

Self-organized TiO₂ nanotube layer on Ti-6Al-7Nb for biomedical application



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ABSTRACT

In the present study, a self-organized nanotube TiO₂ layer on Ti-6Al-7Nb was fabricated. The influence of acidic electrolytes including glycerol (G) and ethylene glycol (EG) on the anodization, microstructural features and surface wettability was explored. The phase compositions and morphological characteristics were characterized by X-ray diffraction (XRD) and field emission scanning electron microscopy (FE-SEM), respectively. According to the results, due to the intrinsic amorphous feature of ceramic oxide, the characteristic TiO₂ peaks were not detected in the XRD profiles. After annealing in normal atmosphere at 600 °C for 2 h, TiO₂ crystallized and consequently, nanotubular TiO₂ arrays containing anatase and rutile phases formed. From a microstructural point of view, the average length and diameter of the nanotube array ranged from 2.23 to 4.22 μm and 160 to 170 nm, respectively. Besides, the type of acidic electrolyte and subsequent annealing noticeably affected the surface wettability of the products.

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1. Introduction

Titanium alloys are widely used as implant materials for failed hard tissue owing to their good physiochemical stability, mechanical integrity, good biocompatibility and excellent corrosion resistance [1]. Commercially pure titanium, Ti-6Al-4 V and Ti-6Al-7Nb alloys are the most favored materials for many biomedical applications [2]. Among them, Ti-6Al-7Nb alloy was developed to achieve the following aims [3]: (i) a dense and stable passive surface layer with the presence of all alloying elements, (ii) high resistance to corrosion, (iii) $\alpha + \beta$ grain structure with the possibility of superplastic deformability, (iv) mechanical properties comparable with those of the high-strength, wrought Ti-6Al-4 V alloy, and (v) economical production of semi-finished materials for implant components [4]. Moreover, cell and tissue responses are affected not only by the chemical properties of the implant surface, but also by the implant's surface topography or roughness. Therefore, various surface modifications can be made to enhance the usefulness of implants [5].

It has been found that implant osseointegration occurs through the natural oxide TiO₂ layer, but it is a long process [6]. Accordingly, to enhance implant bioactivity and bone growth, the surface layer can be modified by sand blasting [7], calcium phosphates coating [8] and chemical approaches like acid etching and alkali treatment [9]. According to literature, generating a self-organized TiO₂ nanotube layer is an appropriate surface modification achievable by various techniques, such as sol-gel method [10], electrophoretic deposition [11] and anodization [12]. Among them, anodization is suitable for creating nanotubular oxide layers for biological applications, as it facilitates the highest layer adhesion strength compared to other techniques [13]. In nanotubular TiO₂ arrays, there are some gaps between adjacent nanotubes (~15 nm), which play an important role in minimizing the interfacial stresses between two joined, dissimilar materials. In addition, these gaps create pathways for body fluid supplies of ions, nutrients and proteins [14]. On the other hand, the nanotubular morphology combined with an anatase structure leads to the formation of apatite layers with a thickness of greater than 6 nm in less than 2 days, while no stable apatite layer was observed on amorphous TiO₂ films [15]. In terms of corrosion resistance, TiO₂ nanotube layers on titanium exhibit better corrosion resistance in simulated bio-fluid than smooth Ti [16]. In fact, the functional specifications of nanotubular arrays may be manipulated by varying the process parameters [15]. For instance, a vertically aligned TiO₂ nanotube array can be fabricated on the surface of titanium substrate by anodization in slightly dissolving fluoride-containing

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electrolyte [17]. Electrolytes without fluoride, e.g. sulfuric acid [18], are extensively utilized to create a compact non-porous TiO₂ layer at low potential and porous oxides at high potential due to the oxide's electrical breakdown [19,20].

