TiO₂ nanostructured surfaces for biomedical applications developed by electrochemical anodization

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Abstract. Present research demonstrates the formation of self-ordered nanostructured oxide layer on the surface of two phase Ti6Al4V alloy by using electrochemical anodization in H₃PO₄/HF electrolytes. Our results show that the ordered oxide nanotubes grow on large areas on the samples surface, on both phases of (α+β) Ti6Al4V titanium alloy. We developed nanotubes of 70 nm (internal diameter) using 0.3 wt% HF and of 80 nm using 0.5 wt% HF additions to 1M H₃PO₄, at an anodization potential of 20 V, and an anodization time of 2 hours. We show that anodization potential has a strong influence on nanostructures morphology. Our results show that nanotubes' internal diameter is ∼30 nm at 10 V potential, ∼40 nm at 15 V potential, and ∼70-80 nm at 20 V potential in anodization process performed in 1M H₃PO₄ + 0.5 wt% HF, 2 hours. The thickness of the developed nanostructured oxide layer is in 200-250 nm range.

1. Introduction

Titanium based implants are of great importance in craniofacial surgery and orthopaedics, providing excellent outcomes in terms of functionality. These devices utilize the unique biocompatibility properties of titanium and titanium alloys, which facilitate the apposition of bone directly onto the metal surface, a phenomena known as osseointegration. The modification of the implant surface at the micro level has been shown to have a major effect on the rate and degree of osseointegration. Recent studies demonstrate that surface modification at nano scale level in order to produce an ordered nanostructured surface, promotes further enhanced bone apposition during the early stages of osseointegration when compared with those seen on micro-rough surfaces [1-9].

Nowadays the use of commercially pure titanium (CpTi) is dominant in dental implants, while the use of Ti6Al4V (Ti grade 5) alloy is of major importance in orthopaedics, due to its increased mechanical properties [10].

Electrochemical anodization of titanium and titanium based alloys can shape the morphology, structure and chemical composition of oxide layers to enhance the surface properties [11, 12]. Several recent studies have shown that nanostructured (nanoporous or nanotubular) surfaces can be developed by optimizing the process parameters of anodization [13-16]. These nanostructures combine very well with osseous tissue and can be the perfect basis for osteoblasts integration during the process of bone regeneration.
The mechanism of nanotubes formation is a very complex one and occurs in interdependent conditions. In a simple approach, the formation of nanotubes can be viewed as being governed by the competition between anodic oxide formation and chemical dissolution of the oxide as soluble complexes. Briefly explained, the nanotubular layer develops in three stages: first is compact oxide formation, second is the initial porous structure formation, and third is self-organized nanotubes growth [17]. In recent studies Kulkarni, Krasicka, and Lee emphasize that 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 highly-organized nanotubular oxide structures on titanium [1, 11, 15]. Moreover, the formation of self-ordered nanostructures on two phase titanium alloys 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.

Phosphate-fluoride solutions proved to be very effective on TiO$_2$ nanotubular structures development. As during the electrochemical anodization process a competition between oxide formation and dissolution exists, in H$_3$PO$_4$/HF electrolytes hydrofluoric acid is the key factor which causes nanoporous or nanotubular oxide layer development.

In this context our major research direction is enhancement of surfaces of biomedical titanium based implants, both at micro and nano level, in order to improve their osseointegration. Our recently reported research led to successful development, using sand blasting and acid etching (SLA) processes, of micro-rough SLA surfaces with an average surface roughness $R_a$ of 1-2 $\mu$m, surface topography with micropits less than 10 $\mu$m (these micropits are essential for a proper osseointegration), large valleys of $\sim$50 $\mu$m and different size peaks, and enhanced hydrophilic properties [18-20].

Presently, the major goal of our current research work is to develop an effective and efficient procedure to prepare modified implant surfaces with uniform, self-organized nanotubular oxide layers. The objective of the present paper was to develop ordered TiO$_2$ nanotubes on the surface of two phase Ti6Al4V alloy for biomedical implants, using electrochemical anodization procedure. Our results show that the goal was accomplished; our nanotubular structures for medical implants are fully comparable with the latest results reported by several research teams working in the field of nanostructured titanium based modified surfaces [1, 2, 8, 13, 16].

2. Methodology

For the present set of experiments we prepared $\varnothing$16 x 3 mm disc samples of Ti6Al4V titanium alloy. The roughness of samples was measured using a Surtronic 25 (Taylor Hobson) roughness tester. The weight of samples was measured using Kern ARJ 220-4M laboratory balance with a reproducibility of 0.1 mg. Before the anodization all samples were subjected to a cleaning process in distilled water followed by ethanol, and drying.

The anodization process was performed in an electrochemical cell having two electrode configuration. The samples were connected to the anode of the cell, while the cathode was in form of $\varnothing$16 x 3 mm disc, made of high purity copper (99.99%) rod. For all experiments the distance anode-cathode was 15 mm. We used a direct current stabilized power supply, and voltmeter and ammeter for electrical parameters control and registration. 1M H$_3$PO$_4$ with different concentration of HF was used as electrolyte in anodization experiments. All electrolytes were prepared from reagent grade chemicals (Chemical Company) and DI water. Experiments were carried out at room temperature.

