Thin Solid Films 517 (2009) 5038–5043

Contents lists available at ScienceDirect

Thin Solid Films

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

Electrochemical characteristics of nanotubes formed on Ti–Nb alloys

Seung-Hyun Jang [a], Han-Cheol Choe [a,*], Yeong-Mu Ko [a,c], William A. Brantley [b]

[a] Department of Dental Materials and Research Center of Nano-Interface Activation for Biomaterials, College of Dentistry, 2nd Stage of Brain Korea 21 for College of Dentistry, Chosun University, Gwangju, South Korea
[b] College of Dentistry, Ohio State University, Columbus, OH, USA
[c] Research Center for Oral Disease Regulation of the Aged, College of Dentistry, Chosun University, Gwangju, Korea

ARTICLE INFO

Available online 26 March 2009

Keywords:
Electrochemical anodization
Nanotube
Corrosion behavior
Ti–xNb alloy

ABSTRACT

Titanium and Ti alloys have been used extensively as bone-implant materials due to their high strength-to-weight ratio, good biocompatibility and excellent corrosion resistance. In this work, we have investigated the effects of the β-stabilizing element Nb on the morphology of nanotubes formed on Ti–xNb alloys using 1.0 M H_3PO_4 electrolyte containing 0.8 wt.% NaF and various electrochemical methods. Oxide layers consisting of highly ordered nanotubes with a wide range of diameters (approximately 55–220 nm) and lengths (approximately 730 nm–2 μm) can be formed on alloys in the Ti–xNb system as a function of Nb content. The nanotubes formed on the Ti–Nb alloy surface were transformed from the anatase to rutile structure of titanium oxide. The titanium oxide nanotube surface was observed to have lower corrosion resistance in 0.9% NaCl solution compared to titanium oxides surfaces on Ti–xNb alloys without the nanotube morphology.

1. Introduction

Titanium and its alloys (particularly Ti–6Al–4V) are widely used as implants in orthopedics, dentistry and cardiology due to their high strength, enhanced biocompatibility, and high level of hemocompatibility [1,2]. The biocompatibility and hemocompatibility result from a thin titanium dioxide-based layer that is always present on the metal surface [3]. The addition of alloying elements, such as Al and V, improved the mechanical properties of titanium. However, reports of toxicity effects caused by Al and V, and the high elastic modulus of CP Ti and Ti–6Al–4V compared to bone, have stimulated development of more biocompatible titanium alloys with lower elastic modulus for dental and orthopedic applications. Tissue studies have identified Nb as a non-toxic element that does not cause any adverse reaction in the human body [4]. It is well known that recent biomaterials research has focused on β-titanium alloys due to their increased biocompatibility and decreased elastic modulus. A low elastic modulus for an orthopedic implant is desired to minimize bone resorption from stress shielding, which results from bone supporting a much smaller portion of functional stress than the surrounding metallic implant [5].

It has also been reported [6] that the yield strength increases and percentage elongation decreases for Ti–Nb alloys with increasing Nb content.

Titanium and its alloys form stable, dense oxide layers that consist mainly of TiO_2 [7]. The natural oxide is thin (about 3–8 nm in thickness), amorphous, and stoichiometrically defective. It is well known that the protective stable oxides on titanium surfaces provide favorable osseointegration. The stability of this titanium oxide layer depends strongly on its composition, structure and thickness. As a consequence, great efforts have been devoted to thickening and stabilizing the surface oxide on titanium to achieve the desired biological response. Among the various methods to improve the interfacial properties and clinical lifetime of Ti-based implants, anodization methods have attracted great attention due to controllable, reproducible results as well as simple processing [8]. We chose Nb as a β-stabilizer alloying element.

In the present study, electrochemical characteristics of nanotubes formed on Ti–Nb alloys have been researched by using electrochemical methods in 1 M H_3PO_4 with small amounts of fluoride ions, and then the corrosion behavior of the anodic TiO_2 layers was also investigated.

