

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

Macak Jan^{1,*}, Hanna Sopha¹, Knotek Petr²

¹ CEMNAT, FCHT, University of Pardubice, Nam. Cs. Legii 565, 530 02 Pardubice, Czech Republic, EU

² KOANCH, FCHT, University of Pardubice, Studentska 573, 532 10 Pardubice, Czech Republic, EU

*e-mail: jan.macak@upce.cz

Abstract

In the present work we report on the influence of repetitive anodization cycles on the dimensions and morphology of self-organized TiO₂ nanotube layers. Electrolytes based on ethylene glycol (containing water and NH₄F) and widely used Titanium thin foils as substrates were utilized. These substrates were repetitively anodized, in total 3 times, and the resulting layers were after each anodization step removed and analyzed. Investigations by SEM show that overall nanotubes within nanotubes 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 profilometer show that repetitive anodization lead to significant smoothening of initially coarse substrates – this aspect is somewhat surprisingly not discussed in 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 layers uniformity.

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

1. INTRODUCTION

Self-organized TiO₂ nanotube layers have attracted in past decade enormous scientific attention, as they represent 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 that make them suitable candidate for a range of other applications, not necessarily related with photo-catalysis or dye-sensitized solar cells which are typical applications for TiO₂ nanoparticles. For the anodization itself, a variety of different electrolytes combined with optimized anodization conditions were applied past 10 years that yielded to 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 NH₄F instead of HF. Within the development of new tube geometries and aspect ratios, efforts have been carried out to alter morphologies of TiO₂ nanotubes, for example to produce nanotubes as double layers by subsequent anodization steps in two electrolytes [9]. By repetitive anodizations also the highly ordered TiO₂ nanotube arrays were 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 characteristic [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.

Up to date, there is no published work that would explore dimensional or morphological differences between nanotube layers grown by repetitive anodization of identical starting substrates, no matter, whether they are foils, sheets or artificially produced layers (by sputtering, or evaporation) and no matter 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 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 cm² 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 NH₄F were used. All electrolytes were prepared from reagent grade chemicals. Before the first 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 hours 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 TiO₂ 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 H₂SO₄, 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

Figure 1 demonstrates a typical current behavior, when anodizing one Ti substrate three times in a row at 60 V for various times in ethylene glycol (containing 88 mM NH₄F and 1.5 vol% DI water). It has to be noted that for the each next 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 behaviour 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 is not seen for currents recorded during the 2nd and 3rd anodization. They show considerably different features, as there are no current peaks observed anymore. Instead, they current gradually increase and level-off during the sweeping and once the final potential (60 V) is reached, they begin 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 than 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 the Ti surface after previous anodization and the originally rough surface originating from rolling of the surface becomes smoother. Eventhough, some rolling lines in Ti can be still imprinted on its upper surface before 2nd or 3rd anodization, the oxide growth proceeds on smoother and smaller surface area. In addition, the pore formation on the surface resulting in the tube growth later one 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.

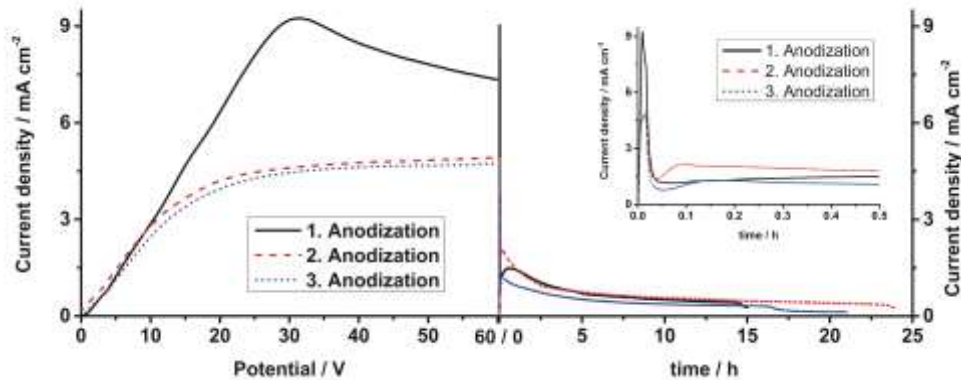


Fig. 1 Current – voltage curve (left) and current transients (right) recorded during 3 repetitive anodizations of one identical Ti substrate in ethylene glycol (containing 88 mM NH₄F and 1.5 vol% DI water).

