

Influence of electrical parameters on morphology of nanostructured TiO₂ layers developed by electrochemical anodization

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Abstract. Ti6Al4V alloy micro rough surfaces with TiO₂ self-organized nanostructured layers were synthesized using electrochemical anodization in phosphate/fluoride electrolyte, at different end potentials (5V, 10V, 15V, and 20 V). The current – time characteristics were recorded, and the link between current evolution and the morphology of developing oxide layers was investigated. On flat surfaces of Ti6Al4V alloy we developed TiO₂ layers with different morphologies (random pores, nanopores of 25...50 nm, and highly organized nanotubes of 50...100 nm in diameter) depending on electrical parameters of anodization process. In our anodization cell, in optimized conditions, we are able to superimpose nanostructured oxide layers (nanotubular or nanoporous) over micro structured surfaces of titanium based materials used for biomedical implants.

1 Introduction

Titanium and its alloys are nowadays widely used for manufacturing of dental and orthopedic implants manufacturing, due to their excellent biocompatibility, good mechanical strength, and high corrosion resistance. Ti6Al4V alloy is of major importance in hard tissue (teeth, bones) replacement and surgery, as it presents increased mechanical properties [1, 2].

The unique biocompatibility of titanium based materials is a result of the formation of a native TiO₂ compact layer, with a thickness of 2...10 nm, on their surface. The process of implants osseointegration of implants can be enhanced by modifying their surface at the micro level, in order to obtain a micro rough surface, with a large bone-to-implant contact

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area. Recent results demonstrate that surface modification at nano scale level, by producing an ordered nanostructured surface, promotes enhanced bone apposition [3-12].

Electrochemical anodization method is used for surface modification of titanium and titanium based alloys, as it can control the morphology, structure and chemical composition of TiO₂ layers, leading to enhancement of the surface properties [13, 14]. By optimizing the process parameters of anodization, highly order and self-arranged nanostructured (nanoporous or nanotubular) surfaces can be developed [15-19]. These nanostructures combine very well with osseous tissue and can be the perfect basis for osteoblasts integration during the process of bone regeneration. Recent literature arguments the favorable osseointegration around TiO₂ nanotubes of 15...100 nm diameters modified surfaces by over-expression of genes related to high activity of osteoblasts and mesenchymal stem cells, and by fast kinetics of hydroxyapatite (basic bone component) formation, surrounding titanium implant.

Nanostructures formation is governed by a very complex mechanism that occurs in interdependent conditions. Phosphate-fluoride solutions used as electrolytes proved to be very effective on TiO₂ nanoporous/nanotubular self-organized structures development. Inside the anodization cell the formation of nanostructures is determined by the competition between anodic oxide formation and chemical dissolution of the oxide, and the presence of hydrofluoric acid is the key factor which causes nanoporous or nanotubular oxide layer development. The nanotubular TiO₂ layer develops in three stages: first is compact oxide formation, second is the initial porous structure formation, and third is self-organized nanotubes growth. A proper combination of electrolyte composition, anodization potential, anodization time, and a perfect balance between potentiodynamic stage and potentiostatic stage are required in order to develop uniform and highly-organized nanotubular oxide structures on titanium [13, 19, 20]. There are many results on development of titanium nanotubes on pure titanium (CpTi) surface. But the formation of self-ordered nanostructures on two phase ($\alpha+\beta$) titanium alloys, such Ti6Al4V is, is a more demanding process, due to the selective dissolution of the less stable phase and/or different reactions rate of the different phases of the alloy [13]. Moreover, the vast majority of results are obtained on extra polished surfaces.

In this context our major research direction is enhancement of surfaces of biomedical titanium based implants, at nano scale level, by developing TiO₂ nanostructures (nanotubes/nanopores) with 15...100 nm diameter, in order to improve implants osseointegration. Our recently reported research led to successful development, using electrochemical anodization, of self-ordered nanostructured oxide layer on the surface of two phase Ti6Al4V alloy by using electrochemical anodization in H₃PO₄/HF electrolytes [21]. Our results have a high degree of novelty, proving nanostructured TiO₂ layers deposition on surfaces with less demanding preparation prior to anodization, such are turning and milling, surfaces that presents a roughness R_a in 1...1,5 μ m range. Also we developed nanostructured layers on sand blasted and acid etched surfaces (SLA) [22].

