SELF-ORGANIZED TITANIUM DIOXIDE NANOTUBE LAYERS: INFLUENCE OF REPETITIVE ANODIZATIONS

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Abstract

In the present work we report on the influence of repetitive anodization cycles upon the dimensions and morphology of self-organized TiO_2 nanotube layers. Electrolytes based on ethylene glycol (containing water and NH_4F) and widely used Titanium thin foils as substrates were utilized. These substrates were repetitively anodized, a total 3 times, and the resulting layers were removed and analyzed after each anodization step. Investigations by SEM show that, overall, nanotubes within nanotube layers produced by the repetitive anodization on one identical substrate, grow so that the tube diameter becomes gradually smaller. In addition, investigations carried out by AFM and mechanical profilometry show that repetitive anodization lead to significant smoothing (or polishing) of initially coarse substrates - this aspect is somewhat surprisingly not discussed in the existing literature. As a result, before each new anodization step, the nanotube layers grow on gradually smoother substrates with positive implications on the overall nanotube layer uniformity.

Keywords: Titanium dioxide; Nanotubes; Anodization; Roughness, Smoothening

1.   INTRODUCTION

Self-organized TiO_2 nanotube layers have attracted enormous scientific attention in past decade, as they represent a material with manifold applications - for an overview, several comprehensive reviews are available [1-3]. In addition, they display interesting morphological features compared to their nanoparticulate counterparts, which make them a suitable candidate for a range of other applications, not necessarily related with photo-catalysis or dye-sensitized solar cells which are typical applications for TiO_2 nanoparticles. For the anodization itself, a variety of different electrolytes combined with optimized anodization conditions were applied over the past 10 years, which yielded nanotubes with different lengths and diameters. This electrolyte range included the use of aqueous electrolytes [4,5], glycerol based electrolytes [6,7], and ethylene glycol electrolytes [8] with NH_4F instead of HF. Within the development of new tube geometries and aspect ratios, efforts have been carried out to alter morphologies of TiO_2 nanotubes, for example to produce nanotubes as double layers by subsequent anodization steps in two electrolytes [9]. By repetitive anodizations, highly ordered TiO_2 nanotube arrays were also achieved by removing the nanotubes after the first anodization of the Ti foils, and applying a second anodization step [10,11]. From some pioneering reports exploring the influence of crystallographic orientation of titanium substrates on the growth characteristics [12, 13] and the growth rate [14], it has become evident, even though there is no direct study devoted to this aspect that the quality and uniformity of the nanotube layers must arise from the quality and homogeneity of the substrate. In particular, it appeared to matter strongly for the oxide growth rate (oxide in the form of nanotubes [15] or flat anodic layers [16]), whether the substrates were as-received rough foils or electropolished substrates.

To date, there has been no published work that would explore dimensional or morphological differences between nanotube layers grown by repetitive anodization of identical initial substrates, whether on foils, sheets or artificially produced layers (by sputtering, or evaporation), and regardless of how smooth they are. In addition, there is no work that would report on the roughness of the regular substrates used for anodization - titanium thin foils - and how the roughness changes upon the anodization. In order to provide more insight into these issues, sets of experiments have to be carried to out.

Therefore in this work we investigate dimensional and morphological changes of nanotube layers grown by repetitive anodizations of identical starting titanium substrates. In addition, we investigate roughness changes of these substrates between multiple anodization steps.

2.   EXPERIMENTAL

Titanium foils (Sigma-Aldrich 0.127 mm thick, 99.7 % purity) were first degreased by sonication in isopropanol and acetone, then rinsed with isopropanol and dried in air. The anodization setup consisted of a 2 electrode configuration using a platinum foil as the counter electrode, while the titanium foils (working electrodes) were pressed against an O-ring of the electrochemical cell, leaving 1 cm^2 open to the electrolyte. Electrochemical experiments were carried out at room temperature employing a high-voltage potentiostat (PGU-200V, IPS Elektroniklabor GmbH). Electrolytes based on ethylene glycol containing 1.5 vol% deionized water and 88 mM NH_4F were used. All electrolytes were prepared from reagent grade chemicals. Before the initial use, all electrolytes were aged for 9 hours by anodization of blank Ti substrates at 60 V under the same conditions as for the main anodization experiments. Titanium foils were anodized for different times, after sweeping the potential from 0 V to 60 V with a sweeping rate of 1 V/s. After anodization, the titanium foils were rinsed and sonicated in isopropanol and dried. The structure and morphology of the TiO_2 nanotubes was characterized by a field-emission electron microscope (FE-SEM JEOL JSM 7500F). Dimensions of the nanotubes were measured and statically evaluated using proprietary Nanomeasure software. For each condition used in this work, we calculated average values and standard deviations from at least 3 different locations on 2 samples of each condition, with a high number of measurements (n≥ 100). Removal of the nanotube layers between anodization steps was carried out by applying a cathodic step of -5 V for 2 minutes in 1M H_2SO_4, followed by cleaning of surface by sonication in isopropanol. The surface topography was measured using Atomic Force Microscope (AFM, Solver Pro M, NT-MDT; Russia) on the area of 5x5 µm and using SSC-01 mechanical profilometer (RMI, CZ) on the length scale 500 µm, with the step of 0.5 µm. The raw data from the profilometer were corrected for the long-distance deflection of the material's surface by the 2nd order polynomial function.