2. Experimental details

The starting raw materials were 99.99% Ti and 99.9% Nb. A series of Ti–xNb alloy (10, 20, 30 and 40 wt.%) ingots of 10 mm diameter were prepared by arc melting on a water-cooled copper hearth under an argon atmosphere with a non-consumable tungsten electrode. (Alloy compositions are specified throughout this article in weight percent.) Each ingot was melted six times after inverting the metal to ensure homogeneous melting. After water quenching, ingots were heat treated for 6 h at 1000 °C for homogenization of the microstructure. They were then cut into specimens having a diameter of 10 mm and a thickness of 2 mm, followed by degreasing with acetone. One group of specimens (10, 20, 30 and 40 wt.% Nb), serving as the control, was prepared by polishing the Ti–xNb disks with up to 2000 grit SiC paper and

---

* Corresponding author. Tel.: +82 62 230 6896; fax: +82 62 230 6896.
E-mail address: hcchoe@chosun.ac.kr (H.-C. Choe).

0040-6090/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2009.03.166

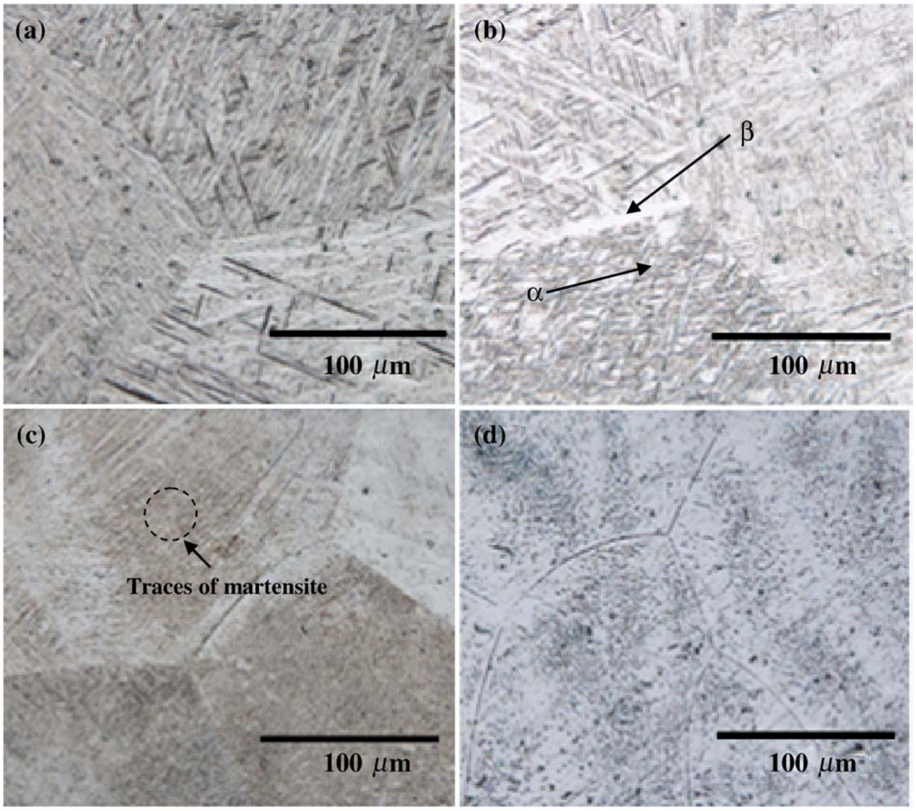

Fig. 1. Optical microscope photographs showing the microstructure of heat treated (water-quenched) Ti–xNb alloys: (a) Ti–10Nb, (b) Ti–20Nb, (c) Ti–30Nb, and (d) Ti–40Nb.

ultrasonically cleaning in ethanol and distilled water. Microstructures of the alloys were observed by optical microscope, and phases were identified by an X-ray diffractometer (X'Pert Pro, Philips) utilizing Cu Kα radiation.

