

# Effects of $\beta$ - Stabilized Alloying Element on the Nanotube Morphology of Ti-Alloy

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## ABSTRACT

Titanium alloys show attractive properties for biomedical applications where the most important factor are biocompatibility, corrosion resistance, low modulus of elasticity, very good strength-to-weight ratio, reasonable formability and osseointegration. The aim of this study was to investigate the effects of Nb content (10, 20, 30 and 40wt%) on microstructure and nanotube formation of Ti-xNb alloy samples. Electrochemical anodization of the Ti-xNb alloys were carried out by potentiostatic experiments in 1M H<sub>3</sub>PO<sub>4</sub> + 0.8wt% NaF electrolyte at room temperature. Under specific sets of conditions highly self-organized titanium oxide nanotubes are formed with diameters varying from approx. 55 to 220 nm and length from approximately 727 nm to 2  $\mu$ m.

**Keywords:** anodization, nanotube, Ti-Nb alloy

## 1 INTRODUCTION

Titanium and its alloys have been widely used for structural biomaterials such as artificial hip joints and dental implants due to their excellent specific strength and corrosion resistance. Amongst conventional biomaterials, pure Ti as well as Ti-6Al-4V alloy exhibit excellent properties for surgical implant applications. These properties are achieved by a thin titanium oxide based layer that is always present on these alloys surface [1]. By adding alloying elements to titanium, such as Al and V, its mechanical properties are improved [2-3]. However, due to toxicity effects caused by Al and V and high elastic modulus, new alloys that present lower elastic modulus and do not contain these elements are receiving a great deal of attention. Tissue reaction studies have identified Ti, Nb, Zr and Ta as non-toxic elements as they do not cause any adverse reaction in human body. It is well known that recent biomaterials research has focused on  $\beta$ -Titanium alloys due to increased biocompatibility and decreased Young's modulus. Some studies have shown that Ti-Nb alloys ranging from 20 to 50 wt% Nb exhibit a modulus of elasticity of about 60GPa [4-6], which is closer to that of

bone when compared to those of other conventional alloys applied to orthopedic implants. The increase on Nb content tends to decrease the modulus of elasticity and stabilizes the  $\beta$ -titanium phase. It has also been reported that the yield strength increases and the elongation decreases with increasing Nb content [7].

The high degree of biocompatibility of Ti alloys is usually ascribed to their ability to form stable and dense oxide layers consisting mainly of TiO<sub>2</sub>. The natural oxide is thin (about 3-8 nm in thickness) and amorphous, stoichiometrically defective. It is known that the protective and stable oxides on titanium surfaces are able to provide favorable osseointegration [8]. The stability of the oxide depends strongly on the composition, structure and thickness of the film. As a consequence, great efforts have been devoted to thickening and stabilizing surface oxide on titanium to achieve desired biological response [9].

Anodic oxidation is efficient to control the thickness, composition and topography of the oxide film on titanium and can be applied for implant surface modification. Using anodic oxidation, TiO<sub>2</sub> is formed with a chemical bond between the oxide and Ti substrate that likely results in enhanced adhesion strength. Indeed, a bone-like apatite layer is formed on TiO<sub>2</sub> in simulated body fluid. Furthermore, researchers have suggested that TiO<sub>2</sub> with a 3D micro/nanoporous structure may enhance apatite formability when compared to dense TiO<sub>2</sub> [10].

In the present study, we chose Nb as a binary alloying element because it has excellent biocompatibility and be expected to act as a  $\beta$ - stabilizer. The purities of the starting raw materials were 99.99% for Ti and 99.9% for Nb. For the purpose of improvement in biocompatibility, the anodic TiO<sub>2</sub> layer on Ti-xNb alloys were fabricated by electrochemical method in 1M H<sub>3</sub>PO<sub>4</sub> with small amounts of fluoride ions, and then the effect of Nb content on the nanotube size, the morphology of Ti oxide layer formed by the anodic oxidation method was investigated.

