International Journal of Technology (2012) 2: 181-185
ISSN 2086-9614

SYNTHESIS OF TiO_2 NANOTUBE ON TI-10Ta-10Nb THIN FILM BY ANODIZATION

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(Received: May 2011 / Revised: June 2011 / Accepted: July 2012)

ABSTRACT
The purpose of this research was to study the synthesis of TiO_2 nanotubes on Ti-10Ta-10Nb thin film and the effect of applied potential on the tube size, length and morphology. The Ti-10Ta-10Nb thin film was deposited by dc magnetron sputtering on the CP Ti substrate. The anodization of this Ti-10Ta-10Nb thin film was performed in the solution containing 1M H3PO4 + 1.5wt.% HF at the potential readings of 4, 6, 8 and 10 V for 10 minutes. The results showed that there was a slight increase in the tube diameter from approximately 25 nm at 4 V to 50 nm at 8 V. The length of nanotube varied from 700-900 nm. Interestingly, at the potential of 10 V, the nanotube diameters were damaged with slight decreases in nanotube lengths (500 nm).

Keywords: Anodization; Nanotube; Synthesis; TiO_2

1. INTRODUCTION
Ti and Ti-based alloys have been widely used as implant materials due to their good mechanical properties and corrosion resistance. In the previous work, we studied the corrosion behaviour of Ti-8Ta-3Nb and Ti-10Ta-10Nb in comparison with CP Ti and Ti-6Al-4V (Karayan et al., 2008). The results showed that the corrosion resistance of Ti-10Ta-10Nb in simulated physiological media was superior to three other Ti based alloys, as characterized by Ti-10Ta-10Nb's lowest passive current density.

Kim et al., (2009) studied the cell adhesion of Ti-10Ta-10Nb and they reported that the sputtered nanoscale Ti-10Ta-10Nb coatings exhibited greater cell attachment compared to Ti-6Al-4V and Ti-10Ta-10Nb disks. A number of attempts have been extensively made to synthesize TiO2 nanoporous on the titanium thin films (Mor et al., 2005; Xiaofeng et al., 2006) in order to increase the protein absorption in medical applications and light absorption in the energy material applications. Unfortunately, no reports of nanoporous synthesis on Ti-Ta-Nb thin film could be found in the literature.

The objective of this research was to study the synthesis of nanoporous formed on the Ti-10Ta-10Nb thin film and the effect of its potential on the pore size and morphology.

2. METHODOLOGY
The Ti-10Ta-10Nb thin film was deposited on CP Ti substrate by using DC magnetron sputtering method within 4 hours at the bias voltage of – 300 V and power of 40 W. The temperature, gas pressure, and argon flow rate were set up at 300° C, 7.5 mTorr, and 30 sccm, respectively.

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The synthesis of nanotubes was performed by anodizing Ti-10Ta-10Nb – coated CP Ti in the solution containing 1M H3PO4 + 1.5wt.% HF at the potentials of 4, 6, 8 and 10 V for 10 minutes. The nanotubes formed on Ti-10Ta-10Nb thin film were characterized by scanning electron microscope (SEM) and energy dispersive x-ray spectroscopy (EDS).

3. RESULTS AND DISCUSSION

The Ti-10Ta-10Nb thin film deposited by dc magnetron sputtering is shown in Figure 1. This thin film with the thickness of approximately 964 nm was formed on the CP Ti substrate.

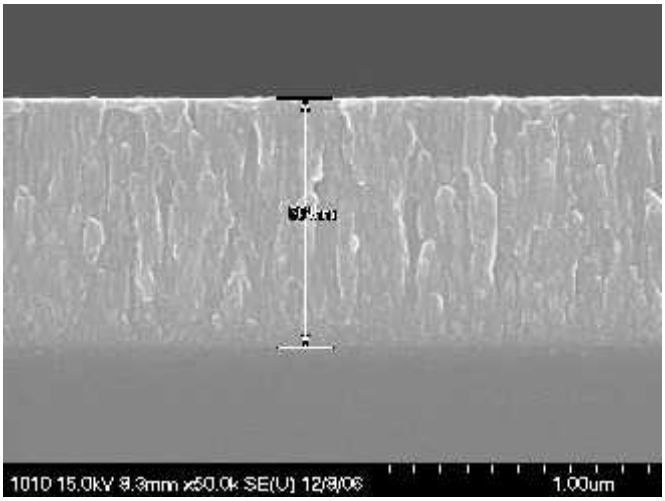

Figure 1 Ti-10Ta-10Nb thin film with the thickness of 964 nm deposited on CP Ti substrate by dc magnetron sputtering