In this study, a self-organized nanotubular TiO₂ layer on Ti-6Al-7Nb was fabricated. In a comparative study, the influence of acidic electrolytes containing glycerol (G) and ethylene glycol (EG) on anodization was investigated. In addition, the microstructural features, surface wettability and reaction mechanism of the formation of vertically aligned TiO₂ nanotube arrays were explored.

2. Materials and methods

2.1. Preparation of the substrate

Ti-6Al-7Nb plates (20 × 10 × 2 mm³, Baoji Liu Wei Special Material and Equipment Produce Co. Ltd China) were used as substrate. Prior to anodization, the samples were polished using SiC emery paper (800–2400 grit) and then wet-polished in a diamond slurry. Afterwards, the polished samples were sonicated in acetone for 14 min at 40 W power. The sonicated specimens were washed three times with distilled water and dried at 100 °C for 1 h.

2.2. Anodization of Ti-6Al-7Nb (Fabrication of TiO₂ nanotube arrays)

Anodization was performed in a two-electrode electrochemical cell, in which a graphite rod (D = 7 mm) and the specimens were connected to cathode and anode electrodes, respectively. The distance between the electrodes was fixed at approximately 20 mm in all experiments. Here, the anodization process was carried out using a direct current (DC) power source (Model E3641A, Agilent Technologies, Palo Alto, USA) at a constant potential of 60 V for different anodization times (1 to 6 h). To investigate the influence of acidic electrolytes on the anodization process, two electrolytes were used: (i) sodium fluoride (NaF, R&M Chemical, 0.5 wt%) electrolyte dissolved in a 90:10 solvent of EG (purity > 99 %, Merck) and distilled water, and (ii) sodium fluoride (NaF, R&M Chemical, 0.5 wt%) electrolyte dissolved in a 90:10 solvent of G (purity > 99.5 %, Sigma-Aldrich) and distilled water. After anodization, all specimens were washed with deionized water to remove surface residual materials. Finally, thermal annealing (heating and cooling rate of 10 °C/min) was conducted at 450 and 600 °C for 2 h in normal atmosphere to detect the crystalline phases.

2.3. Characterization of TiO₂ nanotube arrays

The morphological features of the nanotubes were characterized by field emission scanning electron microscope (FESEM, FEI Quanta, 2 kV). Phase composition and purity were investigated by grazing incidence X-ray (GIXRD) analysis with a PANalytical Empyrean X-ray diffractometer (Cu-K α radiation) over a 2 θ range from 10° to 80°. Surface hydrophobicity was examined by measuring the contact angles with a sessile drop of deionized water deposited on a specimen's surface. Optical wettability was inspected with a video-based optical contact angle measuring system (OCA 15EC). The volume of the liquid was kept constant (10 μ l) through all contact angle measurements of the various samples. Moreover, wettability was evaluated with a dropping velocity of 2 μ l/sec, accuracy of $\pm 1^\circ$, temperature of $26 \pm 1^\circ\text{C}$ and relative humidity of $45 \pm 5\%$.

Grazing-incidence diffraction is a scattering geometry combining the Bragg condition with the conditions for x-ray total external reflection from crystal surfaces. This provides superior characteristics of GID as compared to the other diffraction schemes in the studies of thin surface layers, since the penetration depth of x-rays inside the slab is reduced by three orders of magnitude typically from 1–10 μm to 1–10 nm (10–100 Å).

3. Results and discussion

3.1. Microstructural characterization (FESEM analysis)

Fig. 1 a-c show FESEM top view images of as-prepared TiO₂ nanotubes in EG (Fig. 1a and b) and G (Fig. 1c and d) electrolytes. It is clear that the surface of the specimens is not smooth and mainly coated by lamellar solid matter. The low-magnified FESEM images (top view) display that the nanotubes are distributed uniformly over the anodized surfaces, indicating an extensive dispersion of nanotubes (Fig. 1a and c). Besides, high magnitude FESEM images of the surfaces show that the as-prepared nanotubes have an average diameter of 40 nm in both electrolytes (Fig. 1b and d). At the beginning of the anodization, the formation of compact oxide layers on the surface of the sample was dominant as a result of the interaction within O²⁻ and OH⁻. After that, irregular pits were formed due to localized dissolution of oxide layer and followed by the pits conversion to larger pores, while most of the areas covered with oxide layer. With increasing the anodization time, the compact TiO₂ layer collapsed, after which a porous TiO₂ layer gradually grew and the TiO₂ nanotubular arrays were achieved [21].

