

**Dikova Ts.D.**

## INFLUENCE OF TECHNOLOGICAL PARAMETERS ON TITANIUM NANOTUBES FORMATION

*Present paper deals with investigation of the influence of technological parameters on the titanium nanotubes formation on the surface of pure Ti Grade-2 and Ti-6Al-4V alloy in anodization with graphite cathode. The anodization was done in two concentrations of HF solution in different voltages and process duration. The surface morphology, chemical and phase compositions were investigated by SEM, EDAX and XRD-analyses. It was established that anodization in 0,5% HF solution allows obtaining of oxide layer with nano-tubular structure in narrow voltage range 30V +/-5V for the Ti-6Al-4V alloy and 20-25 V for the pure Ti Gr-2 in a relatively long process duration. The average inner diameter of the nano-tubes is close for the both materials (80 nm - 120 nm) and increases with increasing of process duration. The surface morphology at lower voltages characterizes with nano-roughness in short-term process which changes to TiO<sub>2</sub> nano-fibers with increasing of process duration. At higher voltages - 40 V for Ti-6Al-4V alloy and 30 V for pure Ti porous sponge-like structure of the oxide layer is observed. Higher 1,5% HF concentration leads to formation of nano-tubes after 30min process, while increased duration leads to the areas with different morphology – nano-tubes, porous microstructure and dense oxide layer.*

**Key words:** titanium, titanium alloy, anodization, titanium oxide nanotubes.

### Introduction

Pure titanium is an inert metal with good corrosion resistance which possesses mechanical properties and elastic modulus close to that of the bone tissues. That is why it is preferable material for production of implants. Good corrosion resistance and biocompatibility of titanium depends upon the formation of a solid oxide layer (TiO<sub>2</sub>) to a depth of 10 nm. Geometry, roughness and other characteristics of the implant surface also importantly influence the surface-tissue interaction. Biocompatibility of the implant can be enhanced by surface modification with different methods – mechanical, chemical, electro-chemical [1,2].

The biomimetic approach in surface treatment is the main tendency last years. According to it the surface topography of the implant should consists of hierarchical structure, composed of micro- and nano-components, which mimic the structure of the natural bone [3,4]. The microtopographies can promote osteoblast differentiation and bone-to-implant contact via mechanical interlocking, while they depress osteoblast proliferation [3]. Whereas the last year's investigations show that the nanotopography has played a critical role in accelerating the rate of cell proliferation and enhancing the tissue acceptance [5].

The TiO<sub>2</sub> nanotubes are of increasing interest as they can mimic the dimensions of the components of natural bone, because natural bone is composed of nanophase hydroxyapatite in the collagen matrix [6,7]. The presence of a vertically aligned TiO<sub>2</sub> nanotube surface on Ti foils had improves the proliferation and mineralization of osteoblasts [8]. The cell response depends on the nanotubes' diameter, thus on small-diameter nanotubes, increased cell adhesion and growth with minimal differentiation is prevalent, while on larger-diameter nanotubes, mesenchymal stem cells are forced to differentiate specifically into osteoblast cells [5]. It was established that 70 nm diameter is the optimum size for TiO<sub>2</sub> nanotubes implants to obtain favorable osteoconductivity and osseointegration [6].

The TiO<sub>2</sub> nanotubes can be prepared by various techniques: sol-gel method, electrochemical deposition and anodization [8,9]. Anodization is preferred to the rest two processes because it provides strongly adherent TiO<sub>2</sub> layer. The process itself is a rapid, simple and inexpensive ensuring large array of titanium nanotubes [10-12]. The TiO<sub>2</sub> nanotubes fabricated using this method are highly ordered and oriented perpendicularly to the substrate.