It can be expected, that these differences must have an influence on the resulting structure and dimensions of the nanotube layers. **Figure 2** shows SEM images of the nanotube layers grown as in Figure 1. Even though it may not appear on the first look, by a thorough inspection of the layers and statistical analyses, interesting dimensional changes are observed.

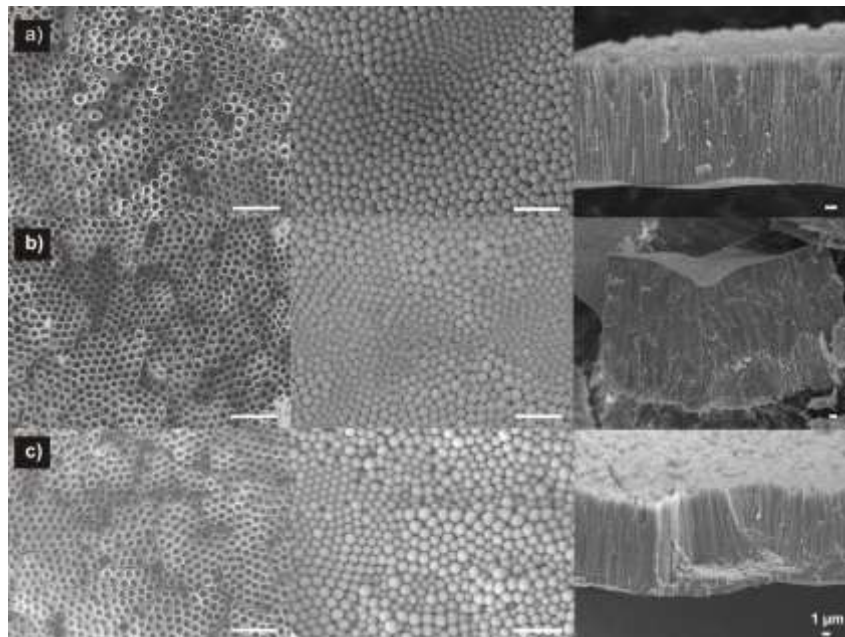


Fig. 2 SEM images of self-organized TiO₂ nanotube layers prepared after 1st (a), 2nd (b) and 3rd (c) anodization of Ti, as in Figure 1. Images show top-view (left column), tube bottoms (middle column) and cross-sections (right column).

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 a part of large electrolyte volume prepared at once and having the same aging time (9 hours). This phenomena must have origin in the different starting quality and uniformity of Ti thin rolled foils as substrates.

Table 1 Dimensions of self-organized TiO₂ nanotube layers shown in Figure 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 distance 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 **Figure 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 more and more smoother, independently on the direction of the rolling lines.