3.   RESULTS AND DISCUSSION

Fig. 1 demonstrates a typical current behavior, when anodizing one Ti substrate, three subsequent times in a row at 60 V in ethylene glycol (containing 88 mM NH_4F and 1.5 vol% DI water). It has to be noted that for the each following anodization step, the previously grown nanotube layer was removed first. As one can see from **Fig. 1**, the C-V curve for the 1st anodization follows the typical behavior reported in earlier papers [17,18]. Briefly, at the beginning of the anodization, when the potential is swept to 60 V, the current strongly increases due to an oxide layer that is spontaneously formed at the surface of the titanium. Once the final potential is reached, a fast current density decay is recorded. During the following period, where the current density proceeds through its first minimum, small pores start to grow randomly in the oxide layer, and shortly after the current density increases due to an increase of the active area, until a maximum number of pores is formed. This stage corresponds to a maximum in the current density. Subsequently, the tubes expand in length, and the current density slowly decays towards a steady-state.

However, this typical behavior has not yet been seen for currents recorded during the 2nd and 3rd anodization. They show considerably different features, as there are no current peaks observed anymore. Instead, the current gradually increases and levels-off during the sweeping, and once the final potential (60 V) is reached, it begins to drop and gradually decrease. In addition, the current recorded during the 1st anodization are higher, in particular during the sweeping period. This is interesting and to the best of our knowledge, this significant deviation has not been previously reported and discussed. It appears as if the surface of Ti in this initial period undergo different morphological changes then usual (as described above). One possible explanation for this can be that the 2nd and 3rd anodization step begins with the Ti surface, with billions of small dimples imprinted on it, after the previous anodization, and the initial rough surface originating from rolling of the surface becomes smoother. Even though, some rolling lines in Ti can be still imprinted on its upper surface before 2nd or 3rd

anodization, the oxide growth proceeds on a smoother and smaller surface area. In addition, the pore formation on the surface is directed by the dimples imprinted in the Ti and presumably it takes also shorter times for the main nanotube growth to begin, compared to the case, when initial rough foils are used.
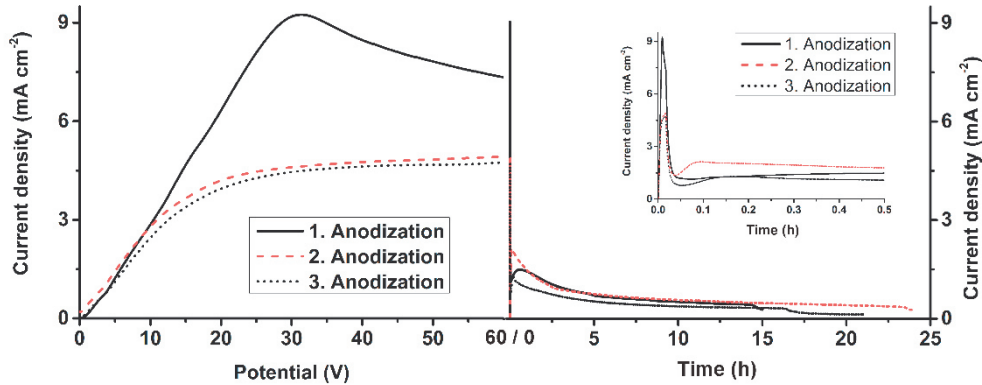
Fig. 1 Current density - voltage curve (left) and current density transients (right) recorded during 3 repetitive anodizations of one identical Ti substrate in ethylene glycol (containing 88 mM NH₄F and 1.5 vol% DI water). The inset in the right part shows a zoom of the initial 30 minutes of the current density transient