The nano-tubular structures are obtained during anodization in fluorine electrolyte solutions with applied voltage lower than the dielectric breakdown. The most of researchers use 0,5% HF electrolyte solution and platinum cathode for anodization process [4,8-12]. S. Oh et al. [5] fabricate nanotubes layers in a mixture of 0,5% hydrofluoric acid and acetic acid, while N. Wang et al. [6] and A. Roguska et al. [13] use glycerol electrolyte containing 0,3% NH<sub>4</sub>HF<sub>2</sub> or 0,86 wt.% NH<sub>4</sub>F respectively. In the most electrolytes containing fluorides, nanotubes can be grown with diameter of 40-150 nm at anodic voltages in the range of 5-30V [4-6, 8-13]. It was found that the diameters of nanotubes were determined by applied voltage while the final length of the tubes was independent of the anodization time. The thickness of the formed tubular-structure oxide layer can be from a few hundred nanometers up to a few microns by controlling pH and electrolytes.

The up to now studies have been focused preliminary on the samples of pure Ti. The data for fabrication of TiO<sub>2</sub> nanotubes on the surface of Ti-6Al-4V alloy, widely used for orthopedic implants, are insufficient.

### **Purpose**

The aim of the present paper is to investigate the influence of the technological parameters on the titanium nanotubes formation on the surface of pure Ti and Ti-6Al-4V alloy in anodization with graphite cathode.

### **Experimental methods**

Round samples with dimensions 24mm x 3mm (diameter x thickness) were made of commercially pure (CP) Ti Grade-2 (99,5%) and Ti-6Al-4V alloy with chemical composition: Al-5,7%; Fe-0,13%; V-3,8%, O-0,089%; Ti-the rest (wt.%). The samples' surface was grinded with sandpaper 300, 600 and

800. After grinding they were ultrasonically cleaned consecutively in acetone, ethanol and deionized water for 15 min in each media and dried with compressed air. On the next stage the samples were etched for 30 min in 0.5 wt.% HF acid, immediately rinsed with deionized water and dried. They were anodized in an electrolyte containing 0.5 wt.% HF acid using a DC power supply with a graphite electrode as cathode. We used different voltages: 20 V, 25 V and 30 V for the CP Ti samples and 20 V, 30 V and 40 V for the Ti-6Al-4V alloy. The process duration varied from 30min to 7 hours. As the anodization for covering the entire sample's surface with nano-tubular structure took too long time we made experiment with 1,5% HF solution for Ti-6Al-4V alloy. Immediately after anodization the samples were rinsed several times with deionized water and dried with compressed air. The surface morphology was observed and EDAX analysis was made on high resolution field emission scanning electron microscope FEI Quanta 400 ESEM FEG (ESEM2). The phase composition was investigated by XRD analyzer Rigaku D/Max in Cu K $\alpha$  irradiation.

### Results obtained

The samples' surface after grinding and etching is shown on Fig. 1. The grinded surface of Ti-6Al-4V alloy (Fig. 1a - 1) is smoother than that of the pure Ti Gr-2 (Fig. 1b - 1). Traces of abrasive paper can be seen on the surface of the both samples. After etching micro-roughness appears on the surface of Ti-6Al-4V alloy (Fig. 1a - 2 and 3) while on the samples of the CP Ti the micro/nano-roughness is observed (Fig. 1b - 2 and 3).

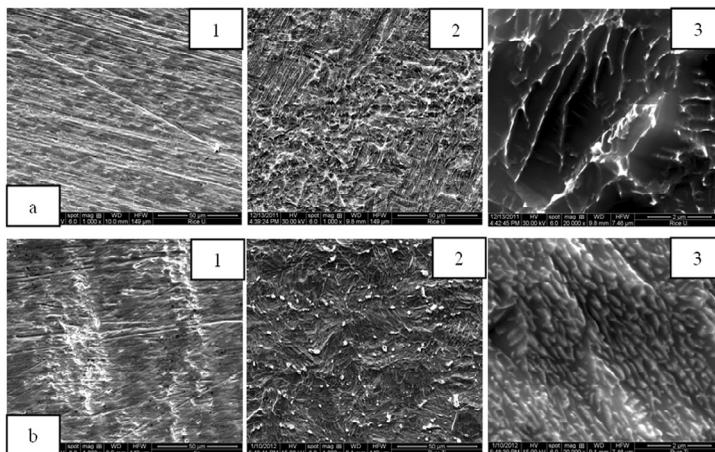


Fig. 1. Samples' surface of Ti-6Al-4V alloy – a and pure Ti Gr-2 – b after grinding – 1 and etching – 2 and 3

