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First-order phase transition in nanotubular titanium dioxide

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Titanium dioxide (TiO_2) nanotubes array with the length of $16\,\mu$m and the outer diameter of 100 nm were synthesized by anodic oxidation of titanium foil in an electrolyte solution containing a fluorine-containing solution of ethylene glycol. The selected synthesis conditions make it possible to separate the nanotubular array from the titanium foil and study it as a homogeneous functional material. The performed scanning electron microscopy study and Brunauer–Emmett–Teller analysis allowed to get data on the morphology of the samples. X-ray diffraction, thermogravimetric, and differential scanning calorimetry analysis made it possible to determine the temperature of the phase transition of the amorphous state into crystalline anatase (sp.gr. $I4/amd$). Observed phase transition of first order takes place at temperature about 350°C.

Keywords: nanotubular titanium dioxide films, anodic oxidation, phase transition, anatase, TG, DSC.

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1. Introduction

At present, nanostructured titanium dioxide TiO_2 is a promising functional material [1] for such areas as renewable energy sources [2], inorganic sorbents [3], resistive memory cells [7], photocatalysts [4,5], including those for hydrogen energy [6].

Currently, there are many methods for the synthesis of nanostructured TiO_2 with different morphology and structure: hydrolysis of titanium salts [9,10], sol-gel [11,12], hydrothermal synthesis [13], as well as anodic oxidation [7,14,15].

There are four most common phase states of titanium dioxide, namely amorphous, anatase, brookite, and rutile. According to the literature, the temperature of the phase transition from the amorphous state to anatase differs for various synthesis methods and depends on the final particle morphology [10,14,16]. At the moment, there are no works on thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) for nanotubular titanium dioxide separated from the substrate, synthesized by the anodic oxidation method. According to the DSC [15] data, there are no direct data on the phase transition to the crystalline phase on TiO_2 nanotubes obtained by anodizing titanium foil. In this regard, the aim of the work is to obtain a nanotubular layer of titanium dioxide by anodic oxidation, to study its morphology and phase transformation during thermal treatment.

2. Experimental part

Nanotubular titanium dioxide was synthesized by anodizing titanium foil 200 mkm thick on a Digma unit, consisting of an electrochemical cell, a thermostat, and a power source [7]. Before being applied, the foil was placed in an acid solution ($HNO_3:HF:H_2O = 1:1:20$), and then washed with distilled water. Anodizing was carried out in a potentiostatic mode at a voltage of 60 V for 60 min while maintaining the electrolyte temperature at a level of 20°C. A fluorine-containing solution of ethylene glycol was used as an electrolyte with adding water in the proportion $NH_4F:H_2O_{dist}:C_2H_6O_2 = 1:2:98$ by mass. All chemical reagents had an analytic grade purity class. After anodizing, the sample was removed from the electrochemical cell and washed with a running stream of distilled water, then dried. Subsequently, the layer of titanium nanotubes was separated mechanically. TiO_2 was annealed in air in a SNOL muffle furnace at temperatures of 180, 240, 300, and 350°C for 4 h.

X-ray diffraction analysis (XRDA) of the synthesized TiO_2 nanotubular layer was performed in $CuK_{\alpha 1,2}$ radiation on a STOE „STADI-P"diffraction instrument. The X-ray diagrams were taken in the step-by-step scanning mode with $\Delta(2\theta) = 0.03^\circ$ in the range of angles 2θ from 10 to 80° with high statistics. Polycrystalline silicon with a lattice spacing of 543.07 pm was used as an external standard. The phases were identified using „Powder Standards Database — ICDD, USA, Release 2016". Phase analysis was carried out using Powder Cell 2.4 software.

The TiO_2 nanotubular layer, previously separated from the titanium foil, was ground in an agate mortar.

A Gemini VII 2390 analyzer was used to determine the specific surface area. The nitrogen adsorption and desorption isotherms obtained at a temperature of 77.3 K were processed in accordance with the Brunauer–Emmett–Teller (BET) theory. Preliminary degasation was carried out at a temperature of 150°C with further use of helium. The study of nanotube morphology was carried out on a scanning electron microscope (SEM) SIGMA VP (Carl Zeiss) in high vacuum mode with a secondary electronic detector (InLens). The studies by differential scanning calorimetry (DSC) and thermogravimetry (TG) were carried out without preliminary heat treatment of the synthesized TiO_2 nanotubes on a Netzsch STA 409 PC Luxx TG-DSC analyzer. The samples of the nanotubular layer were heated in a alumina crucible in an argon atmosphere at a rate of 20°C/min.

