

Nanoporous anodic titania observed at the bottom side of the oxide layer



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ABSTRACT

The morphology and pore arrangement of nanoporous anodic TiO₂ arrays, prepared in the electrochemical cells with different sample alignments by the three-step self-organized anodic oxidation of titanium, were investigated at the bottom side of oxide layers. The quantitative analyses of pore spacing (cell size), pore density and pore arrangement were performed on the basis of FE-SEM bottom view images. The results show that the type of sample alignment and anodizing potential influence the pore spacing, pore density and pore arrangement. On the contrary, the anodizing temperature has a little effect on nanoporous anodic titanium dioxide (ATO) layers. Quantitative information on the nanopore arrangement, based on Delaunay triangulations, is also provided. The cells, which are not six-fold coordinated by neighboring cells, were recognized as defects and the percentage of defects, defined as a ratio between the number of defective pores and number of all pores on the analyzed surface was calculated for all the samples. A quite poor hexagonal arrangement with a relatively high percentage of defective pores (above 30%) was found for all studied anodizing conditions. However, the least percentage of defective pores suggesting the best nanopore arrangement was obtained for the potential of 60 V and 50 V at 10 °C and 20 °C, respectively.

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1. Introduction

Nanotechnology is widely seen as having tremendous potential to bring benefits to many areas of research and application. It allows us to manipulate the matter on a molecular scale, much less than 100 nm, and provides valuable information on the reproducible synthesis of new materials with specific properties. In this regard, an important part of the scientific community is currently focused on a challenging and relevant research direction, which is a fabrication of novel nanostructured materials, especially with a nanoporous/nanotubular architecture [1–3]. Recently, nanostructured materials with periodic arrays of nanopores, nanotubes, nanowires and nanodots have become a research hot spot because of their unique chemical and physical properties, substantially differing from those of corresponding bulk solids. Therefore, they are widely considered as alternative options for various technological applications [4–6].

Nanostructured titanium dioxide materials have a wide range of modern applications. In general, the applications of nanostructured TiO₂ can be divided into two different areas depending on a semi-conductive nature of the TiO₂. In case when the semiconducting

nature of TiO₂ is exploit, typical application examples include self-cleaning, sensing, photocatalysis, and solar energy conversion [7–23]. In the latter case, nanostructured titanium dioxide can be used as templates for deposition of secondary nanomaterials, electrochromic devices, and biocompatible bone implants for medical applications [24–35].

To date, it is well known that among all synthetic procedures anodic oxidation of titanium is an excellent approach to fabricate TiO₂ nanopore/nanotube arrays due to its simplicity and low cost. Under the right conditions, this self-ordering process allows to control the surface morphology and leads to nanopore or nanotube arrays with long-range order. The anodic synthesis of nanotubular/nanoporous TiO₂ with a highly ordered arrangement of straight, parallel channels, and with a narrow distribution of nanochannel diameters has received high scientific attention [36,37]. A typical anodic titanium dioxide (ATO) film fabricated in this way, exhibits a close-packed array of hexagonally arranged tubes or cells containing pores in each cell center [38,39]. Several recent studies have indicated that the performance of nanotubular/nanoporous anodic TiO₂, for above mentioned applications, is strongly dependent on its morphological parameters (structural features) such as pore/tube length, diameter, aspect ratio, long-range order and growth rate [36,37,40]. One major advantage of the electrochemical anodization route lies in its ability to tune the surface morphology of ATO by controlling adjustable experimental conditions. In

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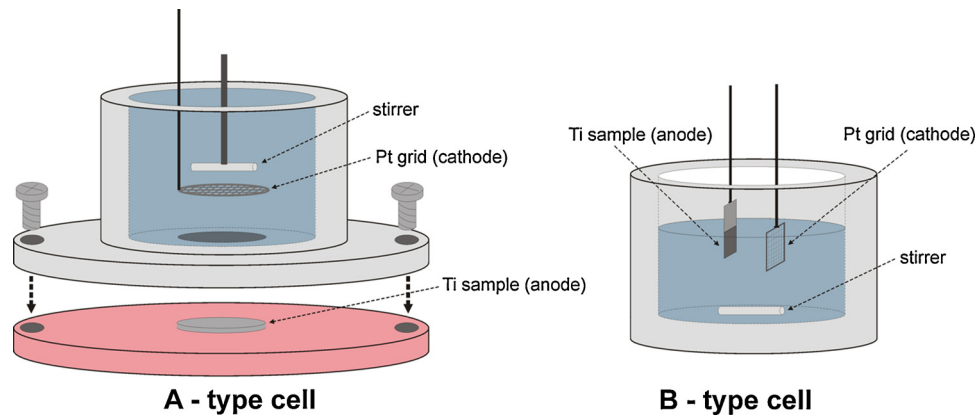


Fig. 1. Schematic illustration of experimental set-ups for anodic oxidation of Ti with the horizontally and vertically aligned anode (anodized sample).

the anodic oxidation method, the most influential parameters on the morphology of ATO films are chemical composition, pH and viscosity of the electrolyte, anodization potentials (DC [41,42], AC [43,44]), time and temperature [45,46]. The optimization of the characteristics of the nanotubular/nanoporous TiO₂ array, in view of their potential applications, requires detailed studies. These kind of elementary investigations are furthermore the basis for improvements of anodic TiO₂ properties.