### *Anodization of Ti-6Al-4V alloy*

The short time anodization of 30 min produced only nano-roughness on the micro-roughened surface of Ti-6Al-4V alloy in the three different voltages applied (Fig. 2). Increasing the duration of 20V process caused nano-roughness on the entire surface and the peaks oxidation (Fig. 2b). The first Nano-Tubes (NTs) were observed after 3h anodization in voltage of 30V (Fig. 2d). Their average internal diameter was about 86 nm (Fig. 3) and they were located in small spots scattered over the whole sample's surface. The rest regions were characterized with nano-roughness of the oxide layer and beginning of tubular structures formation (Fig. 2e).

Increasing the process duration led to increasing of the surface covered with NTs as well as their internal diameter. After 6h anodization 80% of the sample's surface was already covered with NTs (Fig. 2f) with average internal diameter about 109 nm. After 7h anodization nearly 90% of the sample's surface was covered with NTs. They were well shaped with average internal diameter of about 114nm (Fig. 3). Their structure is amorphous, because clearly pronounced peaks only of titanium can be seen on X-Ray diffractograms after anodization of Ti-6Al-4V samples (Fig. 4).

The EDAX analysis of the region on Fig. 2f shows presence of the elements Ti, O, Al and V (Fig. 5a) which is evidence that NTs are made of TiO<sub>2</sub>. But it also means that the all alloying elements take part in the oxidation-reduction processes. After 3h anodization in voltage 40V about 30% of the surface was covered of layer with mainly sponge-like structure (Fig. 2g). Well shaped NTs could be seen in particular regions, while the rest part of the surface was characterized with nano-fibers (Fig. 2h).

The anodization of Ti-6Al-4V in 0,5% HF solution and graphite cathode for coverage of the entire surface of the sample with nano-tubular oxide layer took about 7 hours. To decrease the process's duration the experiments with 1,5% HF concentration of the electrolyte and voltage of 30V were done. The results showed presence of TiO<sub>2</sub> NTs after 30 min anodization (Fig. 6). Their average internal diameter was about 100 nm and they covered about 20% of the samples' surface. To increase the surface, covered with nano-tubes, the anodization time was increased. After 1h anodization the NTs covered about 30% of the surface sample. Nano tubular structure was not observed in further increase of process duration. After 2h anodization the oxide layer possesses rather porous micro-structure which remains in most of the surface after 3h process. But then in some regions dense and thick oxide layer with many cracks could be observed.

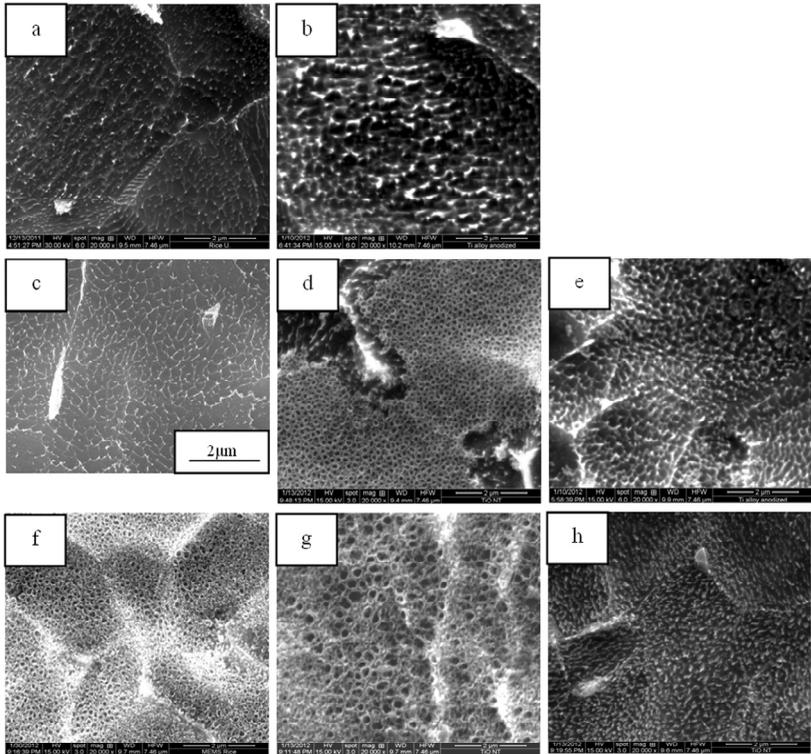


Fig. 2. Surface morphology of Ti-6Al-4V samples after anodization with different voltage and duration: 20V, 30min – a; 20V, 3h - b; 30V 30min - c; 30V, 3h - d and e; 30V, 6h - f; 40V, 3h - g and h

