Influence of Anodizing Potential on Titanium Dioxide Nanotubes Morphology

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The present paper studies the behaviour of titanium pieces anodized in polyethylene glycol 400 at different potentials (50, 40 and 30V) and the morphology of the resulting samples. The surface features were characterized by scanning electron microscopy and transmission electron microscopy. By reducing the potential from 50 V to 40 V and 30 V, the length of the nanotubes is increasing, their internal diameters are changed and the walls become thinner. Regarding the shielding effect which is taking place in the nanotube formations in viscous electrolyte, this process is reduced when applied voltage is decreasing and when sonication is used as well.

Keywords: titanium nanotubes, anodization, polyethylene glycol

One of the most interesting 1D structures is represented by self-organized TiO_2 nanotube layers. These layers can be formed by a simple electrochemical method as anodization, a cheap and convenient procedure to elaborate titanium dioxide nanotubes [1-2]. The great number of papers devoted to the TiO_2 nanotubes structure can be ascribed to the fact that these structures represent a unique combination of the highly functional properties of TiO_2 with a controllable nanoscale geometry which permits the adjustment of the external and internal tube diameter, length and self-ordering[3-4]. Changing the anodizing conditions like the potential, time, electrolyte and pH [5-6], a large variety of TiO_2 nanoarchitectures were fabricated and investigated for different applications [6-7]. More recently, electrochemical anodization was used for fabrication of nanotubes in two steps [8] and for the formation of hexagonally ordered TiO_2 nanocolumnar layers by electrochemical oxidation in a fluoride containing electrolyte, using high potentials and low temperature values [9]. The curent paper investigates the influence of anodizing potential over the titanium dioxide nanotubes formation and their morphology using a viscous polyethylene glycol as electrolyte.

Experimental part

The electrolyte was prepared by using polyethylene glycol with average molecular weight 400 (PEG 400) (Fulka Analytical) as viscous organic compound with ammonium fluoride (NH_4F) (Sigma Aldrich) for fluoride ions and small purified water amount obtained with a Millipore Direct-Q UV3 water purification system.

The titanium specimens used for anodization were cut from a Ti foil (99.7% purity, 2mm thick, Sigma-Aldrich) in small pieces, with a selected working area of 0.385cm^2. Prior to anodization, these specimens were pre-treated as following: mechanically polishing with silicon-carbide papers up to 4000 grit and alumina paste followed by sonication in water, ethanol and acetone (15 min each). The specimens were dried in the air and used immediately.

The specimens were anodized in electrolyte containing PEG 400 with 0.5 wt% NH_4F and 2% v/v purified water by contacting and pressing against an O-ring inside an electrochemical cell (with a platinum plate as counter electrode) and a MATRIX MPS-7163 electrochemical source in series with a VA18B digital multimeter (V&A International with PC-Link soft). The electrochemical treatment consisted in raising the potential from 0 to 30V/ 40V/ 50V end values with a 2V/ 10s step, and maintaining these potential values constant for 2 h. The experiments were performed at room temperature. After the anodization the samples were rinsed with purified water.

For the structural and morphological characterization of the TiO_2 nanotubes a Nova NanoSEM 630 scanning electron microscope with field emission gun and high-resolution imaging capabilities has been used. The cross-section images were taken from cracked surface layers after scratching the samples. Supplementary nanoscale investigations have been conducted by using a Tecnai TM G^2 F30 S-TWIN high resolution transmission electron microscope (HR-TEM) equipped with STEM—HAADF detector, EDX and EELS.

Results and discussions

During the nanotubes fabrication process we used an anodization method involving an increased potential in the beginning of the research, because in this way the anodic current flow can be adjusted avoiding a destabilization of the steady-state situation within the pores, which generally occurs when a galvanostatic approach is used. Considering this, the *p*H value is about 2 at the pore bottom side and about 5 at the pore top side causing a different chemical etching rate [5], so a stabilization of *p*H profile can be also established by sweeping the potential.

The current density evolution during anodization process is presented in figure 1 for anodized samples in PEG 400, for 2 h, at three different voltage values.

