

MICROSTRUCTURAL PROPERTIES OF TITANIUM DIOXIDE NANOTUBES PRODUCED BY ELECTROCHEMICAL ANODIZATION

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The nanotubes of titanium dioxide were produced by electrochemical anodization of metallic titanium in a fluorine-containing electrolyte. The influence of the electrolyte composition, voltage and time of anodization on the geometric characteristics of the synthesized nanotubes was investigated.

Introduction

Recently one of the researchers' attention objects is titanium dioxide nanotubes. Due to its adsorption, optical, electrical and catalytic properties the titanium dioxide is widely used in molecular electronics [1], solar energy [2-5] and photocatalysis [6].

The materials based on titanium dioxide nanotubes exhibit the necessary physical and chemical properties, which depend primarily on its obtaining conditions. There are several methods for producing titanium dioxide nanotubes. One of them belongs to a group of researchers led by Professor Latika Menon [7] from Northwestern University (USA). This method consists in carrying out the electrolysis of the chloride salts solution in the presence of a titanium foil. As a result of the electrolytic reaction (with the release of chlorine in an aqueous medium), the surface of the titanium foil was oxidized, and under certain conditions it was transformed into a highly oriented structure. Another method for the preparation of ordered titanium dioxide nanotubes is electrochemical anodization of metallic titanium in the electrolyte, which includes hydrofluoric acid or concentrated hydrogen peroxide [8]. However, these methods except the positive characteristics, such as controlled geometric characteristics of nanotubes, high surface area, high light absorption ability, also have negative characteristics: toxicity of anodization, the necessity of strict control of the temperature of environment and electrolyte, which requires additional equipment and cost. In addition, synthesized nanotubes have amorphous structure.

One of the methods for the preparation of titanium dioxide nanotubes is the anodic oxidation of metallic titanium in the fluorine-containing electrolyte. Parameters of nanotubes can be controlled by varying the oxidation conditions (voltage, time, composition of the electrolyte). Analysis of publications devoted to the synthesis of TiO₂ nanotubes in the fluorine-containing electrolyte, has shown that many of the works contradict each other and most of their claims are not supported by experimental data.

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This paper presents the results of highly ordered TiO₂ nanotubes synthesis, obtained by a two-step electrochemical anodization of metallic titanium in the fluorine-containing electrolyte while changing the composition of the electrolyte, voltage and anodization time.

Experimental part

The titanium foil with 120 microns thickness was subjected to chemical polishing in 100 ml of a solution which comprises: sulfuric acid - 60%, hydrofluoric acid - 25%, glycerol - 15%. The polishing the surface the titanium foil is mounted on the cathode, the anode was titanium platen. The polishing process occurs at a voltage of 20 V with vigorous solution stirring for 10 minutes. After polishing the sample was washed with distilled water, dried and then it was divided into the 2x1 cm plate. Before anodization the sample was sonicated into a 2 M HCl solution and acetone for 10 minutes to remove the surface dirt and degreasing.

As the electrolyte bases the ethylene glycol with NH₄F content and H₂O was used. Anodic oxidation of titanium was carried out in potentiostatic mode, in an electrochemical cell at temperature of 5-70 C. As the cathode platinum foil was used, as the anode - anodized material. The distance between the anode and cathode was 3 cm.

Electrochemical oxidation process consists of two stages, the first: anodization for 2 hours. The separation of formed film at the first stage was carried out in an ultrasonic bath with 1 M hydrochloric acid solution. The sample was then washed with much deionized water and dried at a temperature of 800°C. The second stage was the same as the first one.

Results and discussion

The surface morphology of the porous titanium oxide obtained by a scanning electron microscope MIRA 3LMU (Tescan, Czech Republic) is shown in Figure 1. The film was prepared in a mixed solution of ethylene glycol, NH_4F (0,5%) and H_2O (3%) at anodization voltage of 50 V.

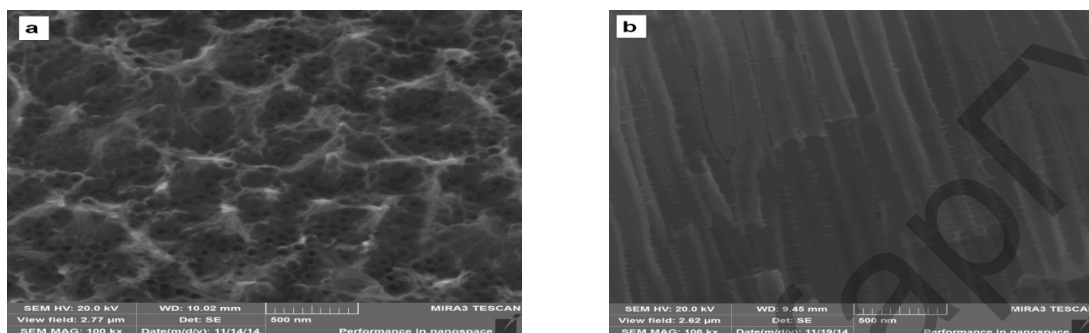


Figure 1. Micrographs of Ti foil after the first stage of anodization: a) the surface; b) cross-section.