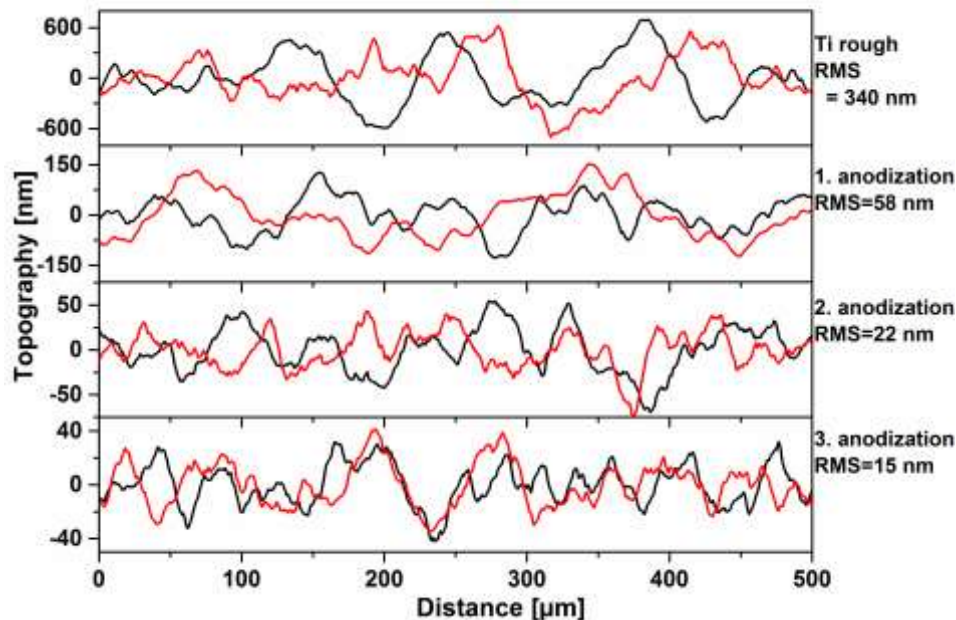


Fig. 3 Roughness profiles obtained by profilometer on Ti substrates (thin rolled foils) before and after all three anodization steps. Surfaces were obtained upon anodization shown in Figures 1 and 2. RMS = Root Mean Square = statistical representation of the roughness deviation. Nanotube layers were 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. **Figure 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.

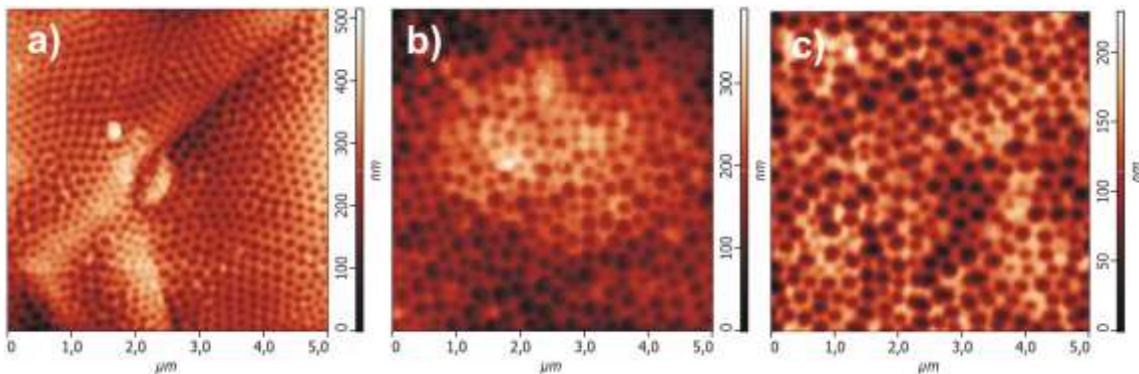


Fig. 4 Topography of identical Ti substrate after all three anodization steps. Measured by AMF on the area of size 5x5 μm . Nanotube layers were quantitatively removed from the surfaces before these measurements.

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, we employed these ones.

4. CONCLUSION

In this work, we demonstrated that 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 the identical starting substrates. These findings might be important for cases, where ultrafine nanotube layers need to be produced and utilized for further applications.

ACKNOWLEDGEMENTS

ERC and Czech Science Foundation is acknowledged for financial support through projects 638857 and 14-20744S, respectively.

REFERENCES

- [1] J.M. Macak, H. Tsuchiya, A. Ghicov, K. Yasuda, R. Hahn, S. Bauer, P. Schmuki, TiO₂ nanotubes: Self-organized electrochemical formation, properties and applications, *Curr. Opin. Solid State Mater. Sci.*, Vol. 11, No. 1-2, 2007, pp. 3-18