In the first part of our research, the current density increases with the increase of the potential in all cases,

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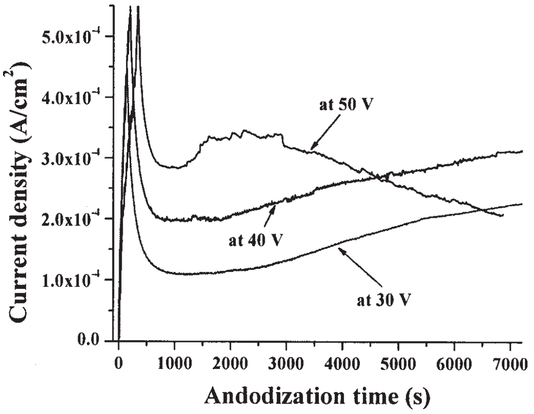

Fig. 1. Current density variation during anodization in PEG 400, for 2 h, at different potentials

achieving a first maximum value, higher in the case of anodised samples at 50V and 40V, but lower for 30V. According to literature data, the intensity of the current is affected by the presence of fluorides in the electrolyte [10], but in our work the fluorides content was the same. In this first stage, an initial oxide layer is formed over the Ti surface [7, 10] and its thickness and corresponding resistive behaviour should be proportional with the applied potential [10].

When the potential reaches 30V, 40V or 50V and remains constant, a fast decreasing of the current density takes place in the circuit, because of the consolidated TiO$_2$ passive layer [7, 11]. Then, a short plateau of about 700s with a constant current of about 0.1 mA/cm^2 for 30V, 0.2 mA/cm^2 for 40V and 0.3 mA/cm^2 for 50V can be observed. The resistance of the oxide layer remains approximately the same in this time lapse suggesting indistinguishable changes in the consolidated oxide layer.

After this first stage, due to the presence of F$^-$ ions in the electrolyte solution, an active electrochemical corrosion takes place, so the Ti-O bond in the oxide layer is weakened [12] and some irregular pores are developed at the TiO$_2$/ solution interface [7] causing an increase of the electric current.

The current starts to increase with almost similar slope for the sample anodized at 30V and 40V suggesting a similar mechanism of nanotube growth. Because of the small water content used in the viscous electrolyte (PEG 400), chemical dissolution of the TiO$_2$ layer is slower as compared with aqueos electrolytes [13].

For the sample anodized at 50V a sudden increase of the current can be observed then the current remains on the plateau for about 1500s. This is an important information which suggests that the chemical etching process is blocked and another resistive behaviour is installed.

In other previous work, we have reported the formation of the shielding layer which covers the self organized TiO$_2$ nanotubes layers by anodizing of Ti in viscous PEG 400 [14] and PEG 600 respectively, at 50V [15].

The formation and consolidation of the shielding layer has, as a consequence, a continuous decrease of the current observed in the last part of the current *vs*. time curve presented in figure 1.

Trying to remove or at least to reduce this superficial layer, we prepared TiO$_2$ nanotubes at lower potentials - 40V and 30V respectively. In the case of all the considered voltage values, we obtained self-organized vertically tubular layers opened at the top and closed at bottom. They were strong adherent on Ti substrate. SEM images from figure 2 shows the results for Ti anodizing in PEG 400 at 40V. The initial barrier oxide layer remaining at the Ti metal surface after removing the nanotubes by scratching is visible in the inset from the figure 2A. In figure 2B, one can observe that the nanotubes are still partially covered. This could be, as it was in the case of anodized sample at 50V, a conglomerate of partially dissolved nanotubes [14] and also some remaining electrolyte from anodization bath. There are also reported cases in the literature where the initial (non-ordered) layer is still partially present, in the case of anodization in glycerol/ 0.5wt.% NH$_4$F [16]. When the voltage was lowered to 30V, keeping the other parameters constant, the resulting nanotubes are less covered, as can be seen from figure 2B.