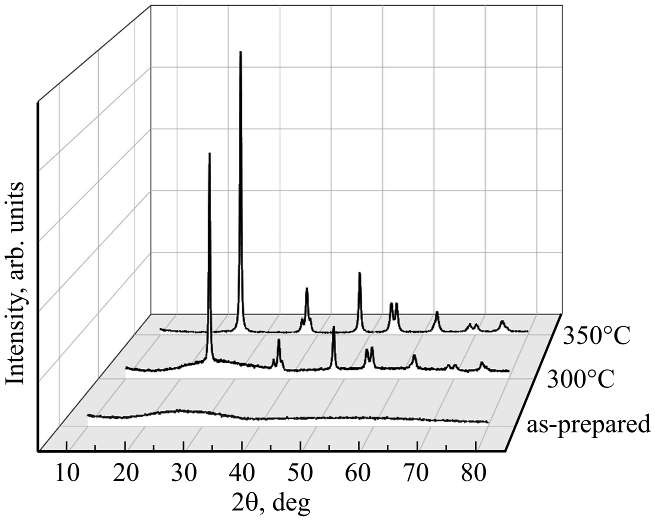

Figure 2. The X-ray diagrams of synthesized nanotubular titanium dioxide and annealed at different temperatures in air.

3. Results and discussion

According to the SEM-micrographs (Fig. 1), the nanotubular layer of titanium dioxide synthesized by anodic oxidation reached a thickness of approximately 16 mkm, the diameter of the nanotubes was approximately 100 nm, and the thickness of the tube walls — approximately 35 nm. The synthesis conditions proposed in this work allowed to obtain large (several cm^2) nanotubular layers that can be easily separated mechanically.

The X-ray diagrams of the synthesized nanotubular layer and samples annealed at temperatures of 300 and 350°C are shown in Fig. 2. According to XRDA data, the synthesized TiO_2 nanotubular layers have an amorphous structure. Annealing at 300°C for 4 h leads to the formation of the anatase phase. The presence of a diffuse halo after annealing at 300°C for 4 h in air indicates incomplete crystallization. Annealing in air at a higher temperature, namely at 350°C for 4 h leads to the completion of the phase transition from the amorphous state to the crystalline state, the formation of a completely crystalline phase anatase occurs. According to full-profile analysis data, as a result of the phase transition, titanium dioxide was formed in the anatase phase with a tetragonal structure (sp. gr. $I41/amd$) with crystal lattice parameters: $a = b = 379.29$ pm, $c = 948.46$ pm, $\lambda = \beta = \gamma = 90°$, which corresponds to the anatase phase according to the literature [6].

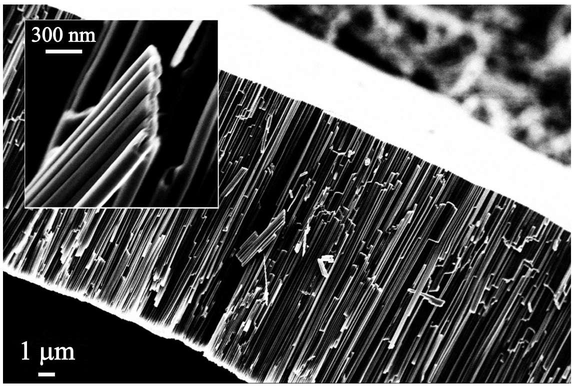

Figure 1. Micrograph of the TiO_2 nanotubular layer cross section. The inset shows individual nanotubes.

According to the analysis of the specific surface, the value of the specific surface area of the synthesized nanotubular layer of titanium dioxide is approximately 14 m^2/g, annealing at 180 and 240°C for 4 h does not significantly change the value of the specific surface area, and increasing the temperature to 300°C slightly increases the value of the specific surface area to 18 m^2/g (Fig. 3). Annealing at a temperature of 350°C leads to a significant increase in the specific surface area to 51 m^2/g. An increase in the specific surface area can be caused by several factors: firstly, nanotubes that are tightly adjacent to each other as a result of heating and further cooling are partially separated from each other, which leads to the formation of new surfaces, secondly, at heat treatment, organic electrolyte residues decompose into carbon dioxide and water, which leads to purification of the inner surface of nanotubes.

Figure 4 shows the results of TG-DSC analysis of nanotubular titanium dioxide. According to the TG curve, the mass loss occurs in several stages. At the first stage, up to 250°C, physically adsorbed water and ethylene glycol are removed from the surface of the TiO_2 nanotubular array. The weight loss due to this desorption is approximately 1.3%. This process is accompanied by an extensive endothermic peak on the DSC curve. At the second stage, an active weight loss occurs in the temperature range from 250 to 400°C — by 8.4%, associated with the thermal decomposition of ethylene glycol into water and carbon dioxide. This section corresponds to three exothermic peaks on the DSC curve.