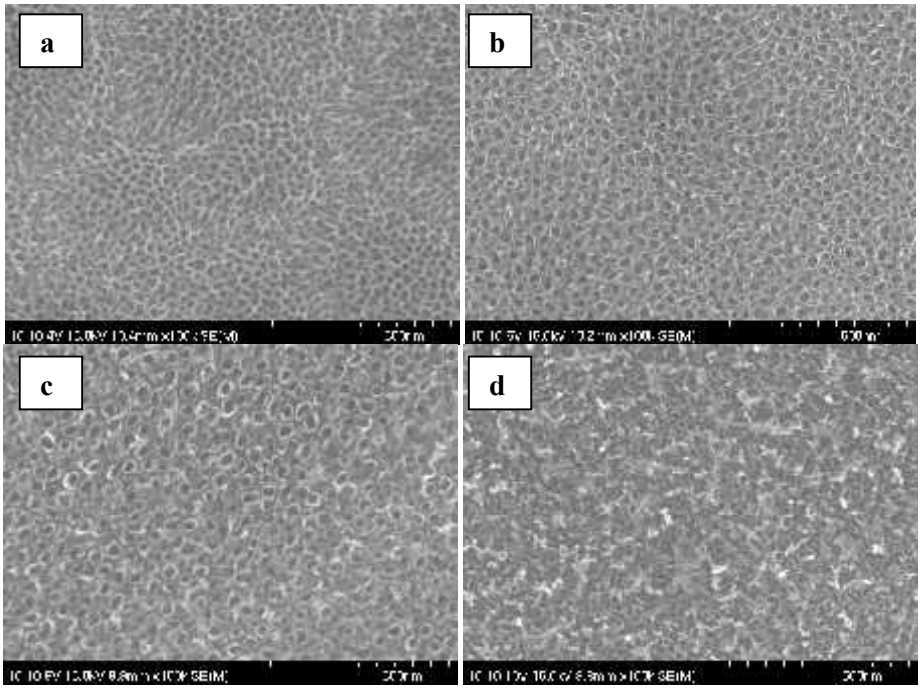

Figure 2 Size of nanotubes on Ti-z10Ta-10Nb thin film by anodization in the solution containing 1M H3PO4 + 1.5wt.% HF at the applied potential of (a) 4 V, (b) 6 V, (c) 8 V and (d) 10 V

The EDS spectrum of nanoporous , as shown in FigURE 3, showed the presence of Ti, Ta and Nb, suggesting that the nanoporous was formed on the Ti-Ta-Nb thin films instead of CP Ti substrate. A significant amount of titanium and oxide in the EDS spectrum might suggest that the nanoporous formed on Ti-10Ta-10Nb mainly composed of TiO_2 along with a small amount of TaO and NbO. Further more detailed studies are needed to explore the type of metal oxide that plays the most important role in nanoporous synthesis on Ti-10Ta-10Nb thin films.

Informal transit services, which compete with regular buses was used as an alternative mode for commuting. Even though informal transit services are illegal, they are necessary. Rather than banning informal transit services, transportation authorities could legalize and control their operations, providing a much needed additional (and more organized) commute mode.

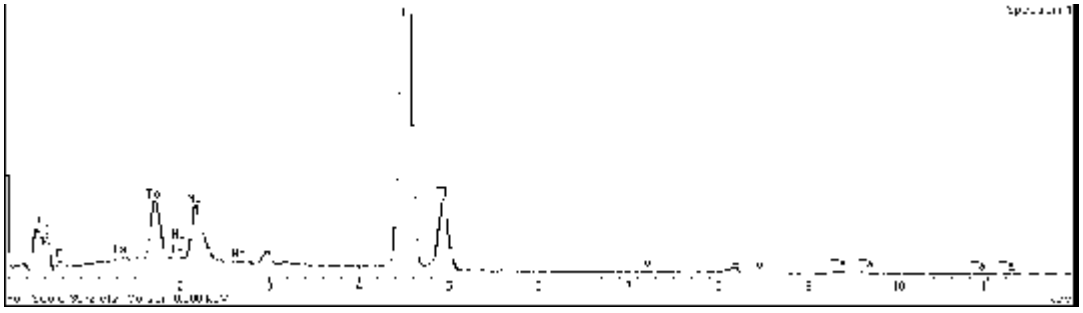

Figure 3 EDS spectrum of nanoporous formed on Ti-10Ta-10Nb thin film showing the presence of Ti, Ta, Nb, O and F.

