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Mixture of Oxides with Different Valence States in Nanotubes

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Oxide nanotubes with different diameters and lengths were fabricated on the biomedical Ti2448 alloy by anodic oxidation in neutral electrolyte. Similar to oxide nanotubes fabricated on pure titanium and its alloys, the as-grown nanotubes on Ti2448 also exhibit gradually changing chemical distribution along the direction of tube growth. Furthermore, several kinds of oxides with different valence states ($MxOy$) are formed simultaneously for each alloying element M , while their volume fractions vary gradually along the tube-growth direction. The findings of this study would provide insight into the effect of valence states on the desired nanotube properties and help develop ways to enhance the properties of the preferred oxide.

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1. Introduction

Oxide nanotubes can be easily fabricated by electrochemical oxidation on pure metals and their alloys^[1–21]. Because they have potential applications in many fields, the formation of highly ordered and self-organized nanotubes on titanium and its alloys has been investigated extensively^[22–27].

The morphology of oxide nanotubes grown on pure Ti is generally different from that of nanotubes grown on its alloys. The self-organized nanostructure on pure Ti has a uniform size or a continuous size distribution^[1]. On its alloys, the nanostructure dimensions, e.g., tube diameter, length, and wall thickness can be controlled by varying the solution chemistry, applied potential, anodization time, and solution temperature^[5,7,11]. Thus, the morphology can be customized to enhance some desired nanotube properties^[6,10,11,28].

Besides the above morphological contribution, alloying also has a high impact on amorphous–crystalline transitions, the types of oxides formed, and their high-temperature stability. The thermal stability of nanotubes and the transformation temperature of TiO₂ from the anatase to rutile crystal structure can also be enhanced by alloying^[5]. Adding large amounts of Nb can prevent the nucleation and growth of anatase crystallite from the initial amorphous titania nanotubes, resulting in a higher transition temperature^[29].

Zirconium titanate ($Zr_{1-x}Ti_xO_2$), with excess TiO₂ and ZrO₂, is formed on the Ti–Zr binary alloy whereas Nb addition (to form a Ti–Zr–Nb ternary alloy) results in TiO₂ and three kinds of complex ternary oxides^[7,10]. Such a significant difference in the types of oxides seems impossible for titanium alloys containing large amounts of Nb. For example, the oxide nanotube layer mainly consists of TiO₂ and Nb₂O₅ in the Ti–Nb binary alloy and extra Ta₂O₅ in the Ti–Nb–Ta–Zr quaternary alloys^[5,12].

The Ti2448 alloy (Ti–24Nb–4Zr–8Sn, wt%) is a kind of multi-functional β -type biomedical titanium alloy, which has a high strength and an ultralow elastic modulus that is similar to that of human bone^[30–32]. In our study, oxide nanotubes with different tube diameters and lengths were fabricated on Ti2448 by anodic oxidation in a neutral electrolyte. The kinds of oxides, their thermal stability, and their impact on the morphology and composition along the tube growth direction were studied.

2. Experimental

All samples with a diameter of 10 mm and thickness of 1 mm were prepared from the hot-forged Ti2448 alloy with a single β phase^[31]. They were polished using SiC water-proof papers of up to #1200 grit; ultrasonically cleaned in acetone, ethanol, and deionized water, successively, for 10 min each; and then dried in air. Anodic oxidation was performed at room temperature in a neutral electrolyte containing 1 mol/L (NH₄)₂SO₄ and 0.15 mol/L NH₄F (pH = 6.7) prepared from analytical-grade chemicals and deionized

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water. A direct current (DC) power supply was used to keep the potential at a constant value for several cycles after the potential was swept from the open-circuit potential to the desired final potential at a sweep rate of 0.5 V/s. A two-electrode system consisting of a stainless steel cathode and the sample as the anode was used to fabricate the nanotube oxide layer without stirring. All samples were cleaned using deionized water after anodization. Some samples were annealed in air at a temperature between 550 °C and 750 °C for 2 h to investigate the effect of annealing temperature on the morphology and phase transformation of nanotube oxide layers. The morphology and microstructure of the nanotube layer were characterized using a field-emission scanning electron microscope (FESEM; LEO SUPRA35, Zeiss, Germany) and a transmission electron microscope (TEM) equipped with an energy-dispersive X-ray (EDX) detector (Tecnai G2 F30, FEI, USA). The diameter and length of the nanotubes were measured from the SEM images, and more than 50 tubes were measured to obtain the experimental accuracy. The phase compositions were analyzed with a glancing angle X-ray diffractometer (GAXRD; D/max2400, Rigaku, Japan) using a $\text{CuK}\alpha$ radiation source with an accelerating voltage of 40 kV and a current of 250 mA. The samples were also subjected to X-ray photoelectron spectroscopy (XPS; Escalab250, Thermo Fisher Scientific, USA) analysis in a vacuum chamber at a base pressure of $\sim 3.5 \times 10^{-8}$ Pa. To analyze the chemical distribution along the nanotube, the oxide layers were removed by sputtering with Ar^+ ions (2 kV, 2 μA) at an angle of $\sim 45^\circ$.