## 2 EXPERIMENTAL

### 2.1 Materials and surface preparation

The purities of the starting raw materials were 99.99% for Ti and 99.9% for Nb. A series of Ti-xNb alloys (10, 20, 30 and 40wt%) (in this study, all the percentages are shown in weight %) were prepared. Ti-xNb alloys of 10 mm in diameter were prepared by arc melting on a water-sealed copper hearth under an argon gas atmosphere with a non-consumable tungsten electrode. Each ingot was melted six times by inverting the metal to ensure homogeneous melting. The ingots were heat-treated for 6h at 1000 °C for homogenization after water quenching. They were cut to a diameter of 10 mm and a thickness of 2 mm followed by degreasing with acetone. The as-received group specimens (10, 20, 30 and 40wt%Nb), which were used as the control groups, were prepared by polishing the Ti-xNb disk surfaces with up to #2000 SiC paper and ultrasonically cleaning in ethanol and distilled water.

## 2.2 Nanotube formation treatment

Electrochemical experiments were carried out with a conventional three-electrode configuration with a platinum counter electrode and a saturated calomel (SCE) reference electrode. Experiments were performed in 1M H<sub>3</sub>PO<sub>4</sub> with small additions of NaF(0.8wt%). All experiments were conducted at room temperature. Electrochemical treatments were performed by using a scanning potentiostat (EG&G Co, 362, U.S.A). The electrochemical treatment consisted of a potential ramp from the open-circuit potential (*E*<sub>ocp</sub>) to an end potential at 10 V with a scan rate of 500mV/s followed by holding the sample at 10V for 2h.

## 2.3 Surface characterization

Structural characterization of the nanotube formed samples was carried out with a field emission scanning electron microscope (Hitachi FE-SEM 4800, Japan). The scanning electron microscope was capable of energy dispersive spectrometer (EDS). The cross-sectional and surface of Ti substrate images were obtained from mechanically scratched samples. In order to identify the phase constitutions of the Ti-xNb alloys, x-ray diffractometer (XRD, philips, X'Pert Pro) analysis with a Cu-K  $\alpha$  radiation were performed.

# 3 RESULT AND DISCUSSION

## 3.1 Microstructural observations

Fig. 1 shows the optical microstructures of Ti-xNb alloys with different Nb contents (10, 20, 30 and 40 wt.%). It was controlled by heat treatment at 1000 °C for 6hr in Ar atmosphere followed by water quenching. Fig. 1(a, b) shows the average microstructure, which is mainly composed of  $\alpha$ + $\beta$  colonies. The microstructure is formed by very fine and almost continuous grain boundary  $\alpha$  and  $\alpha$  parallel plates, which grew from the grain boundary, dispersed in a  $\beta$  matrix. The clear

needle-like traces of martensite in the  $\beta$  grain were observed in the image of Fig. 1 (c). However, in Ti-40Nb alloys (Fig. 1(d)), no trace of martensite phase is seen compared to Ti-10Nb and ti-20Nb due to complete  $\beta$ -phase formation. The apparent volume fraction of martensite decreased with increasing Nb content in Ti-xNb alloys, as seen in Fig. 1. This may be associated with  $\beta$ -phase stability, i.e., the stability of  $\beta$ -phase would be enhanced with increasing Nb content, since Nb is known to be a  $\beta$ -phase stabilizer [11-12].

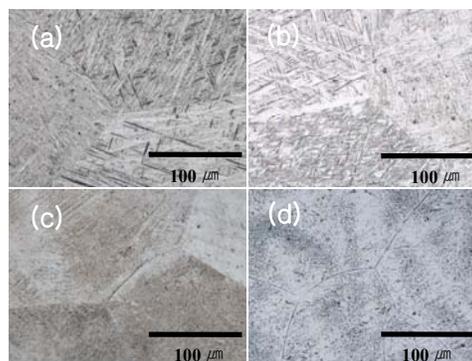


Fig. 1. OM micrographs showing the microstructure of heat-treated (W.Q) Ti-xNb alloys. (a) Ti-10Nb (b) Ti-20 Nb (c) Ti-30 Nb (d) Ti-40 Nb

Fig. 2 Shows the XRD profiles for Ti-xNb alloys in which solution treatment was carried out at 1000 °C for 6h followed water quenching. We prepared samples, varying Nb content, in order to investigate the alloying element effect on phase formation behavior. The structure of alloy was changed from  $\alpha$ -phase (100) to  $\beta$ -phase (110) with increase of Nb content. It can be explained that Nb acted as  $\beta$ -phase stabilizer like Nb and Ta[12].