The mechanism of metal nanotubes formation by anodization has been well documented (Sul et al., 2001; Chen et al, 2006; Grimes et al., 2009). With the onset of anodization a thin layer of oxide forms on the titanium surface (Figure 4a). This oxide formation follows the reaction shown below Eequation 1) (Jaroenworaluck et al, 2007):

$$Ti + 2H_2O = TiO_2 + 2H_2 \quad (1)$$

The localized dissolution of TiO2 oxide leads to small pit formation, as represented by the reaction (3.2) (Lohrengel, 1993) and as shown in Figure 4b making the barrier layer at the bottom of the pits relatively thin which, in turn, increases the electric field intensity across the remaining barrier layer resulting in further pore growth, (Figure 4c).

$$TiO2 + 6F- + 4H+ = TiF62- + 2H2O \quad (2)$$

The pore entrance is not affected by the electrical field assisted dissolution andhence remains relatively narrow, while the electrical field distribution in the curved bottom surface of the pore causes pore widening, as well as deepening of the pore [5]. The result is a pore with a scalloped shape (Sul et al., 2001; Chen et al., 2006; Grimes et al., 2009). As the Ti–O bond energy is high (323 kJ/mol), in the case of TiO_2, it is reasonable to assume that only pores having thin walls can be formed due to the relatively low ion mobility and relatively high chemical solubility of the oxide in the electrolyte, hence un-anodized metallic portions can initially exist between the pores. As the pores grow deeper the electrical field in these protruded metallic regions increases, enhancing field-assisted oxide growth and oxide dissolution, hence simultaneously with the well-defined pores, inter-pore voids start forming (Figure 4d). Thereafter, both voids and tubes grow in equilibrium. The nanotube length increases until the electrochemical etching rate equals the chemical dissolution rate of the nanotube top surface. After this point is reached,

the nanotube length will be independent of the anodization duration, as determined for a given electrolyte concentration and anodization potential (Grimes et al., 2009). Figure 4e shows the fully developed nanotubes with a corresponding top view.

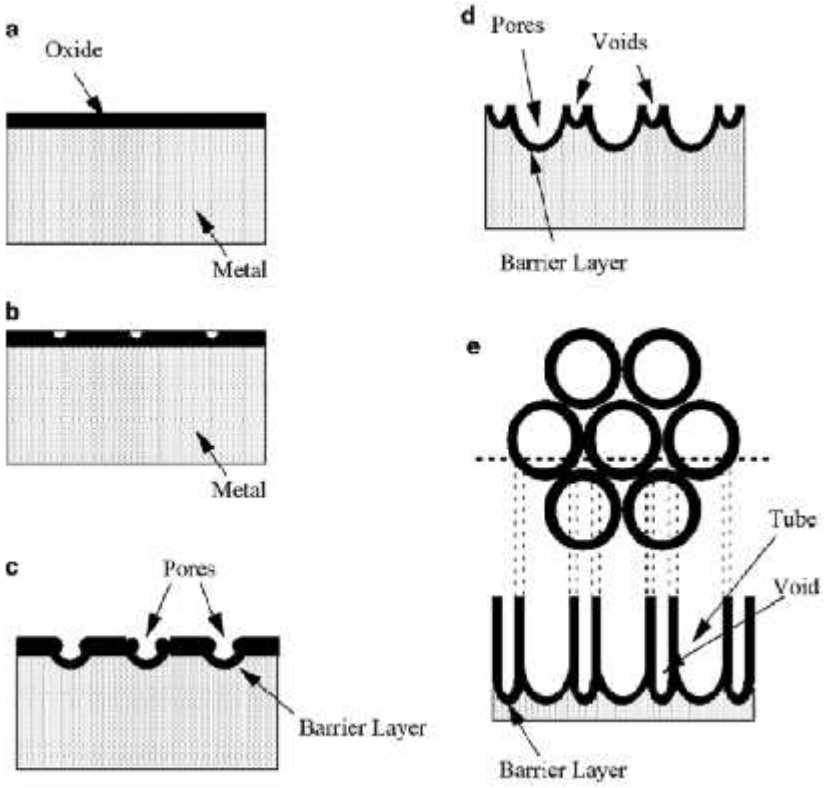

Figure 4 Schematic diagram of nanotube evolution at constant anodization voltage: (a) Oxide layer formation, (b) Pit formation on the oxide layer, (c) Growth of the pit into scallop shaped pores, (d) The metallic region between the pores undergoes oxidation and field assisted dissolution, (e) fully developed nanotubes with a corresponding top view (Mor et al., 2003).

4. CONCLUSION

The maximum potential for nanoporous synthesis of Ti-10Ta-10Nb by anodization in the solution containing 1M H3PO4 + 1.5wt % HF was 8 V. We found that at this potential, the diameter of nanoporous was approximately 50 nm. The length of nanotubes varied from 700 – 900 nm, with an exception at the potential of 10V where a slight decrease was noticed.

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