3. Results and Discussion

Highly ordered and vertically oriented nanotubes were successfully fabricated on the Ti2448 alloy (Figs. 1(a–c) and 2(a–c)). The insets in Fig. 1(a–c) show that the nanotubes were conical, as evidenced by their diameters at the bottom, which were larger than those at the top. Similar to nanotubes grown on pure Ti in aqueous electrolytes^[33,34], both the tube diameter and length varied linearly with the applied potential that ranged from 10 to 80 V

(Fig. 1(d)). The influence of anodization time on the tube length can be fitted to a curve, which represents a typical behavior of such kind of chemical process. At a potential of 40 V, for example, the nanotubes grew rapidly in an early stage (up to 2 h from the beginning), following a linear relation; the growth then proceeded slowly with further increase in the anodization time (Fig. 2(d)). An additional study showed that the anodization time had no obvious effect on the tube diameter. These results can be explained by the growth mechanism of nanotubes that was based on the competition between oxide growth at the metal–oxide interface and oxide dissolution at the tube-bottom–electrolyte interface^[1,34].

The GAXRD pattern (Fig. 3(a)) shows that an amorphous layer characterized by a halo at 2θ of 20° – 35° was formed on Ti2448 after anodization. This is further confirmed by the selected area diffraction (SAD) pattern with a continuous halo (inset in Fig. 2(b)). Widely spaced ridges on the tubes' outside walls, which formed during nanotube growth, were also observed by TEM (Fig. 3(b)).

High temperature annealing for 2 h at 550 °C and 650 °C resulted in the transition from the amorphous phase to anatase (Fig. 3(a)). With the increase in annealing temperature up to 750 °C, small amounts of both rutile and Nb_2O_5 were detected in addition to anatase, which remained a major phase in the tube layer (Fig. 3(a)). This shows that the anatase–rutile transformation temperature of Ti2448 was ~ 750 °C, which is much higher than that of pure Ti (~ 430 °C^[35]) and slightly higher than that of the Ti–Nb binary alloy (~ 650 °C^[5]). This suggests that alloying elements in titanium alloys hinder the nucleation and growth of rutile from anatase because of the barrier effect on the diffusion of Ti and O atoms. The alloying also had a significant effect on the nanotube thermal stability. TEM images in Fig. 3(c) show that the tubular structure was still stable when being annealed at temperatures ≤ 750 °C, which is much higher than the annealing temperature of ~ 580 °C for pure Ti^[35]. Furthermore, the ridges (Fig. 3(b)) almost disappeared after the annealing treatment at 750 °C for 2 h (Fig. 3(c)).

XPS results (Fig. 4(a)) show that the as-grown oxide layer contained mainly Ti, Nb, Zr, Sn, and O, and a small amount of F. The

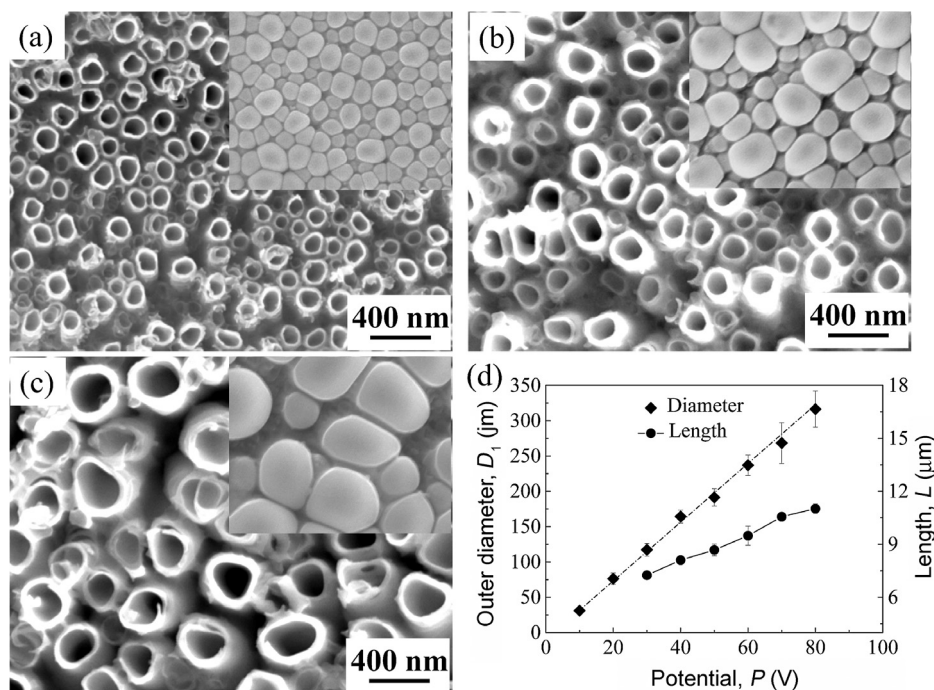


Fig. 1. SEM images showing the nanotube layer formed on Ti2448 at different applied potentials: (a) 30 V; (b) 50 V; (c) 80 V for 1.5 h (the insets show the bottom view of nanotubes) and (d) variations in tube diameter and length with applied potential over a period of 1.5 h.

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