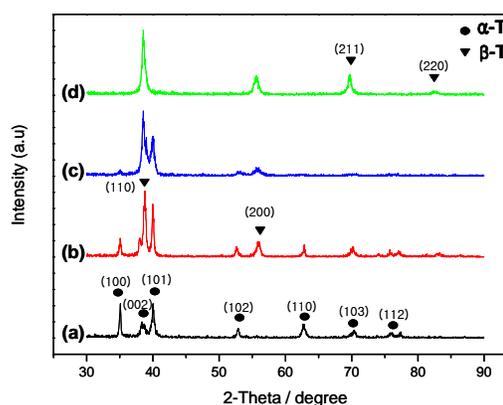


Fig. 2. XRD diffraction patterns of Ti-xNb alloys . (a) Ti-10Nb (b) Ti-20Nb (c) Ti-30Nb (d) Ti-40Nb

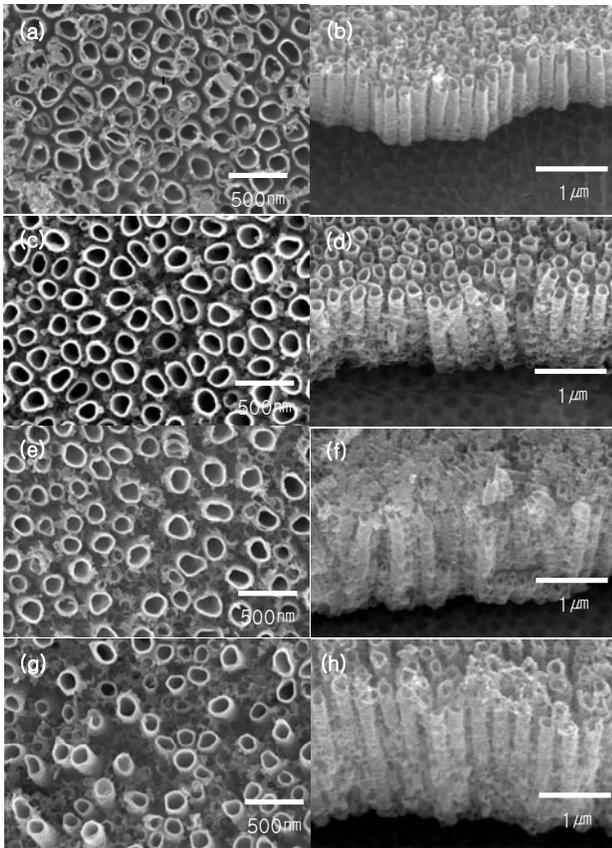


Fig. 3. SEM images of titanium oxide obtained by anodization in 1M  $H_3PO_4$  + 0.8wt% NaF at room temperature. (a,b) Ti-10Nb (c,d) Ti-20Nb (e,f) Ti-30Nb (g,h) Ti-40Nb

Fig. 3 and 4 show SEM images of top, cross-sectional and bottom view. The cross-sectional and bottom views were taken from mechanically scratched samples where some pieces flaked off and were upside down. It is apparent Fig. 3 and Fig. 4 that the nanotubes are open on the top while on the bottom they closed. Fig. 3 shows SEM images of the resulting layer formed at 10V in 1M  $H_3PO_4$  containing 0.8wt% NaF. Under specific sets of conditions highly self-organized titanium oxide nanotubes are formed with diameters varying from approx. 55 to 220 nm and length from approx. 727 nm(Ti-10Nb) to 2  $\mu m$ (Ti-40Nb). It is obvious that the amount of Nb strongly influences the pore formation process and morphology of the porous surfaces. As the Nb contents increase to 10 (Fig. 2-a,b), 20 (Fig. 2-c,d), 30 (Fig. 2-e,f) and 40wt% (Fig. 2-g,h), the average nanotube length varies : 727 nm, 944 nm, 1.5  $\mu m$  and 2  $\mu m$  respectively. The average pore spacing(un-nanotube formation area, initially) increases from 55 nm to 432 nm, as Nb content increases. According to Fig.3, higher contents of Nb in Ti alloy cause a increase in pore spacing and pore length. Fig. 4(a) shows an SEM image of nanotube bottom with pore size of approx. 225 nm prepared using anodization voltage of 10V for

2h. It can be seen that the nanotube array is uniform over the substrate.