Present paper aims to investigate the influence of electrical parameters on the morphology of developing oxide layers on flat micro rough surfaces, of Ti6Al4V alloy, in order to optimize the conditions of electrochemical anodization.

2 Methodology

In present set of experiments our samples of Ti6Al4V titanium alloy were cut from a round bar, using a CNC turning machine. They have disc shape of 16 mm in diameter and 3 mm in height. Surtronic 25 (Taylor Hobson) roughness tester was used for roughness measurements.

Before the anodization all samples were subjected to a cleaning process in distilled water followed by ethanol, and after then were dried.

The electrochemical anodization process was performed in a custom built electrochemical cell having two electrode configuration. The samples were connected to the anode of the cell, while the cathode was in form of $\varnothing 16 \times 3$ mm disc, made of high purity copper (99.99%). For all experiments the distance anode-cathode was 15 mm. $1M H_3PO_4 + 0.5$ wt% HF was used as electrolyte in anodization experiments. Electrolyte was prepared from reagent grade chemicals (Chemical Company) and deionized water. Experiments were carried out at room temperature.

For electrical parameters control and registration a direct current stabilized power supply, and voltmeter and ammeter were used. Several experiments were conducted with different anodization potentials: 5 V, 10 V, 15 V, and 20 V, applied with a sweep rate of 0.1 V/s. After the end potential was reached, we applied a potentiostatic stage by holding constant the end potential for an anodization time of 2 hours. After anodization, the samples were rinsed with deionized water, cleaned in ethanol and dried.

The surface morphology was evaluated using scanning electron microscopy (SEM), performed in a JSM 5200 (JEOL) scanning electron microscope, operated at 25 kV. We collected images at magnifications of 100X, 1500X, 10000X, 20000X, and 35000X, using secondary electrons and backscattered electrons. For the visualization of layers thickness we used a tilt angle of 45° . The dimensions of nanostructures developed on the modified surfaces were measured on SEM micrographs using an open source graphical image processing software (Gimp).

3 Results and discussion

Titanium alloy Ti6Al4V is a two phase ($\alpha+\beta$) alloy, with 6 wt% aluminum stabilizing the α phase (hcp), and 4 wt% vanadium stabilizing the β phase (bcc).

Table 1 summarizes the electrical process parameters used in our experiments and results on morphology and diameters of self-organized TiO_2 nanotubes/nanopores that were synthesized by anodization.

Table 1. Electrical process parameters and anodization results.

Electrical parameters			Results	
Sam ple	Potential [V]	Current [mA] in potentiostatic stage	Morphology of TiO_2 layer	Nanostructures diameter D_i [nm]
A	5	2.2...4.4	random pores	< 10 nm
B	10	2.2...3.5	ordered nanopores	25...45
C	15	3.1...6.5	ordered nanopores	30...50
D	20	2.8...9.6	self-ordered nanotubes	60...100

After electrochemical anodization the surface of the samples is covered by TiO_2 oxide layer. The oxide layer grows over the entire surface, as the Figure 1.a, collected at low magnification, shows. At higher magnification the morphology of oxide layers can be examined in details. Figure 1.b presents the SEM micrograph of highly organized, self-arranged TiO_2 layer developed on sample D, using an anodization potential of 20 V. The nanotubes are fully developed, their walls being clearly split one of the other. The internal diameter of the nanotubes is in 60...100 nm range, the external diameter is 100...160 nm, and the wall thickness is 20...30 nm. The thickness of the nanostructured oxide layer, measured on SEM micrographs not shown here, is 200...350 nm.