As was mentioned, the morphology and structural features of ATO are strongly affected by anodizing conditions, especially the applied anodizing potential, temperature, electrolyte composition and the process duration. The effect of anodizing conditions on the structural features of nanoporous anodic TiO₂ formed by a three-step anodization in an ethylene glycol electrolyte containing 0.38 wt% of NH₄F and 1.79 wt% of H₂O was extensively discussed in our previous works [38,39], however, the top side of oxide layer was analyzed only. In this work we focused mainly on the investigation of oxide morphology and pore arrangement at the bottom side of oxide layer (pore bottoms) at various anodizing potentials and temperatures. To our best knowledge, the quantitative analysis of pore order at the bottom side of anodic titanium dioxide was not studied yet.

2. Experimental

A 0.25 mm thick titanium foil (99.5% purity, Alfa Aesar) were cut in coupons (1.5 × 2.5 or 1 × 1.5 cm) with a selected working area of 0.8 cm² and 0.5 cm². Prior to anodization, the Ti coupons were degreased in acetone and ethanol, then dried in the air. The specimens were electrochemically polished in a mixture of acetic acid (99.5 wt%), sulfuric acid (98 wt%), and hydrofluoric acid (40 wt%) (60:15:25 in volume) at a constant current density of 1.40 A cm⁻² and 20 °C for 1 min, followed by chemical polishing in a mixture of HF (40 wt%) and nitric acid (65 wt%) (1:3 in volume) for 10 s until mirror finish was achieved. The anodization was carried out using a conventional two-electrode configuration where a titanium plate and platinum grid were used as the anode and cathode, respectively. The electrochemical oxidation process was conducted in a home-made Teflon electrochemical cell (volume of 100 cm³), where anodized samples laid horizontally on the metallic cooled plate (A-type cell, Fig. 1). Some experiments were performed in an electrochemical cell with a vertically aligned anode (B-type cell, Fig. 1). The backside of the sample was insulated with a non-conducting polymer varnish. A three-step self-organized anodization under potentials ranging between 30 V and 70 V was used for generation of nanoporous titanium dioxide layers in an ethylene glycol solution containing NH₄F (0.38 wt%) and H₂O (1.79 wt%) at 10 °C and 20 °C. A three-step anodization

consists of two cycles of initial anodizing at the constant cell potential and a subsequent mechanical removal of the grown oxide layer by an adhesive tape. After the removal of oxide layer, hexagonally self-ordered patterns formed on the metal surface serve as nucleation sites for the formation of nanopores during the next anodization. Immediately after the oxide removal, the titanium sample was re-anodized under conditions identical to those in previous anodization steps. The duration of the first and second anodizing steps was 3 h. After the first and second anodizations, the grown oxide layers were removed. Then, immediately, the titanium samples were re-anodized for 10 min. After completing the anodization, the samples were rinsed with water and dried in the air.

The morphological and structural characterization of as-prepared TiO₂ layers includes an extensive characterization of ATO morphology by field emission scanning electron microscopy (FE-SEM, Hitachi S-4700) and evaluations of structural features of ATO (cell diameter, pore density and regularity of pore arrangement) by using software. In order to observe the bottom side of ATO, a one side of double sided adhesive conductive carbon tape was glued onto the ATO top layer. Then, the oxide layer was mechanically removed from the Ti support and the second side of adhesive tape was attached to the disk holder. The ATO sample was sputtered with gold to ensure good electrical contact during FE-SEM observation.

The characteristic parameters of ATO layers were estimated directly from at least six different FE-SEM images. ImageJ 1.37 v software [48], combined with the dedicated computational experiment, and corresponding executable publication powered by the GridSpace2 platform [49,50] and Collage Authoring Environment [51] were employed for determination of cell sizes (pore to pore distance), pore density, percentage of defective pores and for obtaining cell maps based on color coding algorithm. 3D representations of nanoporous TiO₂ layers were obtained directly from FE-SEM images by using WSxM 4.0 Develop 12.0 [47].

3. Results and discussion

Typical FE-SEM top- and bottom-views images together with 3D representations of anodic titanium dioxide layers after 10 min of the third anodization carried out in the ethylene glycol solution containing NH₄F (0.38 wt%) and H₂O (1.79 wt%) at 40 V and 20 °C are shown in Fig. 2a and b, respectively. As can be seen, a dense array of nanopores is formed during the anodizing process. Moreover, a compact oxide layer at the pore bottoms is also formed (see Fig. 2b), similarly to anodization of aluminum [52].

Fig. 3a–c shows FE-SEM bottom-view images of ATO layers after the third step of anodization performed at different applied potentials. The process was carried out at 10 °C in the A-type

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