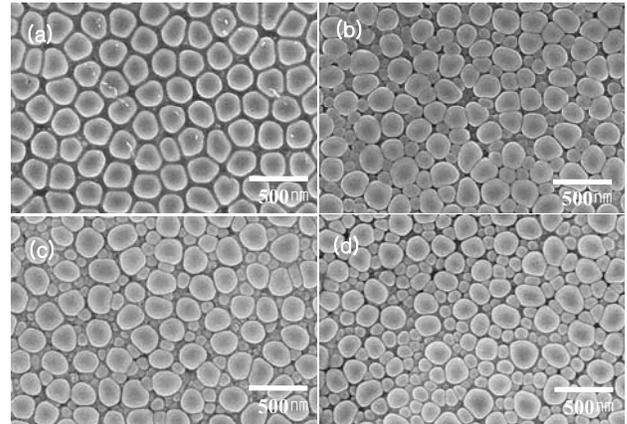


Fig. 4. SEM bottom-view image of  $TiO_2$  nanotubes formed at 10V for 2h in 1M  $H_3PO_4$  + 0.8wt% NaF. (a) Ti-10Nb (b) Ti-20Nb (c) Ti-30Nb (d) Ti-40Nb

However, from a careful look at Fig. 4(b-d), it can be seen that the self-organized nanotube layers consist of arrays with two distinctly different tube diameters of 220 and 55 nm at the bottom. A regular assembly is formed where the 220 nm large nanotubes are surrounded by several 55 nm small tubes. Also at the bottom, smaller nanotubes appear to protrude as Nb content increased. Our results indicate that the composition of the alloys has a great influence on the two-size-scale structure, and two-size-scale structure appeared predominantly as Nb content increased as shown in Fig. 4(d). We think that the site of small size tube was at un-nucleated area(large interspaced tube in Fig. 3-g). This area is necessary for such self-organization in the fluoride-containing electrolyte.

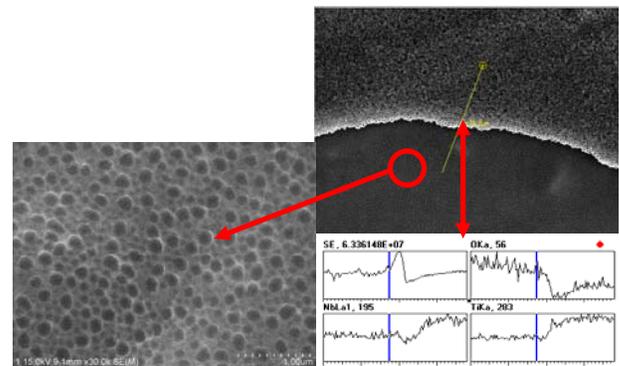


Fig. 5. Line analysis showing the  $TiO_2$  nanotubes formed Ti-30Nb alloy at 10V for 2h in 1M  $H_3PO_4$  + 0.8wt% NaF.

Fig. 5 shows the line profile at nanotube covered and uncovered area after  $TiO_2$  nanotubes formation in 1M  $H_3PO_4$  + 0.8wt% NaF solution. On the nanotubed surface,

Nb content was lower than that of uncovered nanotube film surface, whereas oxygen content was higher on the nanotubed surface. It is confirmed that nanotubed surface mainly consisted of TiO<sub>2</sub> oxide and Nb<sub>2</sub>O<sub>5</sub> oxide film. In the matrix, Ti and Nb content were same before nanotube formation like manufactured alloy.

#### 4 CONCLUSION

1. The structure of alloy was changed from  $\alpha$ -phase to  $\beta$ -phase with increase of Nb content. The structure of alloy was changed from  $\alpha$ -phase(100) to  $\beta$ -phase(110) with increase of Nb content.
2. Titanium oxide nanotubes were formed with diameters varying from approx. 55(nm)(small tube) to 220 nm(large tube) and length from approx. 727 nm(Ti-10Nb) to 2  $\mu$ m(Ti-40Nb).
3. The composition of the alloys has a great influence on the two-size-scale structure, and two-size-scale structure appeared predominantly as Nb content increased, and small size nanotube was nucleated at pore spacing area un-nucleated, initially.
4. From the line profile analysis, on the nanotubed surface, Nb content was lower than that of uncovered nanotube film surface, whereas oxygen content was higher on the nanotubed surface.

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