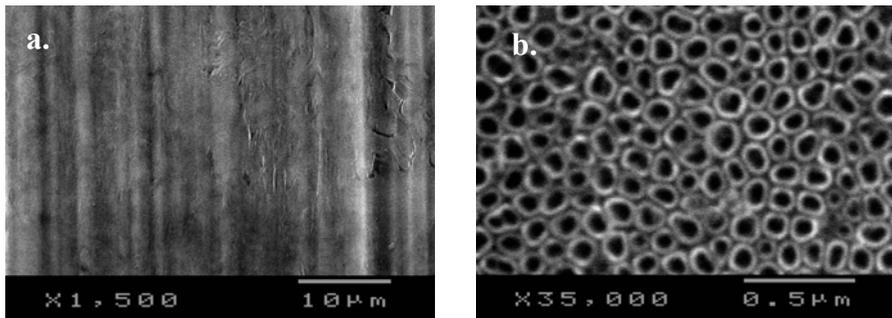


Fig. 1. SEM micrographs of TiO₂ nanotubular layer developed on micro rough surface of Ti6Al4V alloy by electrochemical anodization in 1M H₃PO₄ + 0.5 wt% HF, anodization potential 20 V, anodization time 2 hours (a – 1500X magnification; b – 35000X magnification)

Our results obtained by monitoring the current in the process of titanium layer development using an anodization potential of 5 V show that after the reaching of the end potential (50 seconds from the start of the process), period in which the current has an oscillated evolution between 0...8 mA (not shown in Figure 2), the current is continuously decreasing from 4.4 mA (at 5 min after the beginning of the process) to 2.2 mA (at the end of anodization). The SEM micrographs of the TiO₂ layer show the development of a compact oxide layer with superficial surface pores with openings less than 10 nm (Figure 3.a).

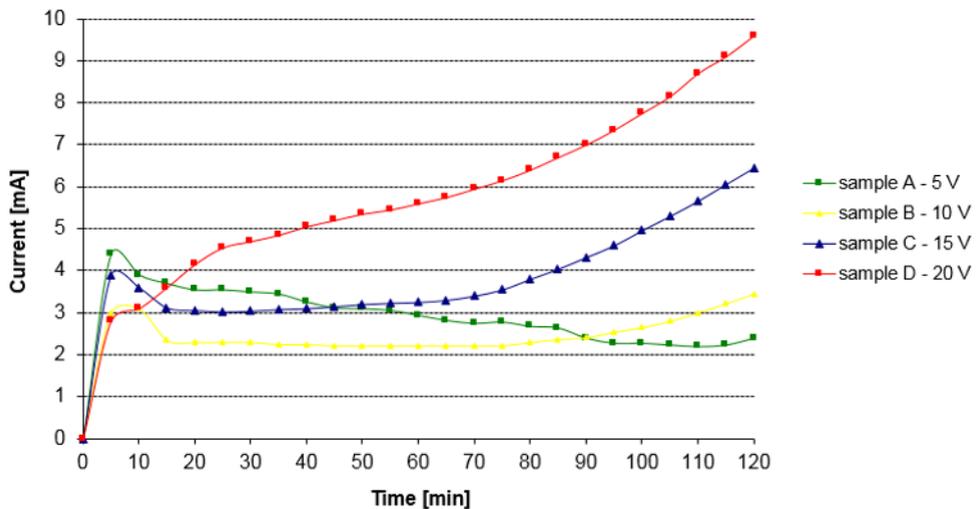


Fig. 2. Current-time characteristic for electrochemical anodization of Ti6Al4V samples in 1M H₃PO₄ + 0.5 wt% HF at different anodization potential, anodization time 2 hours

By using increased anodization potentials, 10 V and 15 V, in the potentiostatic stage, after an initial increase in current, a drop occurs. After that a stabilization of current appears (around 2.2 mA for $U = 10$ V, and around 3 mA for $U = 15$ V), followed by an increase in current, with 0.03 mA/min when anodization potential is 10 V, and with 0.06 mA/min when anodization potential is 15 V. SEM micrographs of developed layers show ordered nanoporous morphology with nanopores diameters in 25...50 nm range (Figure 3.b and 3.c).

By using an anodization potential of 20 V, the current evolution, after the first 200 s needed for reaching the end potential, shows a short stabilization phase (5 minutes) followed by a continuous increase in current with approx. 0.06 mA/min. The SEM micrographs taken

from the TiO₂ layer reveal a well-developed nanotubular topography, with highly organized nanotubes of 60...100 nm in diameter. The tubes wall thickness is of 20...30 nm (Figure 3.d).

