

NOVEL NANO-TiO₂ LAYER PREPARATION ON Ti-6Al-4V SUPPORT ALLOY AND THEIR CHARACTERIZATION

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Ti-6Al-4V alloy is still most widely used for biomedical applications. This alloy can not meet all of the clinical requirements; therefore various surface modifications have been attempted for improving the specific properties. In this study, nano porous oxide films were produced on a Ti-6Al-4V surface using an anodic oxidation treatment. Four different voltages were applied in sulphuric acid electrolyte to obtain oxide films. The surface morphology, chemical composition and thickness of the anodically oxidized film on the substrate alloy were evaluated.

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1. Introduction

Titanium and its alloys have been used for dental and orthopaedic implants because of their good mechanical properties, high corrosion resistance and their excellent biocompatibility [1-3]. However, being bioinert metallic materials, they cannot connect with the bony tissue directly into a host body nor induces bone growth [4-5]. Ti-6Al-4V alloy because of its poor wear resistance and a high co-efficient of friction can cause problems [6]. In addition, it is dangerous for Ti-6Al-4V to stay in the human body for a long time because undergoes electrochemical exchange releasing metallic ions in the physiological environment and is known that Al element has strong neurotoxicity and V is a strong cytotoxin, and over time, the alloy produced adverse reactions in the body tissues [7-8]. The greater corrosion resistance for titanium and its alloys derives from the spontaneous formation of a titanium oxide film on their surface as long as oxygen is present, and its thickness has been evaluated to be approximately 5 nm [9-11]. However, the naturally formed TiO₂ film is not effective in improving the bioactivity of a titanium implant due to its small thickness [4]. Therefore, oxide films need to be formed intentionally using various techniques. Recently, anodic oxidation has become an attractive method for preparing oxide films on titanium or its alloys, because the porous oxide films insure apatite formation in physiological environment in order to improve implant bioactivity for biomedical applications [5, 12-13]. This paper describes a quickly method of synthesizing nano porous anodic oxide layer on Ti-6Al-4V substrate by applying four different voltages in sulphuric acid electrolyte. The oxide surface morphology as well as chemical composition and thickness are studied in this work.

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2. Material and methods

2.1 Materials

Ti-6Al-4V plates with size 2.5 x 2.5 cm and 2 mm in thickness were mechanically polished to a mirror finish by using SiC grinding paper, then diamond paste, and finally a suspension of SiO₂. The polished plates were then cleaned with ethanol in an ultrasonic bath for 5 min and finally dried in air. Then, specimens were subjected to anodic oxidation treatment by connecting them as anode for an electrochemical cell and applying four DC voltages ranging from 25 V to 100 V with the steps of 25 V, for 2 minutes with a DC power supply, and a Ti-6Al-4V plate in a size of 5.7 ×4 cm and 2 mm in thickness as the counter electrode to complete the electrolytic cell. Anodic oxidation was done in an electrochemical cell containing ~0.5 L aqueous solution of 1M H₂SO₄. Schematic representation of obtaining nano porous titanium oxide on Ti-6Al-4V alloy support is presented in Fig. 1.

During the anodic oxidation treatment the electrolyte was mixed with a magnetic stirrer to achieve a homogeneous electrolyte and to accelerate escape of gas produced in the electrochemical reaction from the surface of the titanium alloy substrates [5]. All experiments were carried out at room temperature.

2.2. Surface characterization

Philips scanning electron microscope (SEM) XL 30 FEG with energy dispersive X-Ray analysis (EDAX) system was used to characterize the surface morphology and to determine the chemical composition of the TiO₂ layers. The thicknesses of the oxidized films were evaluated on the cross-sections of the samples using Scanning electron microscope - Focused ion beam (SEM-FIB).