It can be expected, that these differences must have an influence on the resulting structure and dimensions of the nanotube layers. **Fig. 2** shows SEM images of the nanotube layers grown as in **Fig. 1**. Even though it may not appear on first impressions, but by a thorough inspection of the layers and statistical analyses, interesting dimensional changes are observed.
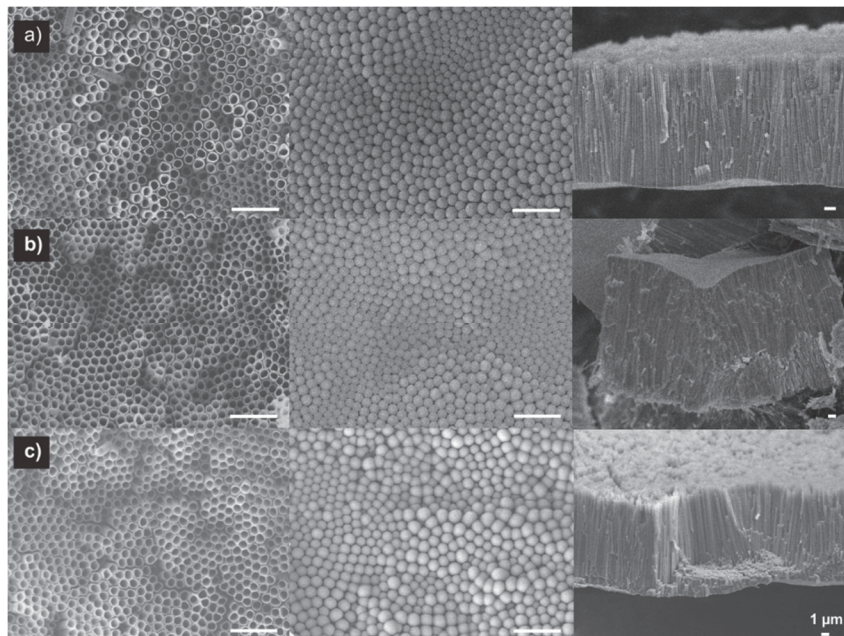
Fig. 2 SEM images of self-organized TiO₂ nanotube layers prepared after 1st (a), 2nd (b) and 3rd (c) anodization of Ti, as in Figure 1. Images show top-view (left column), tube bottoms (middle column) and cross-sections (right column). All scale bars represent 1 μm

As given in **Table 1**, a trend towards smaller tube diameters can be observed with increasing number of anodization steps. For example, the inner diameter evaluated from nanotubes prepared during the 1st anodization is ~ 170 nm, while the inner diameter from nanotubes prepared during the 3rd anodization is ~ 155

nm. This cannot be explained by an increase in the conductivity of electrolytes, as we reported previously [19], since for each anodization step we utilized an aliquot of a larger electrolyte volume prepared at once, and having the same aging time (9 hours). This phenomenon must have its origin in the different starting quality and uniformity of Ti thin rolled foils as substrates.

Table 1 Dimensions of self-organized TiO$_2$ nanotube layers shown in **Fig. 2**

| Anodization	Inner tube diameter (nm)	Tube length (mm)	Duration (hrs)
First	170.5±21.9	10.1±0.9	15
Second	158.3±15.7	17.9±1	24
Third	155±17.9	12±1	21

In the next step, we focused on the Ti substrates themselves. In order to analyze their roughness before anodization and after all anodization steps, profilometric measurements were carried out over relatively long distances of 500 µm. This is such a length scale, that it is significantly larger compared to the scale traceable by AFM within reasonable experimental time. Representative results are shown in **Fig. 3** that provides roughness profiles of investigated surfaces in the parallel direction (red line), to rolling lines imprinted on surfaces or in the perpendicular direction (black line) to rolling lines. The root mean square (RMS) value evaluated here, according to ISO standard [20], is a statistical representation of roughness deviation. As one can see from decreasing RMS value with each anodization step, the original and very rough Ti surface becomes with each individual anodization step increasingly smoother, independent of the direction of the rolling lines.
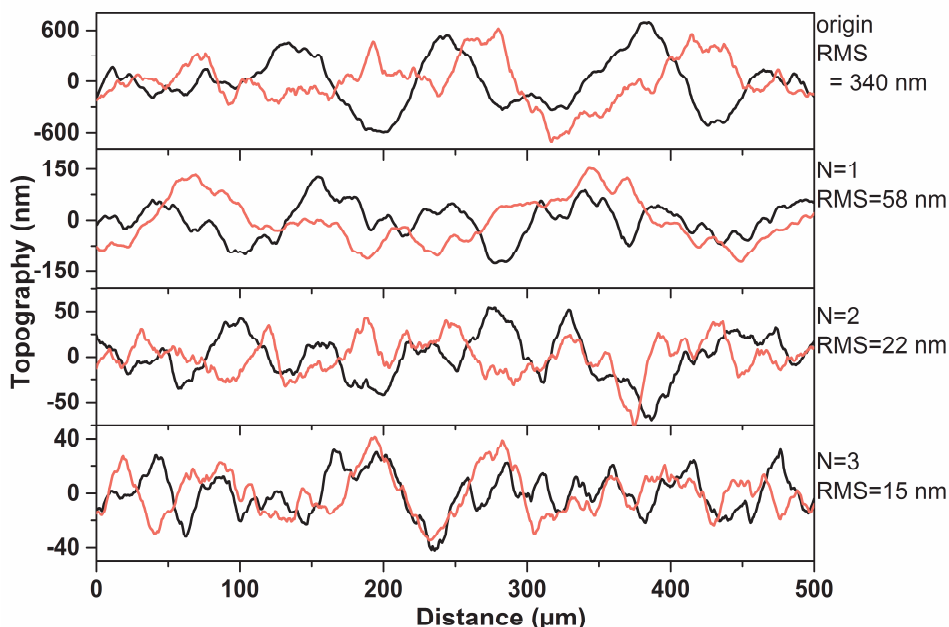
Fig. 3 Roughness profiles obtained by profilometry on Ti substrates (thin rolled foils) before and after all three anodization steps. Surfaces were obtained upon anodization shown in **Figs. 1 and 2**. RMS = Root Mean Square = statistical representation of the roughness deviation. Nanotube layers were quantitatively removed from the surfaces before these measurements