Anodization experiments for nanotube formation employed a conventional three-electrode configuration with a platinum counter electrode and a saturated calomel reference electrode (SCE), and were performed in 1 M H_3PO_4 with small additions of NaF (0.8 wt.%) at 25 °C. The anodization treatment of the Ti–Nb alloys was performed with a scanning potentiostat (Model 362, EG&G Company, U.S.A). This treatment consisted of a linear potential ramp from the open-circuit potential (E_{ocp}) to an ending potential at 10 V, utilizing a potential control mode, followed by holding the sample at 10 V for 2 h.

Structural characterization of the samples after nanotube formation was carried out with a field-emission scanning electron microscope (Model 4800, Hitachi, Japan), which was also capable of energy-dispersive spectrometric (EDS) analyses. The cross-sectional and surface images of the Ti–Nb substrates were obtained from mechanically scratched samples.

The in vitro corrosion behavior of the titanium alloy surfaces containing nanotubes was investigated by potentiodynamic polarization, using a scan rate of 1.66 mV/s from −1.5 V to 2.0 V (SCE). An EG&G Model 263A potentiostat and an 0.9% aqueous NaCl solution at 36.5 ± 1 °C were employed for the corrosion testing.

3. Results and discussion

Fig. 1 shows optical microscope images of the microstructures of the Ti–xNb alloys with different Nb contents (10, 20, 30 and 40 wt.%). As previously noted, the initially prepared Ti–xNb ingots were heat treated at 1000 °C for 6 h in an Ar atmosphere followed by water quenching. Fig. 1 (a) and Fig. 1(b) show the microstructures of the Ti–10Nb and Ti–20Nb alloys, respectively, which were mainly composed of colonies of α and β phases. Very fine and almost continuous grain boundary α and parallel α plates that grew from the grain boundaries are dispersed in a β matrix. Needle-like traces of martensite in the β grains were observed for the Ti–30Nb alloy, as shown in Fig. 1(c). However, Fig. 1(d) shows that no trace of martensite phase was seen in the Ti–40Nb alloy, compared to the Ti–10Nb and Ti–20Nb alloys, due to complete β-phase formation. Thus, Fig. 1 shows that the apparent volume fraction of martensite decreased with increasing Nb content in the Ti–xNb alloys. This may be associated with the enhancement of β-phase stability with increasing Nb content, since Nb is a known β-phase stabilizer [9,10]. These microstructural changes with increased Nb content will be related to the elastic modulus and nanotube morphology. Firstly, some studies

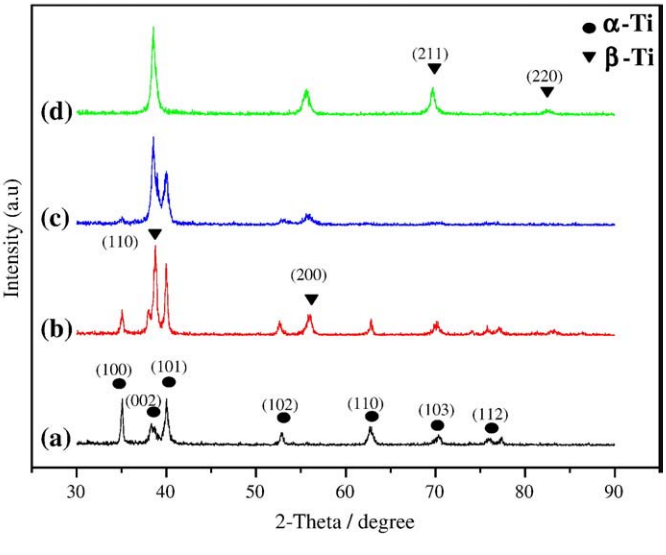

Fig. 2. X-ray diffraction patterns of Ti–xNb alloys: (a) Ti–10Nb, (b) Ti–20Nb, (c) Ti–30Nb, and (d) Ti–40Nb.