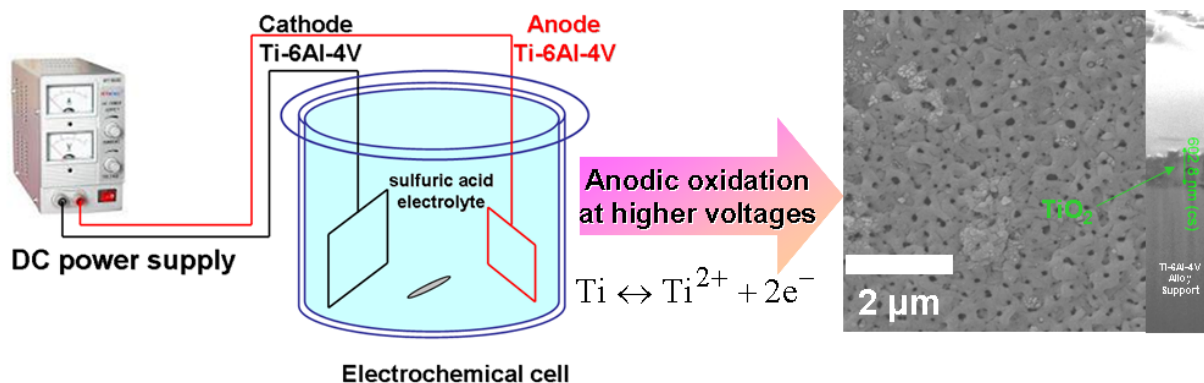


Fig. 1. Schematic representation of the electrochemical preparation of nano porous TiO₂ layer on Ti-6Al-4V alloy support.

3. Results and discussions

The influence of the DC voltage on the morphology, chemical composition and thickness of the titanium oxide films formed on polished Ti-6Al-4V samples was evaluated by SEM and SEM-FIB. Figure 2 shows the change in the morphology of the oxide films as a function of anodic forming voltage.