The picture shows (Figure 1, a) that there are titanium dioxide nanotubes were formed on the surface of the titanium foil. They have a disordered structure and placed perpendicular to the base. On the surface there is a large amount of dirt and cracks. According to the literature [9-10], the source of pollution are by-products of hydrolysis $[\text{TiF}_6]^{2-}$. Their presence leads to low adhesion of the films, which further limits its use. The repeated anodization of titanium foil, after removing the first anodization film, is one of the ways of structuring the surface, removing contaminants and increasing the adhesion of the synthesized nanotubes.

After the second stage of the anodization the obtained TiO_2 nanotubes were sonicated to remove the byproducts and the surface oxide layer, washed with much distilled water and dried in a stream of nitrogen. Crystallization of the amorphous phase of TiO_2 was performed by the thermal treatment of samples in an oven at 450 °C for 3 hours while increasing the temperature at 50 °C per minute.

SEM images of porous titanium oxide are shown in Figure 2.

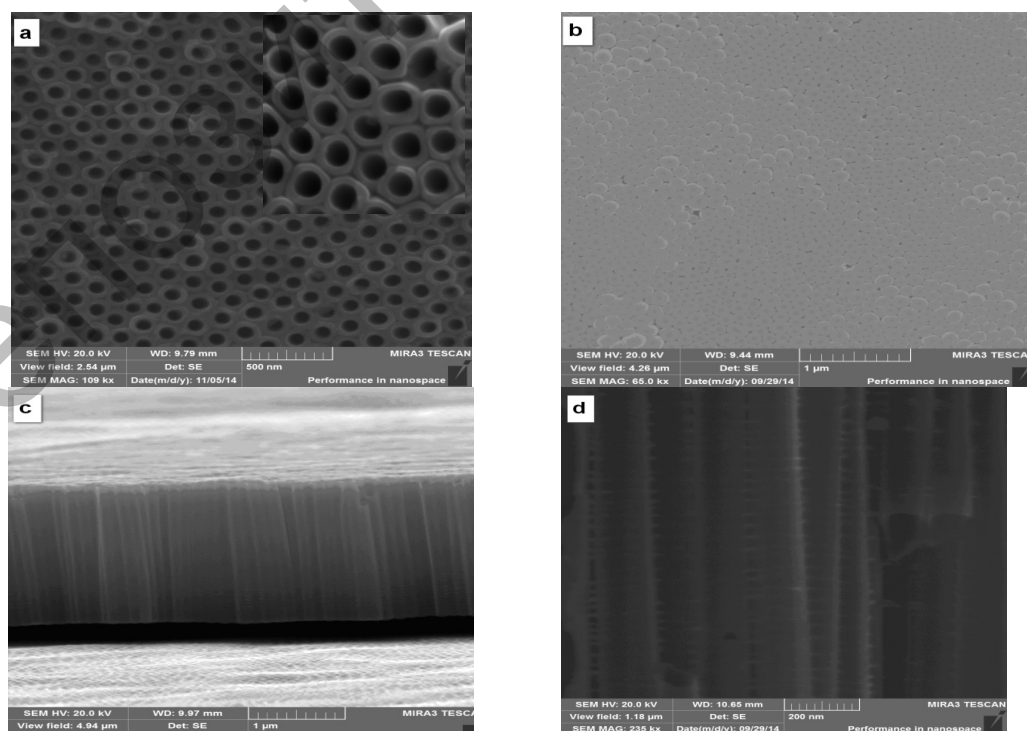


Figure 2. Microstructure of titanium dioxide nanotubes: a – surface; b – barrier layer; c and d – cross-section.

Investigation of the ammonium fluoride (NH_4F) quantity effect in the electrolyte on the geometrical characteristics of obtained TiO_2 nanotubes was performed on samples obtained at 50 V and at temperature 5-7 °C at the duration of the second anodization stage of 1 hour. H_2O and NH_4F content in the electrolyte was varied from 0.1 to 0.5 (wt.%) and 2-6 (wt.%), respectively.

Table 1. NH_4F content effect on the length increasing of titanium dioxide nanotubes

Content of NH_4F , wt. %	The length of titanium dioxide nanotubes, μm				
	Content of H_2O , wt. %				
	2	3	4	5	6
0,1	10	10	2,5	2	1,2
0,2	11	11	6	3	2,2
0,3	12	9	7	6,6	4,5
0,4	3	7	9	8	5,3
0,5	8,5	10	11	9	6

The experimental data presented in Table 1 shows that in the electrolyte consisting of ethylene glycol, 0.3 wt.% NH_4F and 2 wt.% H_2O the titanium dioxide nanotube growth rate is the highest. However, the coatings obtained under these conditions, exhibit poor adhesion to the surface of the metallic titanium, and the drying occurs at a partial TiO_2 peeling from the titanium foil.