Finally, we performed AFM analyses of small spots (5x5 µm) on the anodized surfaces in order to see their local roughness. **Fig. 4** shows representative AFM images showing the obtained topography of these surfaces.

The Z scale (on the right side of each image) provides roughness information which in fact represents the information about the depth of the dimples compared to the rest of the area. As one can see from these images, not only the overall roughness decreases (as shown in **Fig. 3**), but also the local roughness (that stems from dimples in the substrates owing to the tube growth) decreases. It should be pointed out that due to its high initial roughness, non-anodized Ti thin rolled foils cannot be measured by AFM. Moreover, as there are no dimples (that stem from the tube growth), such an image would not fit to the sequence shown in **Fig. 4**.
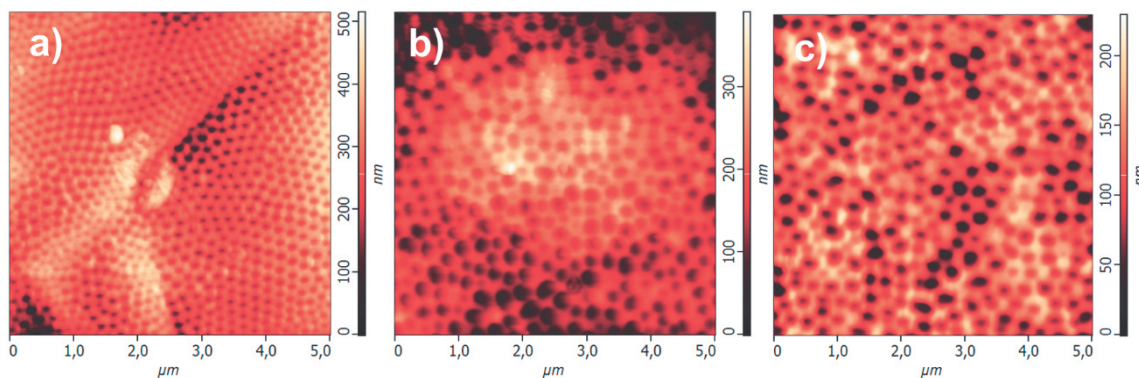
Fig. 4 Topography of identical Ti substrate after all three anodization steps. Measured by AMF on the area of size 5x5 µm. Nanotube layers were quantitatively removed from the surfaces before these measurements

Last, but not least, when looking at the nanotube layer macroscopically, e.g. under an optical microscope or by SEM at very low magnification, one recognizes indeed significant improvement of the uniformity and flatness of the nanotube layers. Some occasional defects in the nanotube layers, such as cracks and local thickness variations (due to grain boundaries of Ti substrates [12-14] and metallurgical defects of Ti) become absent with every additional anodization step. The results presented are not exclusively obtainable just for ethylene glycol based electrolytes, however, as they represent the classical and widely used electrolytes in the field.

4. CONCLUSION

In this work, we demonstrated that the repetitive anodization of Ti substrates in ethylene glycol based electrolytes lead to i) gradual changes of the nanotube dimensions, and ii) significant smoothing of the Ti substrates used for anodization. These two features are reflected also in an improved overall homogeneity of the nanotube layers after each anodization of identical initial substrates. These findings might be important for cases, where ultrafine nanotube layers need to be produced and utilized for further applications.

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