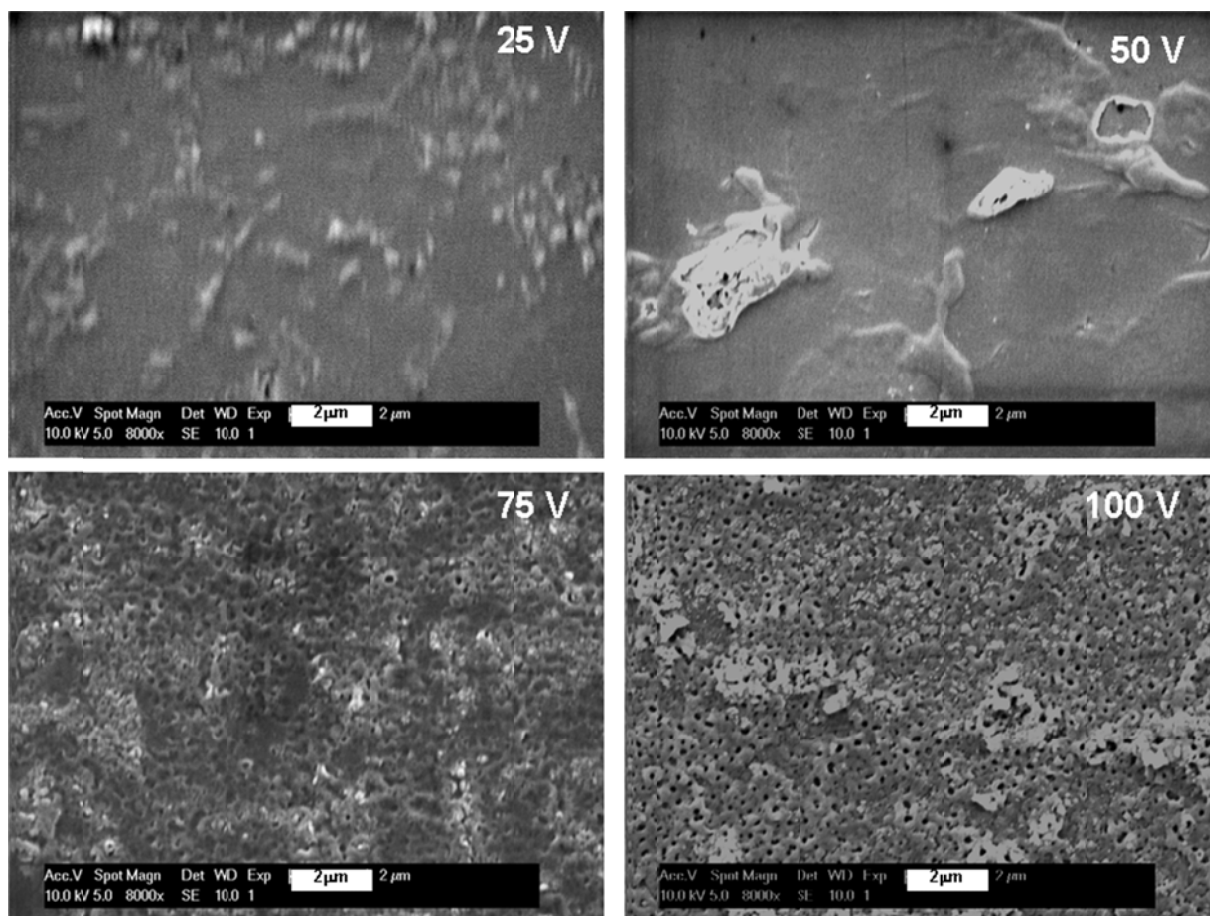


Fig. 2 SEM images of the anodically oxidized Ti-6Al-4V alloy surfaces as a function of anodic forming voltage.

The porosity and the pore size increased with increasing voltage from 25 to 100 V and also the surface of the oxide films became rougher with increasing applied voltage, fact observed also by others for titanium metal using an anodic oxidation method in four different electrolytes and with different voltages [5].

The only one voltage which provides uniform compact oxide films after the Ti-6Al-4V alloys were anodized in H_2SO_4 solutions is at 100 V (Figure 3).

Fig. 4 shows the cross-sectional images of the sample as a function of anodic forming voltage. The thicknesses of the oxidized films were approximately 65 nm, 452 nm and 615 nm for the voltages equal to 50 V, 75 V and 100 V respectively. The thicknesses of the oxide films formed at 25 V could not be determined by SEM-FIB, because they were too thin. The average thickness of the anodic films presented considerable local variations in thickness, especially with the increase in voltage, as can be observed in Fig. 3, similar observation being made also by Kuromoto et al. on commercially pure titanium [14].

