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Research of the TiO_2 nanotubes formation by AC-DC electrochemical anodizing

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Abstract. The present paper has represented results of research of nanoporous TiO_2 formation process under electrochemical anodizing by direct current with an overlapped variable component. It has been shown that overlapping of the variable component with frequency 100 Hz–10 kHz leads to increase of the growth rate and qualitative change of the nanoporous TiO_2 coating structure – open inter-tube space appears, inter-tube “bridges” are generated and form of the nanotube section becomes “rounded”.

1. Introduction

Interest to the titanium oxide is connected with its unique physical and chemical properties. Nanoporous titanium oxide is one of promising and required materials for photocatalysis and adsorption. Traditional method to synthesize nanoporous TiO_2 is electrochemical anodizing by direct current. TiO_2 structure depends on substrate morphology, electrolyte composition and temperature; however main parameter determining structure parameters is a value of anodizing voltage. Possibility to control TiO_2 structure is practically valuable because the structure determines physical and chemical properties of the coating (catalytic activity, etc.) [1–9]. So, search of new methods to control a structure of the nanoporous titanium oxide is important. Most researches of nanoporous TiO_2 formation have been executed under DC anodizing voltage. Papers [10–14] showed a possibility to control a structure by step change of voltage; besides typical time intervals of the voltage change is amounted to tens-hundreds seconds. Influence of AC voltage overlapping with frequency 1 Hz–100 kHz on DC anodizing voltage has not been researched in details. It explains importance and novelty of the performed work directed at study of nanoporous TiO_2 formation process under electrochemical anodizing by direct current with an overlapped AC component.

2. Experiments methods

Specialized test stand (figure 1) has been assembled for experimental researches of the nanoporous titanium oxide synthesis under overlapping of the AC component. The test stand includes two identical cells for performance of anodizing process. Only DC voltage was applied to one of cells and combined AC-DC voltage obtained from a source of DC voltage and generator – to other one. Control of anodizing current was performed by means of current shunts (resistors *R*1, *R*2) and digital oscilloscope. Control of voltage at the cell was performed from the resistor divider output of which was connected to the oscilloscope.

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Electrolyte on the basis of ethylene glycol containing NH_4F 0.3 % (mass.), H_2O 0.5 % (mass.) was used. DC voltage component was varied within 30–80 V, AC component had a sinusoidal form, amplitude 2–10 V and frequency 1 Hz–100 kHz.

Titanium plates of the trademark VT1-0 were used to obtain experimental samples. Final polishing of plates was performed using diamond paste NOM 0,5/0 up. After polishing, plate surfaces were processed by ultrasound in 5 M solution HCl within 40 min. Then within 30 min washing was fulfilled in acetone and after – in ethanol within the same period of time. At the conclusive stage they were washed by distilled water. Obtained samples of the nanoporous TiO_2 coating were researched by a scanning election microscope JEOL JSM-6610LV.

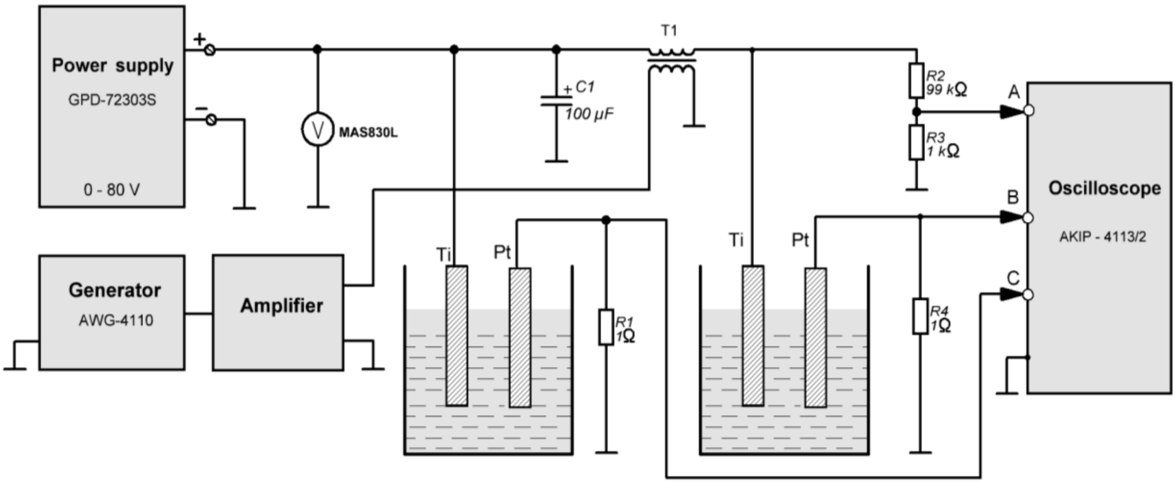

Figure 1. Electric circuit of the experimental test stand for obtaining of the porous TiO_2 under overlapping of the AC voltage component on to DC voltage one.