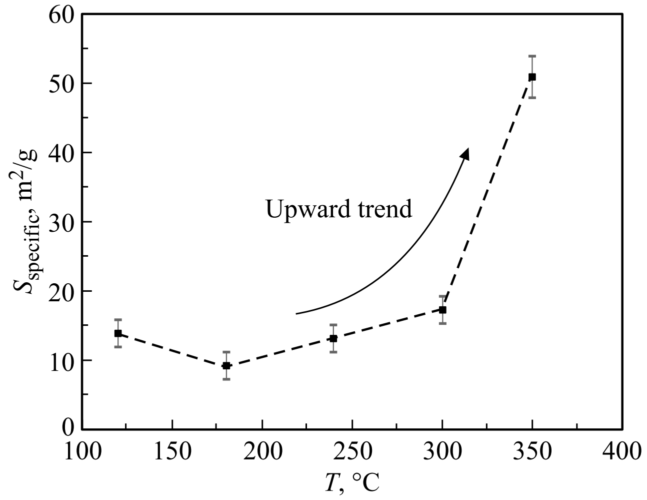

Figure 3. Dependence of the specific surface area of nanotubular titanium dioxide on the annealing temperature in air.

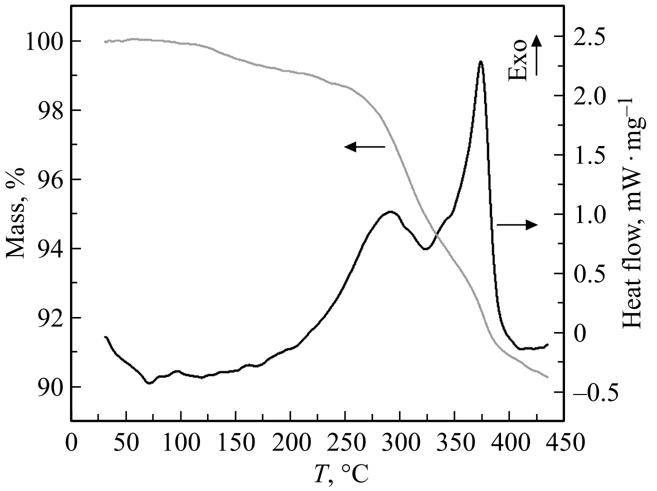

Figure 4. TG-DSC analysis of nanotubular titanium dioxide.

The peaks on the DSC curve with a maximum at 290 and 372°C are accompanied by the highest mass loss rate and refer to the thermal decomposition of ethylene glycol, which is consistent with the data of earlier works [15,11,13]. Between the peaks on the DSC curve in the range from 325 to 350°C, there is a shoulder with a weak exothermic effect, accompanied by a flat section on the TG curve. The phase transition of TiO_2 from the amorphous phase to the crystalline phase with the anatase structure occurs (sp. gr. $I4/amd$) in this temperature range. Since the phase transition is accompanied by a stick-slip heat effect and does not satisfy the Landau criterion for second-order phase transitions, it can be argued that the ongoing phase transition is a first-order phase transition. A slight weight loss in this area is 1.4%, which is associated with the continued desorption of the electrolyte. It should be noted that this shoulder on the DSC curve in the work [15] is absent due to the endothermic peak from the decomposition of the organic solvent on the surface of the nanotubes, which overlaps the crystallization peak exotherm in the temperature range below 300°C. This effect is also confirmed by a strong weight loss — up to 5%. However, in the work [14] the crystallization temperature on TiO_2 nanotubes is comparable with the results of this work and is 343°C. The peak exotherm corresponding to the transition from the amorphous state to anatase is clearly visible on the DSC curve.

There are studies of DSC on nanoscale titanium dioxide with non-tubular particles. The crystallization temperature observed in the form of peak exotherms on DSC during the phase transition from the amorphous phase to the anatase phase is higher than on nanotubes: 385°C [16], 436°C [10], 400–480°C [17], and 360–450°C [9]. This is probably due to the smaller size of nanoparticles and their greater structural disorder.

4. Conclusion

The anodizing conditions proposed in this work allowed to synthesize thick films of titanium dioxide nanotubes (up to 16 mkm), which are easily mechanically separated and allow to use them in practice without titanium foil.

Using XRDA and DSC methods, it was established that the first-order phase transition of the amorphous phase–anatase occurs at temperatures over 240°C, and the maximum intensity of the process is observed at temperatures approximately 350°C.

According to XRDA and BET data, annealing leads to a change in the atomic structure, an increase in the specific surface area from 14 to 51 m^2/g, and surface cleansing of organic impurities, which is very important for the practical application of nanotubular titanium dioxide in photocatalysis.

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Conflict of interest

The authors declare that they have no conflict of interest.

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