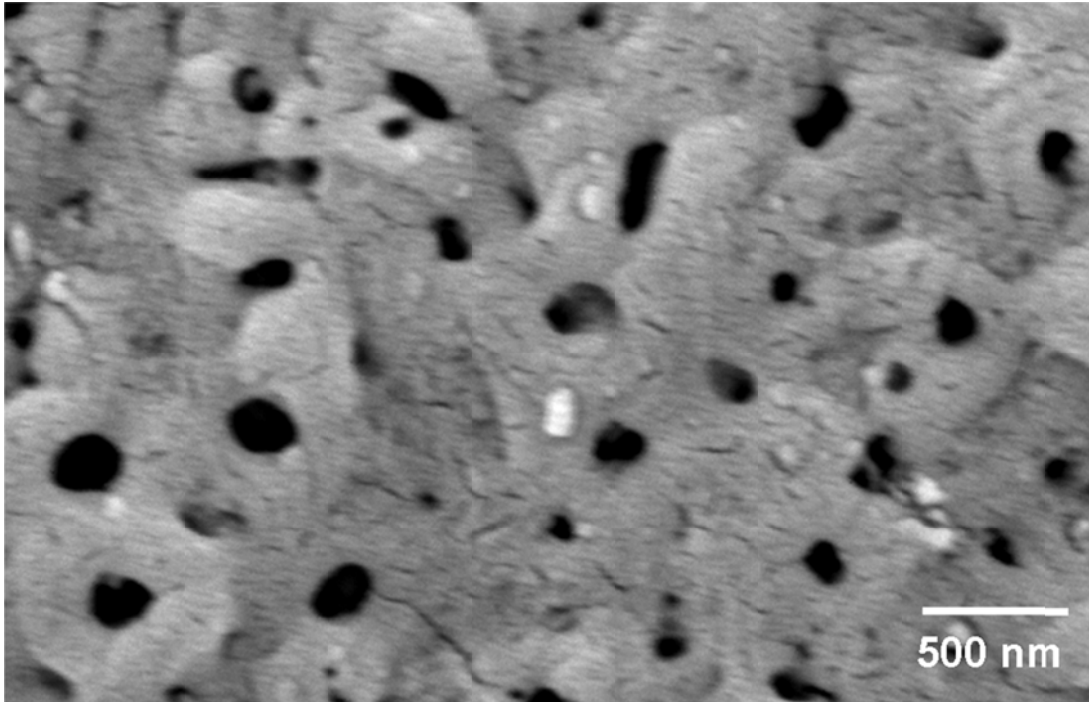


Fig. 3 SEM micrograph of the anodically oxidized Ti-Al-V alloy surfaces at 100 V.

From EDX analyze taken in different zones of oxide films only oxygen shows a major difference in weight percentages, in the sense that this is the only element whose weight percentages increases with increasing applied voltage. For the elements titanium, aluminium and vanadium, their weight percentages decrease with increasing voltage. These statements are supported by Figure 5 from which it appears that the main reactions leading to oxidation of the anode are predominantly for Ti element as follows [15]:

At the Ti/Ti oxide interfaces:



At the Ti oxide/electrolyte interfaces:



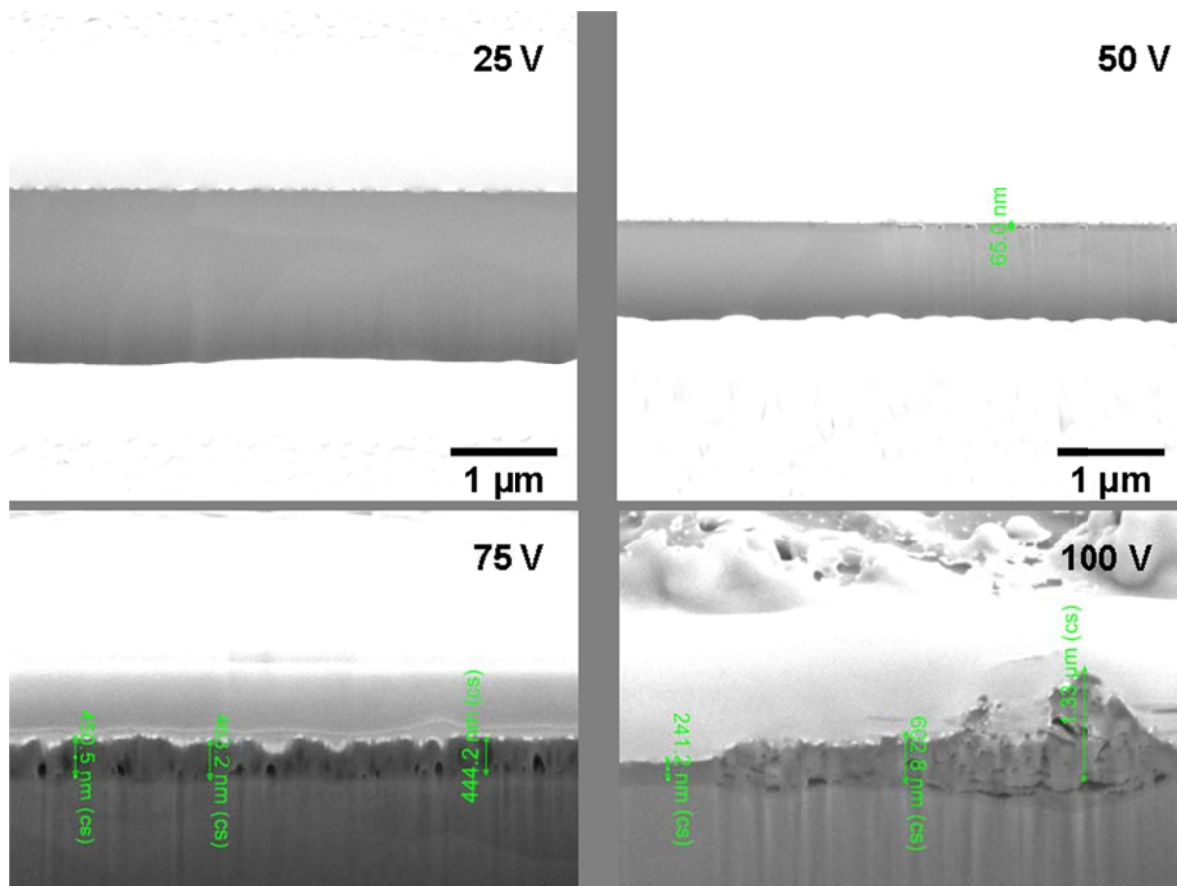


Fig. 4 Cross-sectional SEM-FIB images of the samples as a function of anodic forming voltage

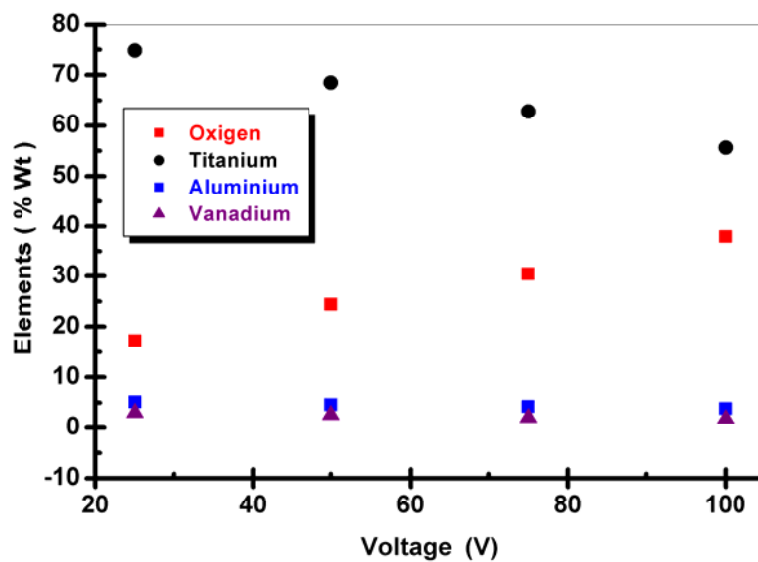
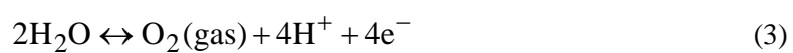


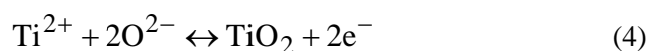
Fig. 5 Weight percentages of the elements of oxide films as a function of anodic forming voltage

Oxygen ions react with titanium to form the oxide.



O₂ gas evolves or sticks at electrode surface.

At both interfaces:



For Al and V elements is observed that their decreasing weight percentages (between untreated samples and those after anodic oxidation) is insignificant. For example, if is taken into account only the voltage of 100 V it is observed that the decreasing weight percentages of aluminium and vanadium are 2.21 and 2.09 respectively, compared with titanium whose decreasing weight percentages is 34.34, and this could means again that the main reactions are titanium oxidation.

The mean diameter of titanium oxide pores was estimated at 50-100 nm from SEM images, Figure 6.