3. Results and discussion

Experimental researches have determined that maximum thickness of coatings under DC and AC-DC modes does not depends on a form of voltage anodizing and it is amounted to 10–12 µm for the present experiment (figure 2).

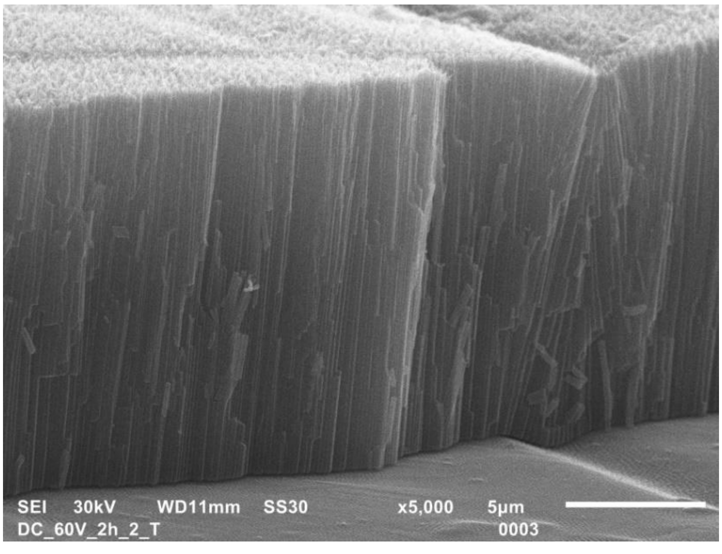

Figure 2. SEM-image of the nanoporous titanium oxide coating (anodizing DC voltage – 60 V).

Analysis of time dependencies of anodizing current for various modes has shown that the initial value of anodizing current under AC-DC mode is higher in 15–20 % in comparison with DC mode and "shelf" is observed with enough high current value (75 % of the maximum value) on time current diagram under AC-DC mode after which current sharply falls and becomes lower than an actual value at direct current. Change of the sample thickness has shown that after current fall growth of the coating terminates. Time to achieve TiO_2 level thickness up to a nominal value under AC-DC mode is less in 5–7 times that under direct voltage (under AC-component being equal to 10 % of DC-component). Figure 3 represents images of sample surfaces of nanoporous TiO_2 obtained under DC and AC-DC anodizing voltages. It is obvious that under overlapping of the AC voltage component typical change of the nanoporous titanium dioxide structure happens: form of nanotubes becomes "rounded", open inter-tube space appears, typical diameter in comparison with direct current slightly changes. Under anodizing voltage 60 V overlapping of the variable component in 10 V (1 kHz) leads to increase of a pore diameter in 25 %.

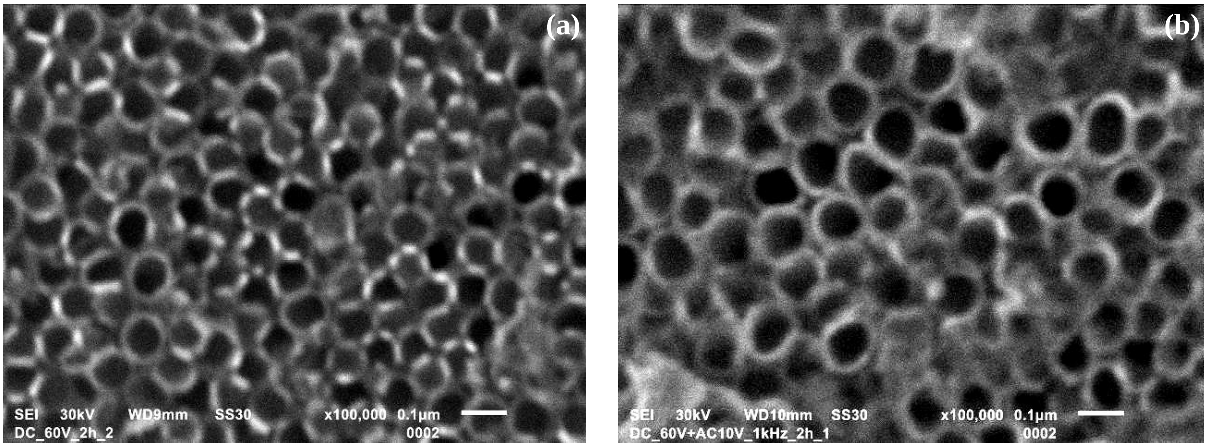

Figure 3. Structure of the nanoporous titanium oxide surface under various modes of anodizing: **(a)** – DC voltage, 60 V; **(b)** – AC-DC voltage (60 V DC + 10 V AC 1 kHz).