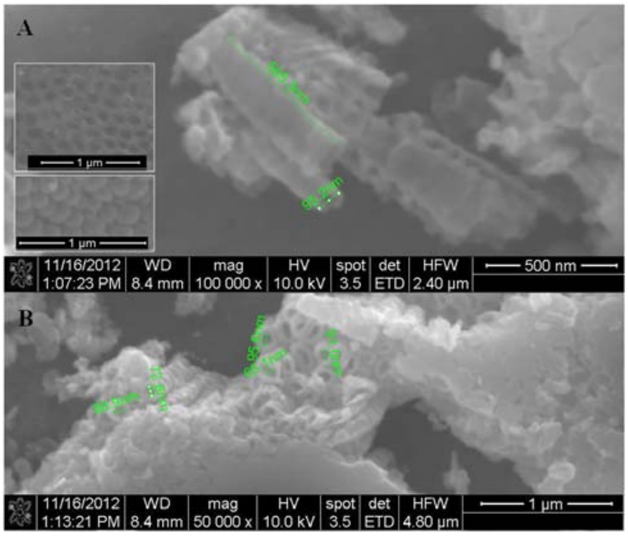

Fig. 2. A- cross-section and B- top-view SEM images of the TiO$_2$ nanotubular layer formed at 40 V. In the inset selected SEM cross-sectional barrier layer and bottom-view

In the figure 2 can be also observed that the side-walls of the tubes are rough, with rings connecting the nanotubes. This phenomenon was described in literature in the case of anodization in viscous glycerol, and can be related with current oscillations occurred during anodization [16]. At 50V, as it was visible in SEM images in other previous work [14] and 40V in current research, the rings on the side-wall of nanotubes can be seen as well, like in the case of nanotubes prepared at 30V, too.

The length of nanotubes is correlated with the working conditions. For example, when anodization was performed in ethylene glycol (other viscous electrolyte) with addition of 0.3wt.% NH$_4$F and 2 vol.% H$_2$O for 18 h at different constant potentials, the tube length grew while increasing the voltage [11]. For the 50V potential, we previously reported short nanotubes of about 300nm[14]. In this work, at 40V, the nanotube length is near 500nm, in cross-section image from figure 2A, taken from the place where the sample was scratched. When the voltage was lowered to 30V, the nanotube's length was increased to around 1µm, as can be seen from figure 2A. It seems that in this electrolyte, the nanotube length is increasing with the decrease of voltage.

From literature data, the dimensions of the nanotube-layers, such as diameter and thickness, are strongly related to the electrochemical conditions employed [16]. In previous work, we reported an internal nanotube diameter, at 50V, around 70nm [14]. At 40V, in the same working conditions (the same electrolyte and potentiostatic anodization with increased voltage from 0 to a certain value with a 2V/ 10 s rate), the average nanotubes internal diameter is around 80 nm. At 30V, the average is around

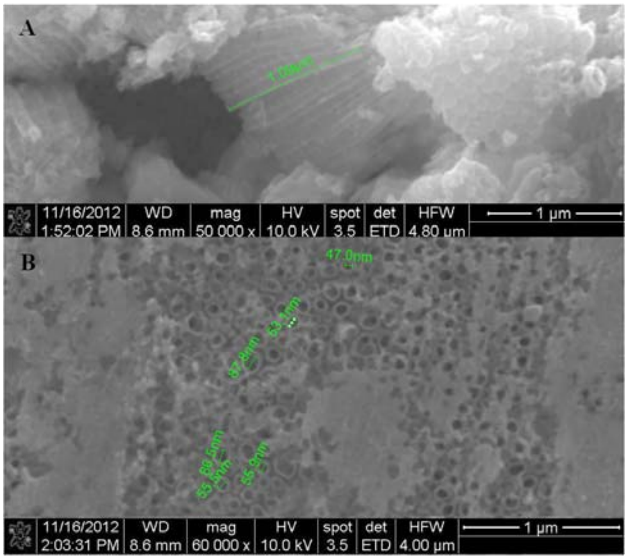

Fig. 3. A - Cross section and B-top-view SEM pictures from a TiO_2 nanotube Layer formed in polyethylene glycol 400 at 30 V

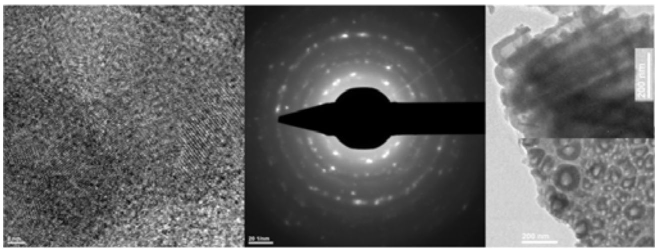

Fig. 4. TEM images for obtained nanotubes layers at 40 V

60nm. From SEM and TEM images in figure 2-5, it is visible that the nanotubes internal diameter is not the same all over the sample. But as can be noticed from the images (fig. 2-5), in the case of 40V and 30V, the nanotubes walls are much thinner, as compared to those reported previously at 50V [14].