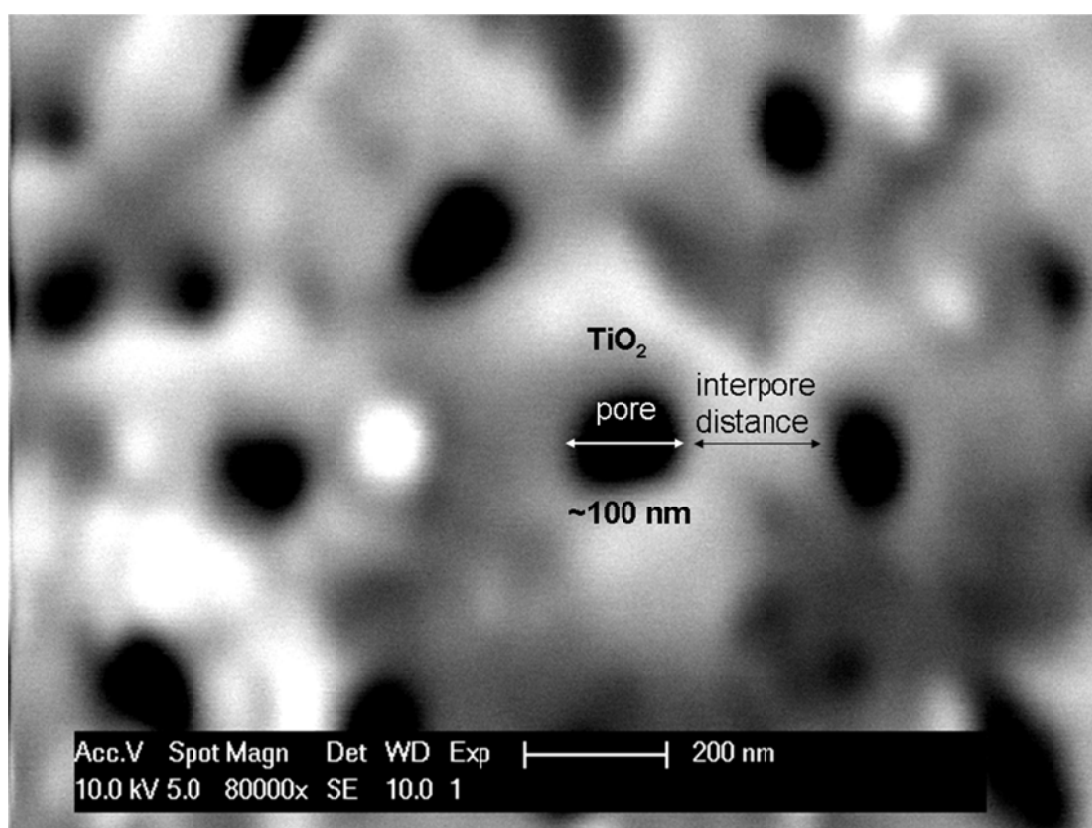


Fig. 6. SEM micrograph of titanium oxide pores formed on Ti-6Al-4V alloy substrate by electrochemical method

Films with homogeneously distributed pores having an average pore diameter of 50-100 nm and interpores distance of about 200 nm were obtained by anodization in an aqueous H₂SO₄ electrolyte solution on Ti-6Al-4V alloy after a comprehensive investigation of the anodization conditions. No similar results were found in the literature for comparison.

4. Conclusions

Novel nanoporous anodic thin TiO₂ films were grown on Ti-6Al-4V alloy substrates in H₂SO₄ acid solution and the films were analysed in terms of the thickness, morphology and chemical composition.

The morphology of the anodic oxide films prepared on Ti-6Al-4V strongly depends on the applied voltage. The thickness of the film as measured with SEM-FIB increased almost linearly with the voltage, varying from 65 nm to 615 nm. With increasing the voltage, oxygen is the only element whose weight percent increases too.

The preponderant reactions which lead to oxidation of the Ti-6Al-4V alloy seems to be predominantly for forming of TiO₂ layer.

The nano porous TiO₂ layer on Ti-6Al-4V alloy support could be further used as antibacterial surface, support for hydroxyapatite formation, bioimplants and biomedical devices.

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