When the water content in the electrolyte is 2–6 wt.% the adhesion of the TiO_2 film to the surface of the titanium foil increases. TiO_2 nanotubes, obtained at the H_2O content of 4 wt. %, have a high bonding strength with titanium substrate. This conclusion is based on the results of measurements of films microhardness by Vickers and by the absence of delamination of the oxide layer from the substrate during drying.

The establishment of voltage influence on the structure of synthesized titanium dioxide nanotubes was carried out at temperature of 5-7 °C in the range from 10 to 80 V in the electrolyte with following composition, 0,5 wt.% NH_4F , 3 wt.% H_2O and 97.7 wt.% ethylene glycol. The duration of the second stage of the anodizing was 1 hour.

Table 2. Influence of voltage on the inner diameter and the density of titanium dioxide nanotubes

№	Voltage, V	Inner diameter of nanotubes, nm	Density of nanotubes, $10^9/\text{cm}^2$
1	10	10	26
2	20	40	25
3	30	60	22
4	40	70	11
5	50	95	6
6	60	105	2,5
7	70	110	0,5
8	80	110	0,5

The formation of highly ordered and open nanotubes occurs at a voltage of 20–60 V. With increasing anodization voltage the inner diameter of nanotubes increases, but the number of nanotubes per unit area falls. The packing density of the titanium dioxide nanotubes was determined from the micrographs obtained by scanning electron microscope.

At voltages < 20 V the closing of nanotubes occurs, due to formation of the byproducts dense layer on the TiO_2 surface, which is formed by the hydrolysis of complex anions $[\text{TiF}_6]^{2-}$. Hydrolysis occurs due to the fact that the nanotube has pH gradient from the lower value at the bottom, to a larger near the mouth of the nanotubes [9]. With increasing the voltage above 60 V the tubes distribution over the surface becomes disordered.

From electron microscopic data it follows that the distance between the centers of the nanotubes depend on the voltage. This makes it possible to obtain arrays of nanotubes with certain packing density of nanotubes per unit area. From the micrographs it was also found that the wall thickness of the nanotubes doesn't depend on the voltage and it is 8-10 nm.

Investigation on the anodization duration influence on the titanium dioxide nanotube structure was carried out on samples synthesized at voltages of 50 V and a temperature of 5-7 °C in an electrolyte with following composition: NH_4F (0,5%) and H_2O (3%). The duration of the second stage of the anodization varied from 1 to 30 hours.

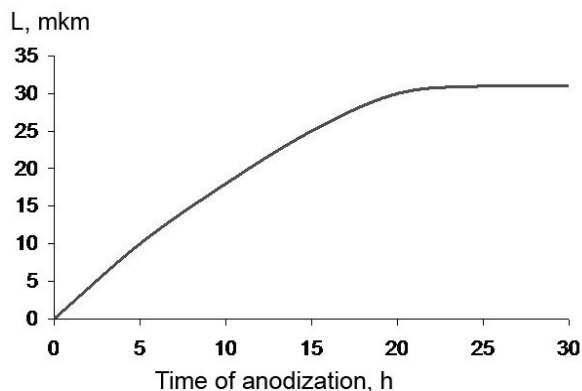


Figure 3. The dependence of the nanotubes length (L) on the duration of the second stage of anodization.

Figure 3 shows that in the early hours of anodization the nanotubes length increases linearly with anodization time and then, reaching 25-30 μm , the rate of nanotubes formation decreases.

The obtained data revealed that with increasing length of the titanium dioxide nanotubes the electrochemical oxidation rate falls. As a result of this the activity of fluoride ions is redirected from the bottom of nanotube to its sidewalls. This leads to the fact that with increasing anodization duration the wall thickness reduces and the inner diameter of the nanotubes is growing.

Conclusion

Thus, by the two stages electrochemical anodizing of metallic titanium in the fluorochemical electrolyte the highly ordered arrays of titanium dioxide nanotubes were synthesized, they were directed perpendicularly to the substrate. It was found that the electrolyte consisting of ethylene glycol, NH_4F (0,3 wt.%) and H_2O (2 wt.%) allows to receive the highest growth rate of titanium dioxide nanotubes. However, the array of nanotubes was characterized by a low adhesion with the metal substrate. When the water content in the electrolyte was 2 – 6 wt. % the adhesion of the TiO_2 film to the foil surface increased. With the growth of the anodization voltage the inner diameter of the nanotubes increased, but the number of nanotubes per unit area decreased. Found that the wall thickness of the titanium dioxide nanotubes depends on the duration of the anodization.

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