- [2] D. Kowalski, D. Kim, P. Schmuki, TiO₂ nanotubes, nanochannels and mesosponge: Self-organized formation and applications, *Nanotoday*, Vol. 8, No.3, 2013, pp. 235-264.
- [3] K. Lee, A. Mazare, P. Schmuki, One-Dimensional Titanium Dioxide Nanomaterials: Nanotubes, *Chem. Rev.*, Vol. 114, No.19, 2014, pp. 9385–9454.
- [4] J. M. Macak, H. Tsuchiya, P. Schmuki, High-Aspect-Ratio TiO₂ Nanotubes by Anodization of Titanium, *Angew. Chem. Int. Ed.*, Vol. 44, No. 14, 2005, pp. 2100-2102.
- [5] J. M. Macak, K. Sirotna, P. Schmuki, Self-organized porous titanium oxide prepared in Na₂SO₄/NaF electrolytes, *Electrochim. Acta*, Vol. 50, No. 18, 2005, pp. 3679-2684.
- [6] J. M. Macak, H. Tsuchiya, L. Taveira, S. Aldabergerova, P. Schmuki, Smooth Anodic TiO₂ Nanotubes, *Angew. Chem. Int. Ed.*, Vol. 44, No. 19, 2005, pp. 7463-7465.
- [7] J. M. Macak, P. Schmuki, Anodic growth of self-organized anodic TiO₂ nanotubes in viscous electrolytes, *Electrochim. Acta*, Vol. 52, No. 3, 2006, pp. 1258-1264.
- [8] S. P. Abu, A. Ghicov, J. M. Macak, P. Schmuki, 250 μm long anodic TiO₂ nanotubes with hexagonal self-ordering, *Phys. Stat. Sol. – Rapid Research Letter*, Vol. 1, No.2 2007, pp. R65-R67.
- [9] J. M. Macak, S. Abu, D. H. Kim, I. Paramasivam, S. Aldabergerova, P. Schmuki, Multilayer TiO₂-Nanotube Formation by Two-Step Anodization, *Electrochem. Solid-State Lett.*, Vol. 10, No. 7, 2007, pp. K28-K31.
- [10] J. M. Macak, S. Abu, P. Schmuki, Towards ideal hexagonal self-ordering of TiO₂ nanotubes, *Phys. Stat. Sol. – Rapid Research Letters*, Vol. 1, No. 5, 2007, pp. 181-183.
- [11] G. Zhang, H. Huang, Y. Zhang, H. L.W. Chan, L. Zhou, Highly ordered nanoporous TiO₂ and its photocatalytic properties, *Electrochem. Commun.*, Vol. 9, 2007, pp. 2854-2857.
- [12] A. Crawford, N. Chawla, Tailoring TiO₂ nanotube growth during anodic oxidation by crystallographic orientation of Ti, *Scripta Mater.*, Vol. 60, 2009, pp. 874 – 877.
- [13] S. Leonardi, A.I. Bassi, V. Russo, F. Di Fonzo, O. Paschos, T. M. Murray, H. Efstathiadis, J. Kunze, TiO₂ nanotubes: Interdependence of substrate grain orientation and growth characteristics, *J. Phys. Chem. C*, Vol. 116, 2012, pp. 384 – 392.
- [14] S. Leonardi, V. Russo, A. L. Bassi, F. Di Fonzo, T. M. Murray, H. Efstathiadis, A. Agnoli, J. Kunze-Liebhäuser, TiO₂ nanotubes: Interdependence if substrate grain orientation and growth rate, *ACS Appl. Mater. Interfaces*, Vol. 7, 2015, pp. 1662 – 1668.
- [15] W.M. Seong, D.H. Kim, I.J. Park, g.d. Park, K. Kang, S. Lee, K.S. Hong, Roughness of Ti substrates for control of the preferred orientation of TiO₂ nanotube arrays as a orientation factor, *J. Phys. Chem. C*, Vol. 119, 2015, pp. 13297 – 13305.
- [16] C.-C. Chen, J.-H. Chen, C.-G. Chao, W.C. Say, Electrochemical characteristics of surface of titanium formed by electrolytic polishing and anodizing, *J. Mater. Sci.*, Vol. 40, 2005, pp. 4053 – 4059.
- [17] K. Yasuda, J. M. Macak, S. Berger, A. Ghicov, P. Schmuki, Mechanistic Aspects of the Self-Organization Process for Oxide Nanotube Formation on Valve Metals, *J. Electrochem. Soc.*, Vol. 154, 2007, pp. C472-C478.
- [18] L.Taveira, J.M.Macak, L.F.P.Dick, P.Schmuki, Initiation and growth of self-organized TiO₂ nanotubes anodically formed in NH₄F/(NH₄)₂SO₄ electrolytes, *J. Electrochem. Soc.*, Vol. 152, 2005, pp. B405-B409.
- [19] H. Sopha, L. Hromadko, K. Nechvilova, J.M. Macak, *J. Electroanal. Chem.*, submitted.
- [20] ISO 4287-1997 „Geometric product specifications (GPS). Surface texture: profile method. Terms, definitions and surface texture parameters“ · ISBN 0-580-28479-4; Published: September 1997.