#### *Anodization of pure Ti Gr-2*

After anodization of pure Ti Gr-2 in voltage of 20V only nano-roughness and nano-fibers could be seen (Fig. 7a and Fig. 7b). The first nano-tubular structure originated after 1h anodization in 25 V. Like titanium alloy, it was located in small spots scattered over the entire sample's surface.

The structure is rather sponge-like consisting of pores with irregular shape and sizes (Fig. 7c). Well-shaped NTs with average internal diameter 82nm could also be observed in some zones. The rest surface was covered with nano-fibers (Fig. 7d). Increasing of the process duration led to the larger surface of the sample covered with nano-structure. After 3h anodization the covered surface is about 50% (Fig. 7e), after 6h: 60%-70%, while after 7h it reaches about 70-80%. With increasing the process duration the structure morphology changes from sponge-like to nano-tubes with regular shape

and sizes (Fig. 7f). The average internal diameter of tubular structures also increases with increasing of anodization time. After 6h anodization the average NTs diameter is 109 nm, while after 7h it is about 121 nm (Fig. 3).

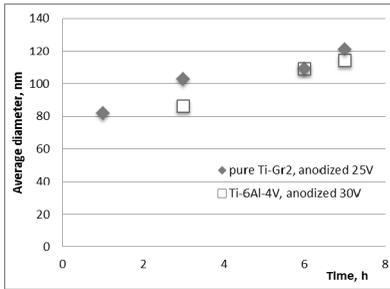


Fig. 3. Average internal diameter of titanium nanotubes after anodization of pure Ti Gr-2 and Ti-6Al-4V

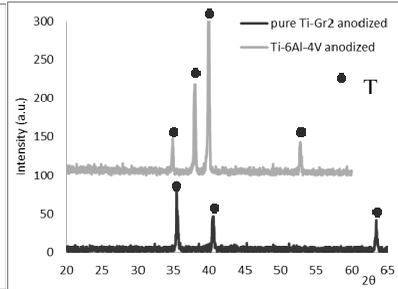


Fig. 4. XRD spectra of anodized pure Ti Gr-2 and Ti-6Al-4V alloy samples

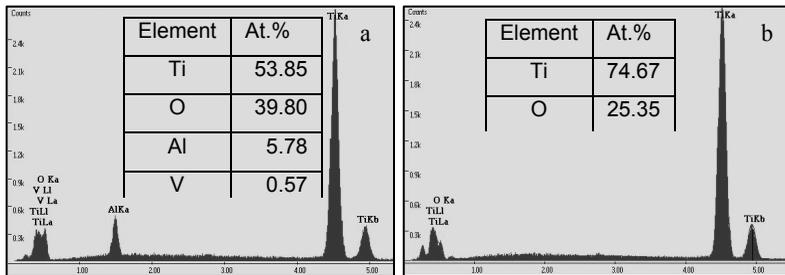


Fig. 5. EDAX analysis of anodized samples of Ti-6Al-4V alloy (30V, 7h, 0,5% HF) – a and pure Ti Gr-2 (25V, 7H, 0,5% HF) – b

EDAX analysis of the NTs region on Fig. 7f shows presence of the elements Ti and O (Fig. 5b) proving the oxide nature of the structure. Like the titanium alloy, it is amorphous, because clearly pronounced peaks only of titanium can be seen on X-Ray diffractograms after anodization of the pure Ti samples (Fig. 4). The first nanostructure after 30min anodization originated after 30min. Its morphology is sponge-like, consisting of pores with irregular shape and sizes. The nano-pores' average inner diameter is about 68nm and it is smaller than that of the NTs. The morphology and sizes of nano-structure do not change with increasing the process duration (Fig. 7g and Fig. 7h). After anodization of 1h, 3h and 6h the porous nano-structure was observed in 30%, 50% and 60% respectively of the samples' surface. The rest regions were covered with nano-fibers (Fig. 7i).