The influences of applied potential over the diameter and length of the nanotubes are summarized in table 1.

In literature it was reported that the as-prepared nanotubes at lower potentials are amorphous but with increasing voltage they can be converted into a crystalline phase such as anatase or rutile [17]. For samples prepared at 40V or 30V, the TEM images from figure 4 and 5 revealed amorphous phases with a certain degree of crystalline phase.

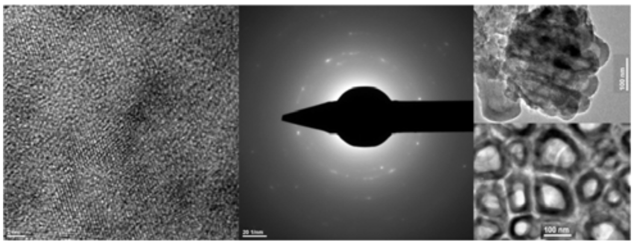

Fig. 5. TEM image for obtained nanotubes layers at 30 V

Table 1

TiO_2 NANOTUBES DIAMETER AND LENGHTS AT 30 V, 40 V and 50 V

	Voltage		
	30 V	40 V	50 v
Nanotubes lenght	1 µm	500 nm	300 nm
Nanotubes Internal diameter	60 nm	80 nm	70 nm

Typical micrographs and EDX spectra are shown in figure 6. It can be seen that C and F atoms from the electrolyte are still present, despite the fact that samples were thoroughly rinsed with purified water after anodization.

For some applications, such as those in the field of solar cells, covered nanotubes are not beneficial [18]. It was shown that when an as-delivered Ti piece is anodized, the surface deformation lead to the formation of the “nanograss” on top of nanotubes [18]. When anodizing is performed on polished Ti samples, a thin rutile layer formed in the beginning of anodization prevents the attack of the tube tips, so uncovered nanotubes are obtained [18]. In our work, all the samples were polished, but still the obtained nanotubes are covered. An attempt to reduce the shielding was by reducing voltage. Because EIS measurements showed changes in nanotubes after they were subject to ultrasonic bubbles [14, 19], another attempt to reduce the shielding was the exposure to ultrasonic treatment in water bath. We have prepared nanotubes by potentiostatic anodizing at 50V and subject the resulting sample to ultrasonic treatment for 10 min. In previous work SEM images revealed that not the entire nanotubes surface