Fig. 2 and 3 show the microstructural evolutions of the anodized samples after thermal annealing at 450 and 600 °C for 2 h for EG (Fig. 2a and b) and G (Fig. 2c and d), respectively. In general, annealing as one of the most widely used post-fabrication processes enhances crystallinity degree of as-prepared amorphous TiO₂ nanotubes and eliminates surface fluorine to improve cell responses [22]. From this figure, it is clear that the crystallization to highly organized structure occurred during annealing in normal atmosphere. This is the same finding as He et al. where they successfully induced crystallization to the anatase structure at temperatures in the range 550–600 °C [23]. In accordance with FESEM images in Fig. 2a and b, the TiO₂ nanotubes obtained in EG showed an average inner diameter of 160 nm and mean tube wall thickness of 15 nm after annealing at 450 °C. Regarding the anodized samples in G (see Fig. 2c and d), the average inner diameter and wall thickness were 167 and 21 nm, respectively. When the annealing temperature rose to 600 °C (Fig. 3a and c), the nanotubular structures remained stable. However, thickening of TiO₂ nanotubes wall took place due to mass transport involving Ti⁴⁺ diffusion at the bottom and wall of the TiO₂ nanotubes as shown (see Fig. 3b and d). In fact, the change in morphological features with annealing temperature is most probably related to the excessive diffusion of Ti ion along with the nanotube walls, which induced oxidation and thus thickened the oxide walls [21].

FESEM cross-section images of TiO₂ nanotubular arrays in different electrolytes after annealing at 450 and 600 °C are shown in Fig. 4. During annealing at 450 °C, the surface was completely filled with self-organized nanotubes with the length of 3.71 μm in EG and 2.23 μm in G (Fig. 4a and b). With increasing the annealing temperature to 600 °C, the tubular structure remained stable and the nanotube arrays length reached to 4.22 and 2.25 μm in the case of EG and G, respectively (Fig. 4c and d). As shown in this figure, the TiO₂ nanotubes displayed a bamboo-shaped structure with good density (an important factor contributing to good mechanical properties), which could result in enhanced chemical activity and stronger interactions [24]. These findings show that the microstructural features of the self-organized TiO₂ nanotubular arrays were influenced by the type of electrolyte and subsequent annealing.

3.2. Phase evolution and structural features (XRD analysis)

Fig. 5 shows the XRD patterns of the samples anodized for different times using dissimilar electrolytes. From this figure, the XRD profiles of the as-prepared TiO₂ nanotubes for both electrolytes were composed of seven peaks located approximately at 35°, 38°, 40°, 52.8°, 62.8°, 70.5° and 76° which were attributed, respectively, to the (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 1 2) and (2 0 1) orientations of the titanium