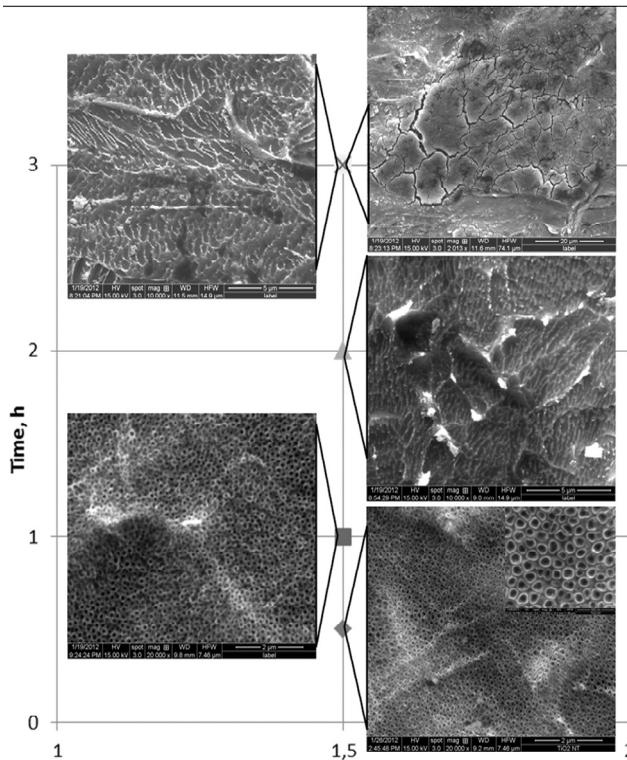


Fig. 6. Surface morphology of Ti-6Al-4V samples after anodization in 1,5% HF solution

### Discussion

During anodization process, when a constant voltage is applied between the anode and cathode, electrode reactions - oxidation and reduction in combination of field-driven ion diffusion lead to the formation of an oxide layer on the anode surface.

The chemical reactions specifically for anodizing of titanium are the following [12]:

At the Ti/Ti oxide interface:



At the Ti oxide/electrolyte interface:



At both interfaces:



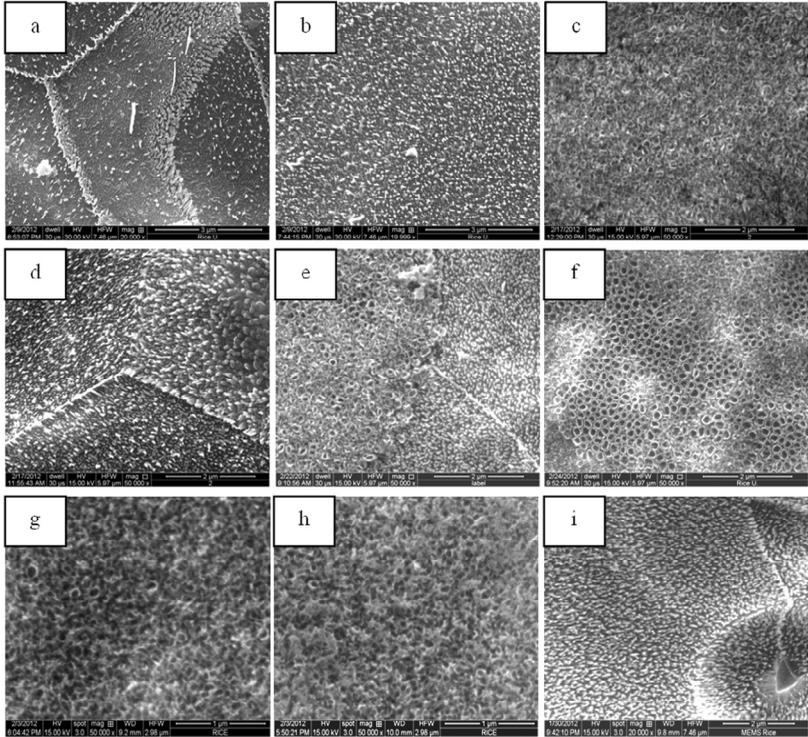


Fig.7 Surface morphology of pure Ti Gr-2 samples after anodization with different voltage and duration: 20V, 1h – a; 20V, 3h – b; 25V, 1h – c and d; 25V, 3h – e, 25V, 6h – f; 30V, 1h – g; 30V, 3h – h and 30V, 6h – i

