



# Highly ordered nanotubular film formation on Ti–25Nb–xZr and Ti–25Ta–xHf



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## ABSTRACT

The purpose of this study was to investigate the highly ordered nanotubular film formation on Ti–25Nb–xZr and Ti–25Ta–xHf, examining the roles of niobium, zirconium, tantalum and hafnium alloying elements. The Ti–25Nb–xZr and Ti–25Ta–xHf ternary alloys contained 0, 7 and 15 wt.% of these alloying elements and were manufactured using a vacuum arc-melting furnace. Cast ingots of the alloys were homogenized in Ar atmosphere at 1050 °C for 2 h, followed by quenching into ice water. Formation of nanotubular films was achieved by an electrochemical method in 1 M H<sub>3</sub>PO<sub>4</sub> + 0.8 wt.% NaF at 30 V and 1 h for the Ti–25Nb–xZr alloys and 2 h for the Ti–25Ta–xHf alloys. Microstructures of the Ti–25Ta–xHf alloys transformed from  $\alpha'$  phase to  $\beta$  phase, changing from a needle-like structure to an equiaxed structure as the Hf content increased. In a similar manner, the needle-like structure of the Ti–25Nb–xZr alloys transformed to an equiaxed structure as the Zr content increased. Highly ordered nanotubes formed on the Ti–25Ta–15Hf and Ti–25Nb–15Zr alloys compared to the other alloys, and the nanotube layer thickness on Ti–25Ta–15Hf and Ti–25Nb–15Zr was greater than for the other alloys. Nanotubes formed on Ti–25Ta–15Hf and Ti–25Nb–15Zr showed two sizes of highly ordered structures. The diameters of the large nanotubes decreased and the diameters of the small nanotubes increased as Zr and Hf contents increased. It was found that the layer thickness, diameter, surface density and growth rate of nanotubes on the Ti–25Ta–xHf and Ti–25Nb–xZr alloys can be controlled by varying the Hf and Zr contents. X-ray diffraction analyses revealed only weak peaks for crystalline anatase or rutile TiO<sub>2</sub> phases from the nanotubes on the Ti–25Nb–xZr and Ti–25Ta–xHf alloys, indicating a largely amorphous condition.

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## 1. Introduction

The principally used bioinert metallic materials are stainless steels, Co–Cr alloys, commercially pure titanium (CP Ti), and Ti–6Al–4V (ELI) [1]. Among these, Ti–6Al–4V is the principal biometallic material for *in vivo* implantation due to its excellent mechanical properties, superior corrosion resistance, and low density [2]. However, there are two concerns with the use of Ti–6Al–4V: (1) potential release of aluminum and vanadium ions that could have negative effects into the human body, and (2) likelihood of adjacent bone resorption resulting from the much higher elastic modulus of this alloy compared to cortical bone (stress-shielding). In order to overcome these concerns, other titanium alloys with non-toxic and non-allergic elements such as Nb, Ta, Zr, Hf, and Mo have been recently developed and studied [3]. Moreover, Ta and Nb have the important effect of reducing elastic modulus by stabilizing the Ti alloys in the  $\beta$  phase; these two elements belong to the

same group as Ti in the periodic chart and are considered biocompatible. There is much current interest in biomedical Ti–Ta alloys [3,4], and the Ti–25Ta alloy is reported to have the best mechanical compatibility [5]. Moreover, Ti alloys with Ta and Zr have potential for dental alloys due to their good mechanical properties and corrosion resistance [3]. Furthermore, Nb is a known  $\beta$ -stabilizer and reduces the elastic modulus of the titanium alloy; the Nb atoms largely occupy Ti sites, resulting in solid-solution strengthening and precipitation hardening [6,7]. It is well known that  $\beta$ -Ti alloys show two stable phases, the body-centered cubic (bcc)  $\beta$  phase at higher temperatures and the hexagonal close-packed (hcp)  $\alpha$  phase at lower temperatures, as well as three metastable phases:  $\alpha'$ ,  $\alpha''$  and  $\omega$  [8]. The additions of Zr and Hf to Ti alloys result in a high level of blood compatibility when used in cardiovascular implants and lead to better corrosion resistance due to formation of stable oxide layers [9].