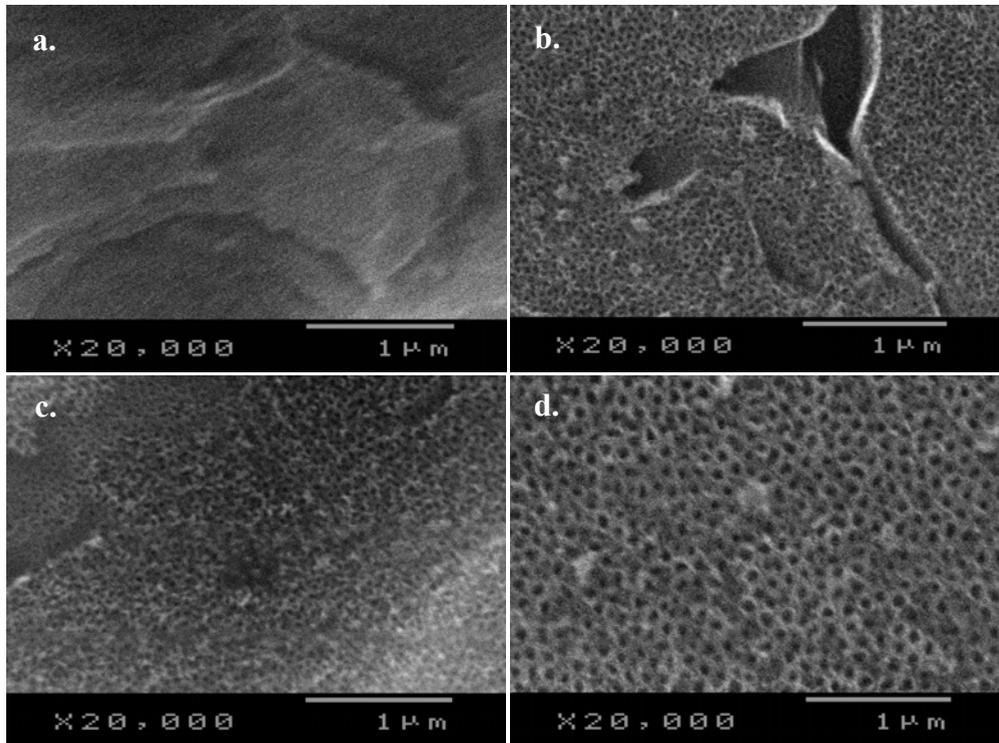


Fig. 3. SEM micrographs of TiO₂ layers developed on micro rough surface of Ti6Al4V alloy by electrochemical anodization in 1M H₃PO₄ + 0.5 wt% HF, anodization time 2 hours, 20000X magnification (a: anodization potential U = 5 V; b: U = 10 V; c: U = 15 V, d: U = 20V)

Analyzing the developed topographies in relation with the current evolution during the process, our results show that, for Ti6Al4V alloy anodized in phosphate/fluoride aqueous solution, when nanotubes are growing the magnitude of the current is higher than when a compact oxide or a nanoporous one is formed.

Our results show that, in optimized conditions, we are able to superimpose nanostructured oxide layers (nanotubular or nanoporous) over micro structured surfaces of titanium based materials for biomedical implants by using electrochemical anodization.

4 Conclusions

We monitored the growth of TiO₂ oxide layer on two phase ($\alpha+\beta$) Ti6Al4V alloy, with micro rough surface, using electrochemical anodization in 1M H₃PO₄ + 0.5 wt% HF solution, and recorded current-time characteristics.

For synthesis of the oxide layers we work by maintaining a constant potential (5, 10, 15, and 20 V) for duration of 2 hours. Our results show that when the current is low (<4 mA) and decrease continuously, the TiO₂ layer is a compact one with superficial nanopores with diameter less than 10 nm. A different evolution of current, an initial decrease, a steady state, and a final step when the current is increasing, leads to the formation of nanoporous structures, with nanopores of 25...50 nm. This ordered nanoporous oxide structures are developing at low currents (2.2 ...3.5 mA, and 3.1...6.5 mA). Higher currents in the

anodization cell (2.8 ...9.6 mA) were recorded by us when highly organized, self-arranged nanotubular oxide layer is developing.

These results allow us to optimize and control the electrochemical anodization process in order to develop nanotubular TiO₂ layer, by means of current control.

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