The titanium oxide is a dielectric and has higher resistivity than the electrolyte and the metallic substrate. Therefore the applied voltage will mainly drop over the oxide film on the anode. As long as the electrical field is strong enough to drive the ion conduction through the oxide, the oxide film will keep growing.

Nano-tubular structures are usually formed in anodizing in fluorine electrolyte solutions when the applied voltage is much lower than the dielectric breakdown [12]. In addition to the electro-chemical oxidation and dissolution, the chemical dissolution of the titanium and titanium oxide in HF acid also takes part.

The processes of tubular nano-structures formation for both materials begin in higher voltages – 30V for Ti-6Al-4V alloy and 25V for the pure Ti Gr-2. Seven hours and more are required for covering the entire surface of the sample. So long process time can be due to the graphite cathode used from one hand. It is inert as working electrode and only indirectly affects the electro-chemical process, unlike platinum electrode, which has a positive electrode potential. On the other hand, etching before anodization produces mi-

cro-roughness on the surface of Ti-6Al-4V alloy and micro/nano-roughness on the surface of the pure Ti. The particular micro-regions are situated at different angle towards the electrode surface which causes running of the field-enhanced oxidation and field-enhanced dissolution with different rate thus leading to a longer time required to cover the entire surface with nano-tubular oxide structure. In the zones, parallel to the cathode surface, intensive dissolution of titanium runs resulting in nano-roughness after short time anodization. With increasing the process duration the oxides in the form of nano-fibers appear on the nano-peaks. In the micro-regions with more intensive oxidation processes the nano-tubular structures originate earlier – after 3h process in 30V for Ti alloy and after 1h in 25V for the pure Ti. The lower process parameters for the CP Ti Gr-2 are probably due to its higher reactivity in comparison with that of Ti alloy. With increasing the process duration the surface, covered with NTs, increases as well as their inner diameter.

Anodization in higher electrolyte concentration leads to formation of nano-tubular structure on the earlier stages – after 30 min. Increasing of process duration does not lead to covering of the entire sample's surface with NTs, but to the appearance of regions with thick oxide layer which confirms our theory about running of different processes at different rates in different areas. So it is difficult to control the process for producing of nano-tubular structure in higher electrolyte concentrations.

With voltage increase the structure of the surface oxide layer of both materials changes from nano-tubes to nano-porous sponge-like, confirming the results of [11]. The nano-porous structure covers Ti-6Al-4V alloy in 40V, while in the pure Ti it originates in 30V. As the anodized layer is not uniform due to existence of micro-roughness, flaws, defects and local stress the formation of nano-porous sponge-like structure is probably due to the blasting process accompanied with intensive gas release at weak points where the potential drop exceeds the dielectric limit [12].

### **Conclusions**

Anodization of pure titanium and titanium alloy in 0,5% HF acid solution using a graphite cathode allows obtaining of oxide layer with nano-tubular structure in narrow voltage range 30V +/-5V for the Ti-6Al-4V alloy and 20V-25V for the pure Ti Gr-2 in a relatively long process duration of about 7 hours for the both materials. The average inner diameter of the nano-tubes is close for the both materials and increases with increasing of the process duration. The first nano-tubes have a diameter of 86nm for Ti-6Al-4V alloy and 82nm for the CP Ti Gr-2, while after 7h anodization their diameter is 114nm and 121nm respectively.