It is known that the protective stable oxides on titanium surfaces provide a favorable environment for osseointegration [10]. The stability of the oxide layer depends strongly on the particular alloying element, along with the structure and thickness of this film [11]. As a consequence, great efforts have been devoted to thickening and stabilizing the surface oxide on titanium to achieve the desired

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biological response using various treatments of the dental implant surface such as sputtering, anodizing (nanotube or micropore formation), grit-blasting, ion implantation, and pulsed laser deposition [12,13]. Among these various surface modification methods to improve the biocompatibility and corrosion resistance of implant materials, anodization has attracted great attention due to the controllable and reproducible results and the simplicity of the process [14]. Anodization has been employed to create titanium oxide nanotubes on Ti and Ti alloy surfaces to improve cell adhesion and proliferation for clinical applications [15]. It should be possible to control the nanotube size and morphology for biomedical titanium implant alloys by controlling the alloying element, applied voltage, current density, anodization time and electrolyte [16]. While previous investigations have examined the effects of applied voltage, current density, time, and electrolyte for nanotube formation by anodization, our study was focused on the factor of alloying element, which has not been studied in a comprehensive manner. Accordingly, in this investigation, we have characterized the nanotubes formed on Ti–25Nb–xZr and Ti–25Ta–xHf, elucidating the roles of these four alloying elements for Ti, and have observed highly ordered arrays of the nanotubes, as will be described.

## 2. Experimental details

The Ti–25Ta–xHf and Ti–25Nb–xZr alloys, having Zr and Hf contents of 0, 7, and 15 wt.%, were prepared using Ti (Grade 4, G&S Titanium, USA), and Ta, Nb, Hf, and Zr (99.95% purity, Kurt J. Lesker Company, USA). These metals were mixed and then fused in a high-purity argon atmosphere using an arc-melting vacuum furnace. Owing to the large difference in the melting points and the densities of these elements in their pure state, the melting operation was carried out 10 times for homogenization, and each time the alloy was held in the molten state for 3–4 min [17]. The resulting ingots were then cut into specimens having a diameter of 10 mm and a thickness of 4 mm. Heat treatment was subsequently performed at 1050 °C for 2 h in an argon atmosphere for further homogenization of the microstructure, and the alloy was then rapidly quenched in 0 °C ice water. The specimens for electrochemical anodization were prepared by polishing with sandpaper having abrasive sizes from 100 to 2000 grit and finishing with 0.3 μm Al<sub>2</sub>O<sub>3</sub> slurry. All polished specimens were ultrasonically cleaned in acetone for 10 min and distilled water and then dried in air.

A direct current (DC) power source (Model E3641A, Agilent Technologies, Palo Alto, USA) was used for anodization to form the surface nanotubes. The titanium alloy specimen was connected to the positive terminal, and a platinum rod was connected to the negative terminal of the power source. Anodization was performed at a constant potential of 30 V and a time period of 1 h for the Ti–25Nb–xZr alloys and a time period of 2 h for Ti–25Ta–xHf alloys. These optimum time periods were determined in preliminary experiments. Self-organized TiO<sub>2</sub> surface nanotubes were then prepared by electrochemical oxidation of the anodized specimens in a 1.0 M H<sub>3</sub>PO<sub>4</sub> + 0.8 wt.% NaF electrolyte at 25 °C.

Microstructures of the alloys were examined with a field-emission scanning electron microscope (FE-SEM, Hitachi 4800, Japan). The specimens for FE-SEM observation were etched in Keller's solution consisting of 2 mL HF, 3 mL HCl, 5 mL HNO<sub>3</sub>, and 190 mL H<sub>2</sub>O. The microstructural phases were subsequently identified by X-ray diffraction (XRD), using a diffractometer (X'pert PRO, Philips, Netherlands) and Cu Kα radiation (λ = 0.15406 nm). Peaks for crystalline phases were indexed using International Centre for Diffraction Data (ICDD) powder standards 44-1288 and 44-1294 for titanium. The chemical composition of the nanotube-formed surfaces was determined by energy-dispersive X-ray spectroscopy (EDS), using a spectrometer (Oxford ISIS 310, England) attached to the FE-SEM, with an accelerating voltage of 15 kV, working distance of 15 mm, and voltage of 137 eV for the detector.