Image of a cross-section of the coating structure (figure 4) shows that under overlapping of the AC component inter-tube "bridges" are formed with thickness about 20 nm at distance 50–100 nm from each other.

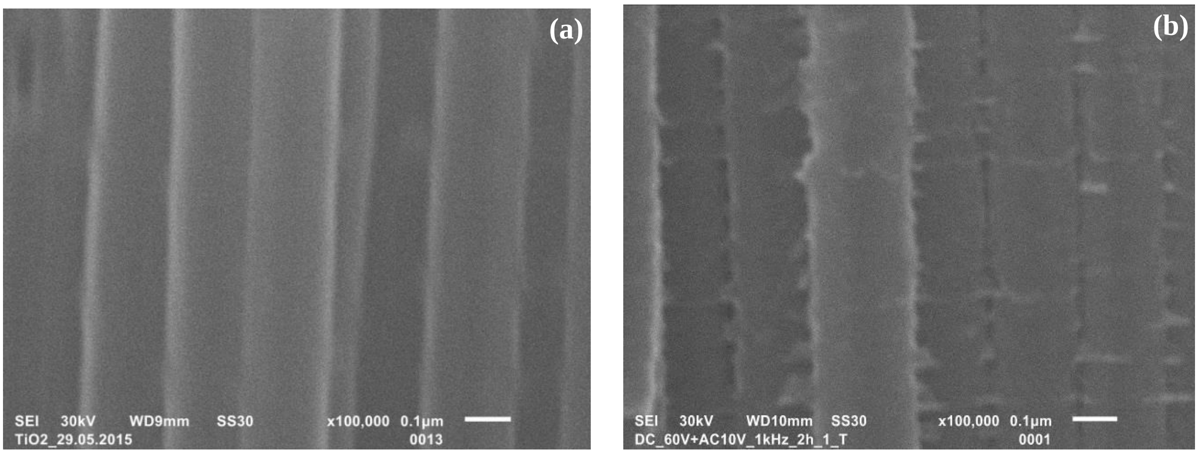

Figure 4. Image of a cross-section of the coating structure of the nanoporous titanium dioxide structure: **(a)** – DC voltage, 60 V; **(b)** – AC-DC voltage (60 V DC + 10 V AC 1 kHz).

Visual influence of frequency on characteristics of the coating structure appears within the frequency range 100 Hz–10 kHz. Under lower and higher values of frequency influence of the variable component is insignificant and geometrical characteristics of the coating structure are not practically different from characteristics under direct current.

Results can be interpreted as increase of the pore growth rate to the deep of titanium under overlapping of the current variable component. Additionally inter-tube space begins to be etched and opened that leads to rounding of the pore form and qualitative change of geometrical parameters of the growing nanoporous titanium oxide surface – appearance of horizontal «bridges» in space between tubes. Explanation of the observed occurrence can be a supposition that capacitive current passing through the lower barrier level of the pore causes a change (increase) of its transport properties in relation to ions penetrating through it that determines an increase of pore growth process rate.

4. Conclusions

Data on influence of overlapping of the anodizing voltage AC component within frequency range 100 Hz–100 kHz on growth rate, surface morphology, structure parameters of the nanoporous titanium oxide have been obtained. Conditions for titanium anodizing have been determined when formation of inter-tube «bridges» with thickness 20 nm at distance 50–100 nm from each other connecting separate tubes in the direction being perpendicular to their axis happens. It has been shown that under overlapping of AC-component (amplitude 10 % of DC-component value) rate of TiO_2 level formation increases in 5–7 times. Visible influence of AC-component appears within frequency range 100 Hz–10 kHz. The paper has determined that within mentioned range of frequencies the form of TiO_2 nanotubes becomes "rounded", open inter-tube space appears. So, the paper has shown that overlapping of the AC component provides a possibility to control characteristics of the coating structure. Obtained results have high practical importance for development of technologies to synthesize new types of catalytically active coatings based on the nanoporous titanium oxide.

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