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# Fabrication of titanium oxide nanotube arrays by anodic oxidation

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**Abstract**

The formation of titanium oxide nanotube arrays on titanium substrates was investigated in HF electrolytes. Under optimized electrolyte and oxidation conditions, well-ordered nanotubes of titania were fabricated. Topologies of the anodized titanium change remarkably along with the changing of applied voltages, electrolyte concentration and oxidation time. Electrochemical determination and scanning electron microscope indicate the nanotubes are formed due to the competition of titania formation and dissolution under the assistance of electric field. A possible growth mechanism has also been presented.


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*Keywords:* A. Nano-tubes; A. Titanium oxide; D. Anodic oxidation

## 1. Introduction

Titanium dioxide is one of the most widely studied chemical substances because of its widely application in catalytic, gas-sensing and corrosion-resistance materials. Moreover, it is gaining considerable interest due to unique and excellent properties in optics, electronics, photochemistry and biology [1–3]. Anodic oxidation is a commonly used surface treatment method especially in forming porous alumina structure. Formation of porous alumina structure has been widely studied. Many kinds of nanostructures including nanowires, nanorods and nanotubes have been fabricated by taking nanoporous alumina as templates [4–7]. There were a few attempts to compare anodic oxide growth on other value metals with porous alumina. Electrochemical oxidization of titanium has been studied in sulfuric acid, phosphoric acid, acetic acid and chromic acid with or without HF solution [2,8–10]. Different morphologies were obtained in oxidized titanium compared with alumina [1,2,11]. A mirror image of the behavior of porous alumina can not be copied in the forming of porous titania.

This paper investigates the oxidation process of titanium in HF aqueous solution via constant-voltage experiments. Under optimized electrolyte and oxidation conditions, well-ordered nanotubes of titania were fabricated. Topologies of the anodized titanium change remarkably along with the changing of applied voltages, electrolyte concentration and oxidation time. A possible growth mechanism is presented.

## 2. Experimental

The high purity titanium foils ($10\times10\times0.5$ mm$^3$) used in this study were obtained from General Research Institute for Nonferrous Metals (Beijing, China). They were polished mechanically to a mirror image and washed in twice-distilled water and acetone by ultrasonic washing before use. Electrochemical experiments were carried out using a direct current (dc) voltage source (DH1722, Dahua Coop., Beijing, China).

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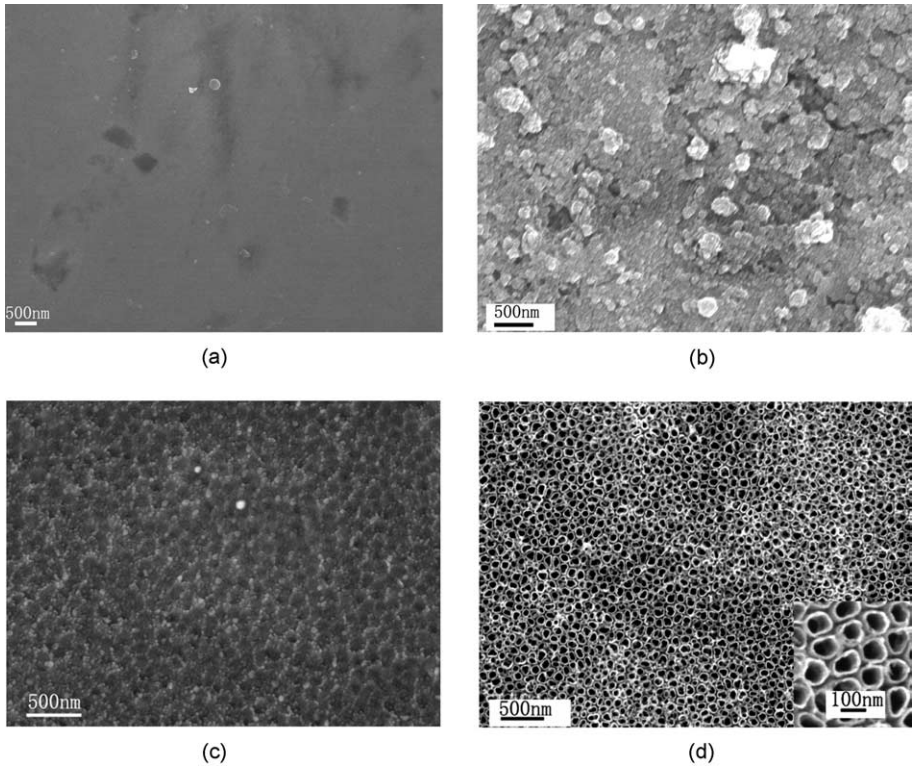


Fig. 1. Titanium microstructure after different treatments (a) titanium metals after being polished mechanically, (b) titanium metals after being anodized at 20 V above the HF solution, (c) titanium metals after being anodized at 20 V and then etched in 1 wt% HF, (d) titanium metals after being anodized at 20 V for 30 min in 1 wt% HF solution.

Titanium foils were used as anodic electrode while platinum ($20\times20\times0.1\ mm^3$) was used as cathodic electrode. The distance between anodic and cathodic electrodes was 20 mm. Electrolyte in this process was $0.1\sim5.0$ wt% HF solution. All solutions were prepared from reagent grade chemicals and deionized water. All anodization experiments were carried out at room temperature. During the experiments, the solutions were stirred using a magnetic stirrer. After the anodization, the samples were rinsed in deionized water, dried and characterized.

Electrochemical measurements were conducted using CHI660a electrochemical analyzer (CH Instruments Inc., Shanghai, China). Raman spectra were obtained on a RM1000 Raman Spectrometer (Renishaw PLC). X-ray diffraction measurements were performed on D/max-RB diffractometer (Rigaku, Rotafles) using Cu $K_\alpha$ radiation (0.15416 nm).The microstructures were observed on field emission scanning electron microscopes (JSM-6301, JEOL Inc., Japan). The cross-section photographs were obtained by observing mechanically fractured sample. The transmission electron microscopy structures and selected area electron diffraction were obtained in TEM-200CX electron microscope (JEOL, Japan).

## 3. Results and discussion

### *3.1. Structures of titanium metals surface after different treatments*

When titanium metals were anodized in HF solution, structures of the anodized titanium change remarkably along with the changing of applied voltages, electrolyte concentration and oxidation time. Fig. 1 shows titanium microstructure after different treatments. The surface of titanium metals is even and smooth after being polished carefully. However, the surface is covered with a compact thin oxide film due to the intrinsic property of valve metal [2]. Fig. 1(c) indicates the compact oxide begins to dissolve and dissolution takes place only in selective area. In a word, compact oxide film at the titanium surface existed with or without the assistance of electric field and HF solution can etch the oxide quickly. But the etching speed was different at different area of the oxide due to the different stress on the surface of oxide film which was called selective etching. Fig. 1(d) shows that the nanotube structure was formed after anodizing titanium metals at 20 V for 30 min in 1 wt% HF solution.