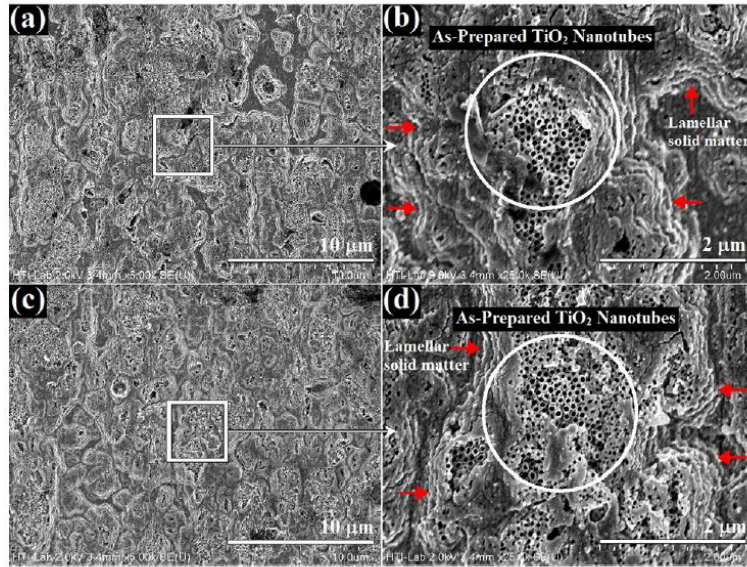


Fig. 1. FESEM top view images of as-prepared TiO_2 nanotubes in different anodization electrolytes, (a,b) EG and (c,d) G.

substrate (JCPDS#005-0682). In fact, no characteristic TiO_2 peaks were observed in the XRD profiles, suggesting that the as-prepared TiO_2 nanotubes were amorphous. Besides, no differences in phase composition were detected between the samples anodized in EG and G.

The XRD patterns of the samples anodized in EG and G after thermal annealing at 600°C for 2 h are shown in Fig. 6. During annealing at 600°C (Fig. 6a), the crystallization of TiO_2 layer occurred and consequently the

characteristic peaks of TiO_2 with anatase crystalline type (JCPDS#01-071-1166) including (1 0 1) at $2\theta = 25.35^\circ$, (0 0 4) at $2\theta = 37.86^\circ$, (2 0 0) at $2\theta = 48.08^\circ$, (1 0 5) at $2\theta = 53.99^\circ$, and (2 1 1) at $2\theta = 55.06^\circ$ were detected. Besides, some characteristic peaks of titanium were also identified. From the magnified XRD profiles in the ranges of $20^\circ \leq 2\theta \leq 30^\circ$ and $46^\circ \leq 2\theta \leq 50^\circ$ (Fig. 6b and c), it is obvious that the preferential orientation of anatase took place along the (1 0 1) plane for both electrolytes. However, the characteristic TiO_2 peaks has changed

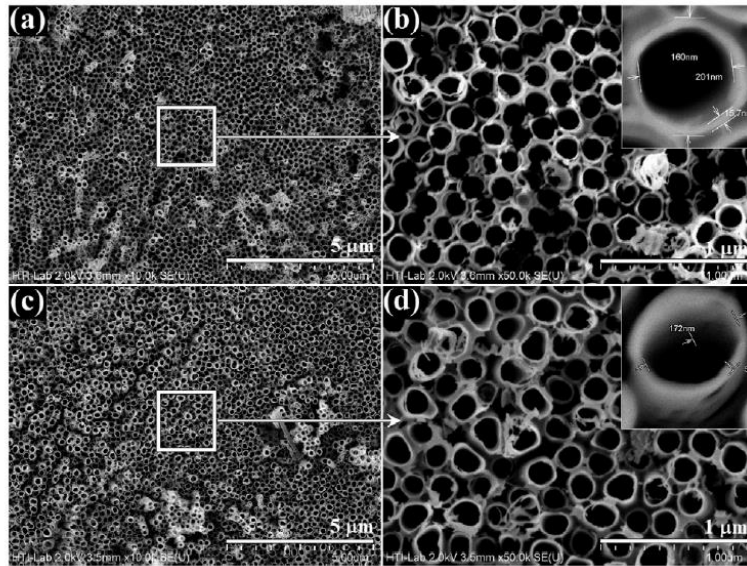


Fig. 2. Microstructural evolutions of the anodized samples after thermal annealing at 450°C for 2 h, (a,b) EG and (c,d) G.