## 3. Results and discussion

Fig. 1 shows the FE-SEM results for the Ti–25Ta–xHf and Ti–25Nb–xZr alloys with varying Zr and Hf contents (0, 7 and 15 wt.%). Fig. 1 (a) shows the microstructure of binary Ti–25Ta without the addition of Hf; Fig. 1 (b) shows the microstructure of ternary Ti–25Ta–7Hf, and Fig. 1 (c) shows the microstructure of ternary Ti–25Ta–15Hf. Fig. 1 (d), (e) and (f) is the corresponding FE-SEM images for the Ti–25Nb–xZr alloys with Zr contents of 0, 7 and 15 wt.%, respectively.

The microstructures of Ti–25Ta in Fig. 1 (a) and Ti–25Ta–7Hf in Fig. 1 (b) show mainly sharp needle-like or acicular structures within the grains, whereas the microstructure of Ti–25Ta–15Hf in Fig. 1 (c) shows mainly an equiaxed structure in which the needle-like structure has somewhat disappeared. It can be seen that the needle-like martensitic structures changed to equiaxed grain structures with increasing Hf content. In previous studies of the Ti–25Ta–xZr alloys it was reported that the effect of increasing Zr content for these alloys might be interpreted as due to an increase in the compositional ratio of (β-stabilizing elements)/Ti [18,19]. The present study suggests that the effect of increasing Hf content in the Ti–25Ta–xHf alloys has the same role of increasing this compositional ratio, which is not surprising since the β-stabilizing Hf has physically and chemically similar properties as Zr [20].

In the case of Ti–25Nb–xZr alloys, shown in Fig. 1 (d) and (f), the α' phase appears within the β-Ti grains and has a needle-like shape similar to a pine-tree leaf. This α' martensitic structure shows a more severe needle-like shape compared to that observed for the Ti–Ta alloys. It is thought that Ta can have a stronger role for forming the β phase in Ti alloys compared to Nb [18]. When Hf is added to Ti–Ta alloys, the β phase is not predominant, compared to the addition of Zr; the latter element can stimulate greater formation of β phase than α' phase [18]. From the FE-SEM image of the Ti–25Nb–15Zr microstructure in Fig. 1 (f), it can be seen that the amount of β phase was greater than that of α' phase. As the Zr content increased, the amount of martensitic α' phase decreased, and the amount of β phase increased. The present results are in agreement with previous studies of phase relationships for Ti–Nb–Zr alloys [21,22].

Table 1 shows the EDS analysis results for the Ti–25Ta–xHf and Ti–25Nb–xZr alloys. The Ti–25Ta–xHf alloy surface mainly consisted of Ti, Ta, and Hf, all compositions were in good agreement with the nominal compositions of the alloys. The Hf alloying element was not detected for the Ti–25Ta alloy, while the Ti–25Ta–7Hf and Ti–25Ta–15Hf alloys showed Hf contents of 7.2 and 15.6 wt.%, respectively. For the two Ti–25Nb–xZr alloys containing Zr, the EDS results of 6.9 and 15.8 wt.% Zr were in good agreement with the nominal values of 7 and 15 wt.%, respectively. These EDS results show that the original melting and heat treatment processes yielded alloys with homogeneous compositions.

Fig. 2 shows the XRD peaks for the Ti–25Ta–xHf and Ti–25Nb–xZr alloys. In Fig. 2 (a), the α' martensitic structure peaks mainly appeared for 2θ angles near 38° and 70° for the Ti–25Ta alloy, corresponding to the needle-like structure shown in Fig. 1 (a). In comparison, while the Ti–25Ta–15Hf alloy also presented α' peaks at similar diffraction angles, there was also a peak at 70° for the β phase, corresponding to the acicular orthorhombic martensitic and equiaxed bcc β structure shown in Fig. 1 (c). Phase transformation of the alloys from α' hexagonal structure to α'' orthorhombic structure or β bcc structure gradually progressed with increasing Hf content, due to the effect of Hf on changing the phase transformation temperature [18]; this behavior accounts for the microstructural changes shown in Fig. 1. Therefore, these results have verified that the phase transformation to the α'' orthorhombic or β bcc phase of the Ti–25Ta–xHf alloys can be controlled by varying the Hf content.

Fig. 2 (b) shows the XRD peaks for the Ti–25Nb–xZr alloys with different Zr contents. The peaks from the Ti–25Nb alloys also corresponded to the bcc β phase and orthorhombic α'' phase. For Ti–25Nb, the XRD peaks have higher intensity for the α'' (020) peak and lower intensity for the α'' (110), (112), (113) and (020) peaks, along with lower

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