At lower voltages and short-time process the nano-roughness is observed on the surface of both materials, on that TiO<sub>2</sub> nano-fibers are formed with increasing the process duration. At higher voltages - 40V for Ti-6Al-4V alloy and 30V for pure Ti porous sponge-like structure of the oxide layer is observed which originates at first in particular regions in short-time process and gradually spread over the entire sample's surface with increasing of the process duration.

Higher 1,5% HF concentration of the electrolyte leads to the formation of nano-tubes in particular regions after 30min process, while increased duration does not lead to coverage of the entire sample's surface with nano-tubes, but to obtaining of areas with different morphology – nanotubes, porous microstructure and dense oxide layer.

Our investigation shows that it is possible to obtain nano-tubular oxide structure on titanium surface by anodization in 0,5% HF solution with graphite electrode. Additional research is needed for precise defining of the technological regimes for obtaining of continuous layer of TiO<sub>2</sub> nano-tubes.

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**Дикова Ц.Д. Вплив технологічних параметрів на формування титанових нанотрубок.**

Досліджено вплив технологічних параметрів на формування титанових нанотрубок на поверхні чистого титану Grade-2 і титанового сплаву Ti-6Al-4V після анодування за допомогою графітного катода. Анодування виконували в двох концентраціях розчину HF кислоти при різних напругах і тривалості процесу. Морфологія поверхні, хімічний і фазовий склад оксидного шару були досліджені за допомогою СЕМ, EDAX і рентгенографічного аналізу. Встановлено, що анодування в 0,5% розчині HF кислоти дозволяє отримати оксидний шар з нанотрубчатогою структурою у вузькому діапазоні напруг 30 В +/-5 В для сплаву Ti-6Al-4V і 20-25 В для чистого Ti Gr-2 при достатній тривалості процесу. Середній внутрішній діаметр нанотрубок близький для обох матеріалів (80 нм - 120 нм) і зростає зі збільшенням тривалості процесу. Морфологія поверхні при більш низьких напругах і меншій тривалості процесу характеризується наношорсткістю, що трансформується у нановолокна TiO<sub>2</sub> зі збільшенням тривалості процесу. При більш високих напругах - 40 В для сплаву Ti-6Al-4V і 30 В для чистого Ti спостерігається пориста структура оксидного шару. Збільшення концентрації електроліту (1,5% HF) призводить до утворення нанотрубок після 30 хвилинного процесу, тоді як збільшення тривалості призводить до формування різної морфології поверхневого шару - нанотрубок, пористої мікроструктури і щільного шару оксиду.

**Ключові слова:** титан, сплав титану, анодування, нанотрубки оксиду титану.

**Дикова Ц.Д. Влияние технологических параметров на формирование титановых нанотрубок.**

Исследовано влияние технологических параметров на формирование титановых нанотрубок на поверхности чистого титана Grade-2 и титанового сплава Ti-6Al-4V после анодирования с помощью графитного катода. Анодирование выполнено в двух концентрациях раствора HF кислоты при разных напряжениях и длительности процесса. Морфология поверхности, химический и фазовый состав оксидного слоя были исследованы с помощью СЕМ, EDAX и рентгенографического анализа. Установлено, что анодирование в 0,5% растворе HF кислоты позволяет получить оксидный слой с нанотрубчатой структурой в узком диапазоне напряжений 30 В +/-5 В для сплава Ti-6Al-4V и 20-25 В для чистого Ti Gr-2 при относительно большой продолжительности процесса. Средний внутренний диаметр нанотрубок близок для обоих материалов (80 нм - 120 нм) и возрастает с увеличением длительности процесса. Морфология поверхности при более низких напряжениях и длительности процесса характеризуется наношероховатостью, которая трансформируется в нановолокна TiO<sub>2</sub> с увеличением продолжительности процесса. При более высоких напряжениях - 40 В для сплава Ti-6Al-4V и 30 В для чистого Ti наблюдается пористая структура оксидного слоя. Увеличение концентрации электролита (1,5% HF) приводит к образованию нанотрубок после 30 минутного процесса, тогда как увеличение продолжительности приводит к формированию различной морфологии поверхностного слоя – нанотрубок, пористой микроструктуры и плотного слоя оксида.

**Ключевые слова:** титан, сплав титана, анодирование, нанотрубки оксида титана.

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