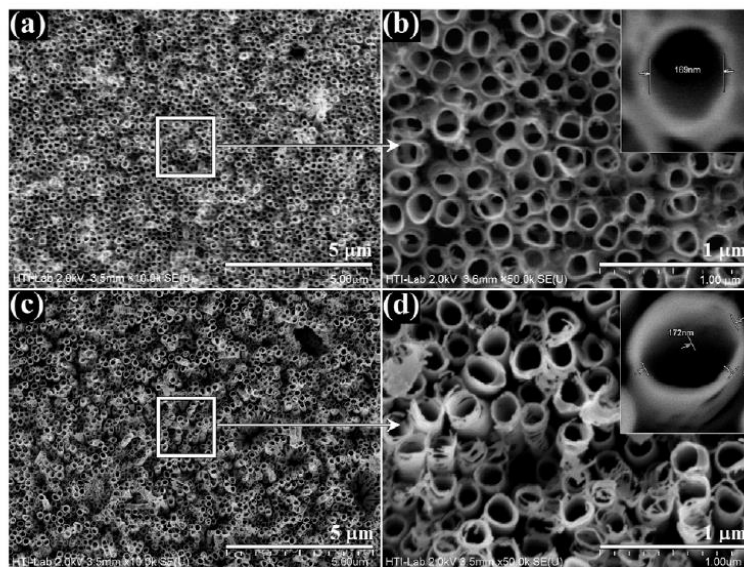


Fig. 3. Microstructural evolutions of the anodized samples after thermal annealing at 600 °C for 2 h, (a,b) EG and (c,d) G.

significantly, indicating that the crystalline phase fraction may be affected by the type of electrolyte. Based on the obtained data, the weight fractions of anatase after annealing at 600 °C were 85 ± 4 and 51 ± 3 % in the case of anodized sample in EG and G, respectively. This result is in good agreement with the previous studies, where the electrolyte composition and subsequent annealing affected on the structural evolutions of TiO₂ nanotubes [25]. For instance, Wang et al. found that in aqueous electrolyte, the anodization potential exerted significant influence on

the formation of TiO₂ nanotube arrays, while little effect from the electrolyte temperature was observed. In contrast, in non-aqueous electrolyte, the electrolyte temperature noticeably affected the TiO₂ nanotube dimensions, while the anodization potential showed slight influence in this regard. Moreover, high temperature annealing has been regarded as an effective route to inducing crystalline formation in as prepared TiO₂ nanotube arrays, converting them into the anatase or rutile phase [26].

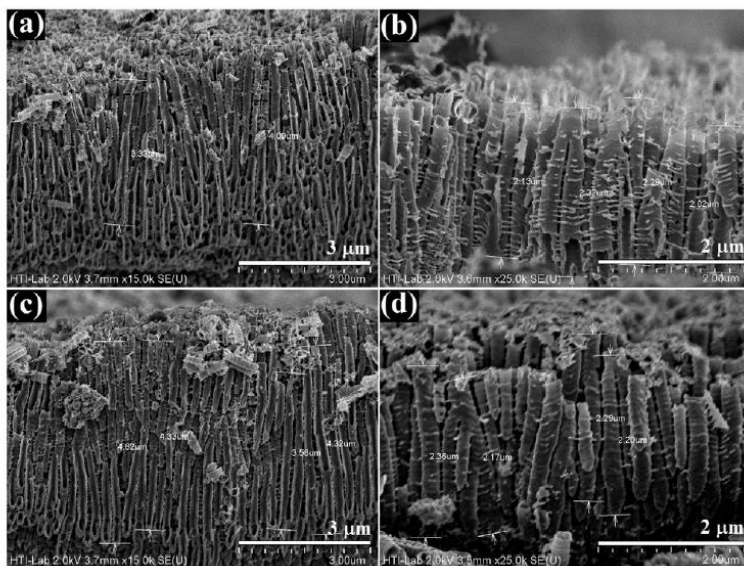


Fig. 4. FESEM cross-section images of TiO₂ nanotubes after 2 h annealing through two electrolytes, (a) EG and (b) G at 450 °C and (c) EG and (d) G at 600 °C.

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