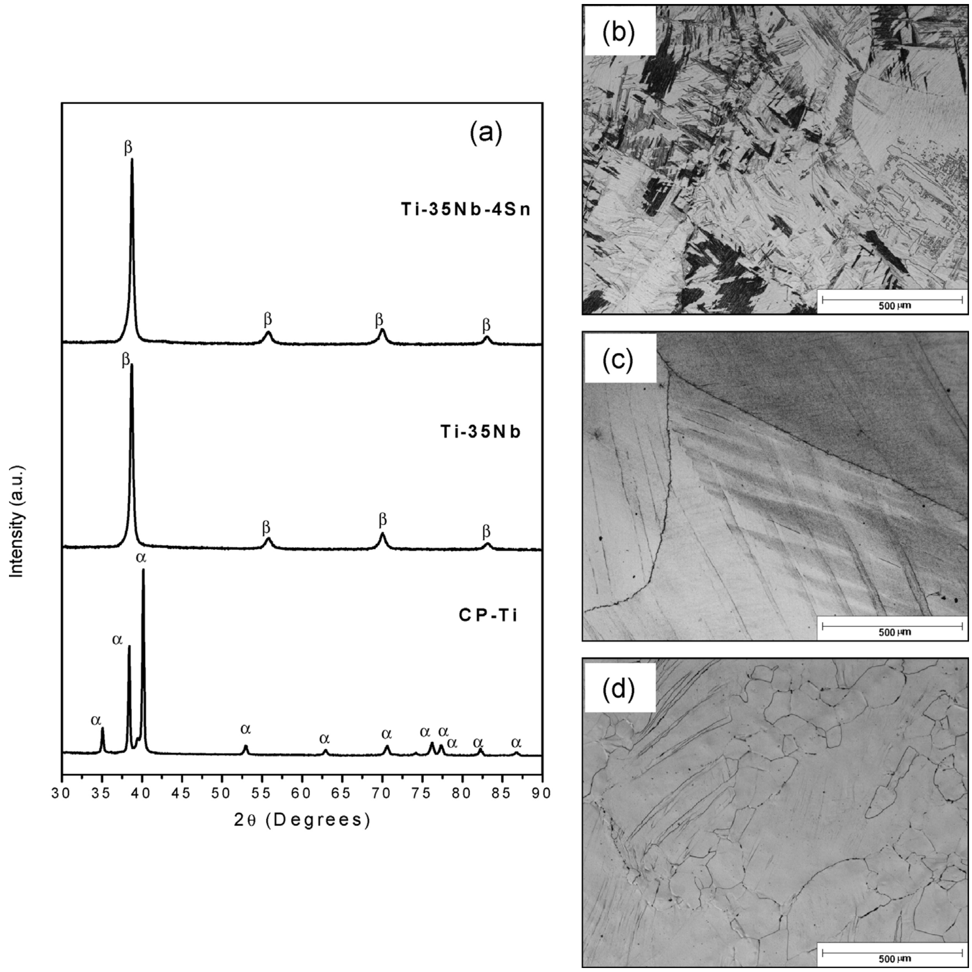

Fig. 1. (a) X-ray diffraction pattern and optical micrographs (OM) of hot-forged (b) CP–Ti, (c) Ti–35Nb and (d) Ti–35Nb–4Sn substrates.

which are directly related to the implant osseo-integration process [8]. Cells in biological tissues, whose dimensions are on the nanometer scale, directly interact with and create nanostructured extra-cellular matrices. Interactions between implant biomaterials and biological tissues are favored by a nanostructured surface because such a surface may stimulate cell growth and therefore tissue regeneration [9,10]. Popat and co-authors have confirmed the ability of nanostructured surfaces to promote osteoblast differentiation and bone matrix production [10].

When Ti or Ti alloys are exposed to oxygen, a passivation layer of TiO_2 is rapidly formed on their surfaces. The controlled formation of TiO_2 by potentiostatic anodization, which leads to nano- or micro-roughness surfaces, provides bioactivity enhancement and also increases the probability of osseo-integration [11,12]. This anodic layer exhibits a high surface-to-volume ratio, and literature results indicate a strong relationship between implant surface characteristics and bone growth [8].

The surface features of the titanium dioxide layer are directly related to its polymorphism. It is well known that TiO_2 exhibits three different naturally occurring polymorphs, i.e., brookite, rutile and anatase, whose formation depends on the synthesis procedure and post-processing conditions employed [13].

According to Uchida and co-authors [14], compared to rutile, anatase is more effective in providing good conditions for nucleating hydroxyapatite on Ti implants. The reason for this more suitable behavior is possibly related to the lattice features of the anatase phase and the hydroxyapatite phase. Implant osseo-integration involves a competition between fibroblast cells and osteoblast cells [15]. Whereas smooth surfaces improve fibroblast cell growth, nanotopographical surfaces favor osteoblast cell fixation and growth [8,10]. The growth of fibrous tissue on an implant surface reduces the possibility of forming a well-established and strong bond between the implant and the bone tissue provided by osteoblast cells [15]. Inefficient mechanical interaction between regenerating tissue and an implant surface may lead to the loosening of the implant device [10]. Consequently, implant success is directly

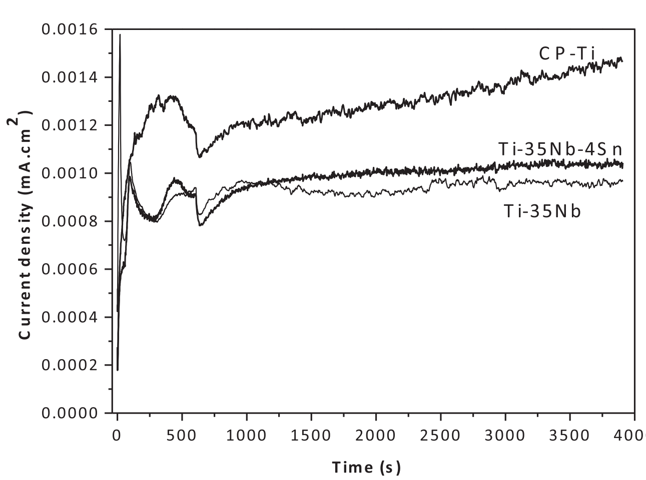

Fig. 2. Current density vs. anodizing time for CP–Ti, Ti–35Nb and Ti–35Nb–4Sn substrates anodized using 0.1 vol.% HF and a constant potential of 20 V.