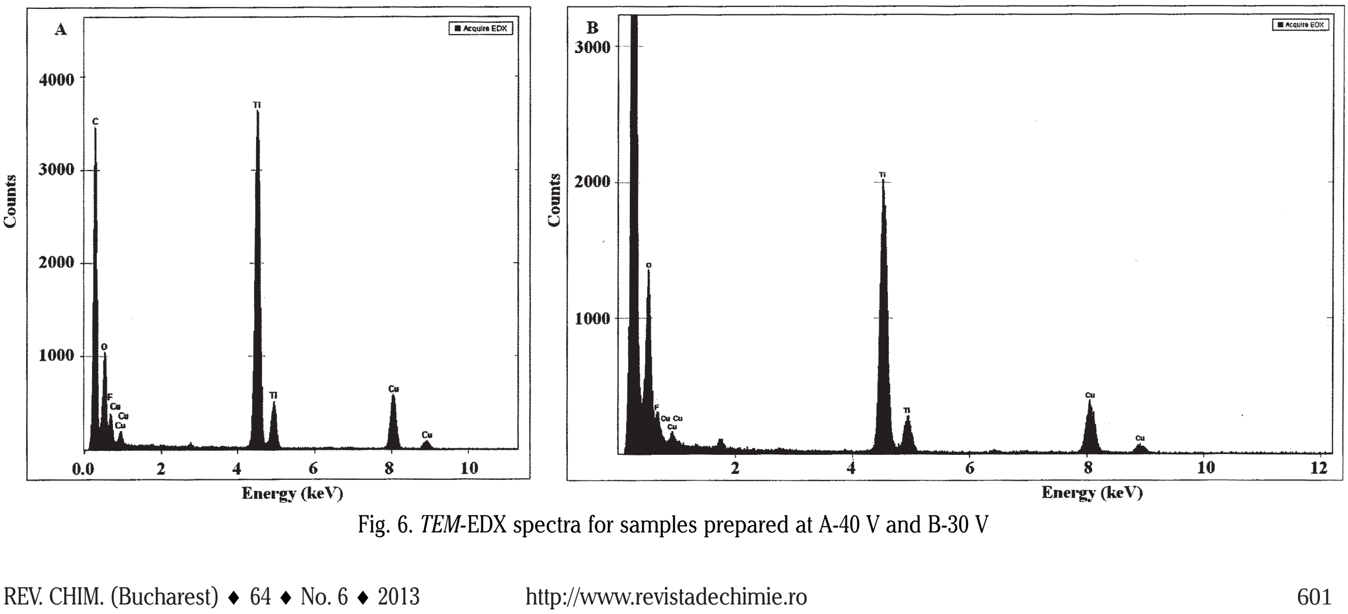

Fig. 6. *TEM*-EDX spectra for samples prepared at A-40 V and B-30 V

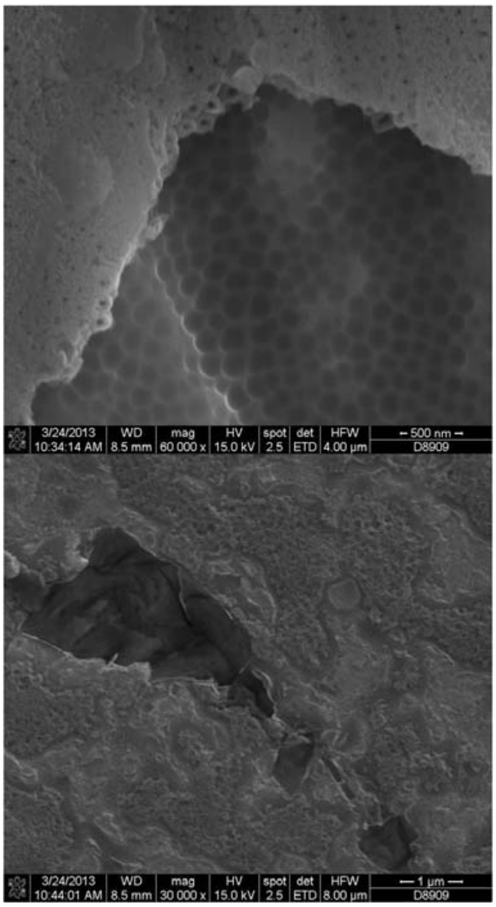

Fig. 7. Top-view SEM pictures from a TiO_2 nanotube layer formed in polyethylene glycol 400 at 50 V, after 10 minutes of ultrasound treatment

the shielded, that the shielding was not continuous [14]. SEM images presented in figure 7 reveal a diminishing of the shielding in some parts (nanotubes are visible below the shielding), but the destruction of nanotubes occurs in other parts were the shielding was not present, after 10 min of ultrasonication.

Conclusions

In this paper well-ordered controlled diameter TiO_2 nanotubes were obtained by potentiostatic anodization of titanium. By reducing the potential from 50V to 40V and then to 30V, the length of the naotubes has been increased and their internal diameters were modified. Also, as the voltage was reduced, the wall thickness of the nanotubes decreased, the surface roughness increased, and visible rings were observed on the side-walls in all the considered situations.

By lowering the voltage, we were able to reduce the shielding effect, without damaging the nanotubes. Also, by ultrasonic treatment, the shielding influences were reduced but in some regions the TiO_2 structures were completely damaged. In any case, in this viscous electrolyte the obtained nanotubes are not completely uncovered.

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