The electrochemical anodization process consisted in an initial potentiodynamic stage, with a sweep rate of 0.1 V/s until the end potential was reached, followed by a potentiostatic stage by holding the potential at the end potential (10 V, 15 V, and 20 V). The total duration for the anodization process was 2 hours for all experiments. After anodization, the samples were rinsed with deionized water, cleaned in ethanol and dried.

The surface morphology was evaluated using scanning electron microscopy, performed in a JSM 5200 (JEOL) scanning electron microscope, operated at 25 kV. For a proper interpretation of the results, the micrographs were collected at magnifications of 1500X, 10000X, 20000X, 35000X, and 100000X using secondary electrons and backscattered electrons. The measurements of nanostructures
developed on the modified surfaces were made on SEM micrographs using a graphical image processing software (Gimp).

3. Results and discussion

The main parameters of anodization processes performed on Ti6Al4V samples in order to develop ordered TiO₂ nanostructures are listed in Table 1. The table shows also the results of the experiments regarding the diameters of the nanotubes developed on the modified surfaces.

| Sample | Electrolyte | Anodization potential | Nanostructures dimensions |
|--------|-------------|------------------------|---------------------------|
|        | [1M H₃PO₄ + HF] | U [V] | Internal diameter Dᵢ [nm] | External diameter Dₑ [nm] |
|        | [% wt] HF | | range mainly | range mainly |
| 60     | 0.5 | 20 | 60-100 | 70 | 100-160 | 120 |
| 61     | 0.5 | 20 | 50-100 | 70 | 90-160 | 120 |
| 63     | 0.5 | 20 | 50-100 | 80 | 90-160 | 120 |
| 62     | 0.3 | 20 | 40-90 | 70 | 70-130 | 100 |
| 65     | 0.5 | 15 | 30-50 | 40 | 60-100 | 70 |
| 64     | 0.5 | 10 | 25-45 | 30 | 50-90 | 60 |
| 70     | chemical etch in 0.5 wt% HF for 30 s (sample for assessment of the initial surfaces) |

Ti6Al4V is a two phase (α+β) alloy, with 6 wt% aluminum stabilizing the α phase (hcp), and 4 wt% vanadium stabilizing the β phase (bcc). Figures 1a and 2a show the SEM micrograph of the surface after etching in 0.5 wt% HF for 30 seconds. On the surface there are regions formed by β phase (bcc) – white areas, and α phase (hcp) – black regions.

After anodization process the surface of the samples is covered by a nanostructured layer, consisting in ordered nanotubular structures. From figure 1b, collected at low magnification (1500X), appear that a continuous TiO₂ layer is formed on the surface of the anodized surface. This layer is interrupted by 1-5 μm micro craters, where, at this magnification, it is not clear if there is or not a nanostructured development of an oxide layer.

Figure 1. SEM micrographs of initial Ti6Al4V samples surface (a) and anodized surface (b) showing the uniform development of nanostructured oxide layer – 1500X magnification (a – sample 70, etched in 0.5 wt% HF for 30 s; b – sample 64 anodized in 1M H₃PO₄ + 0.5 wt% HF, U=10 V, 2 hours)

At higher magnification (10000X), figure 2b, compared with 2a, shows that the nanotubes are developed on both phases of the titanium alloy, even if there are some differences in nanotubes dimensions, depending on which phase they grew. The SEM micrograph presented in figure 2b shows...
more uniform nanotubes development on $\beta$ phase. This phase seems to be more favorable for an ordered nanostructured development of the oxide layer. An explanation for this can be the beneficial influence of vanadium content. More research in order to elucidate the causes of these differences, that occur, probably, from the initial microstructure and/or the processes involved in the initial potentiodynamic stage of anodization, is planned in the nearest future.

**Figure 2.** SEM micrographs of initial Ti6Al4V samples surface (a) and anodized surface (b) showing the uniform development of nanostructured oxide layer – 10000X magnification (a – sample 70, etched in 0.5 wt% HF for 30 s; b – sample 64 anodized in 1M $\text{H}_3\text{PO}_4 + 0.5$ wt% HF, $U=$10 V, 2 hours)

As regard the influence of electrolyte composition our experiments aimed to study its effect on nanostructures morphology in phosphate-fluoride solution containing 1M $\text{H}_3\text{PO}_4$ and different additions of HF (see Table 1). Figure 3 shows the morphology of the surfaces of the samples anodized using the same anodization potential (20 V) and modifying the content in hydrofluoric acid. Our results show titanium oxide development as nanotubular structures on all samples.

Comparing the nanotubes dimensions measurements (made by using Gimp graphical image processing software and presented in Table 1) we found that they only slightly differ when using 0.3 wt% HF (figure 3a) and 0.5 wt% HF (figure 3b) additions to 1M $\text{H}_3\text{PO}_4$.

**Figure 3.** SEM micrographs of anodized Ti6Al4V surfaces showing the development of self-ordered nanotubular oxide layers and the influence of electrolyte composition on surface morphology (a – sample 62 anodized in 1M $\text{H}_3\text{PO}_4 + 0.3$ wt% HF, $U=$10 V, 2 hours – 20000X; b – sample 63 anodized in 1M $\text{H}_3\text{PO}_4 + 0.5$ wt% HF, $U=$20 V, 2 hours – 20000X)
On sample 62, developed at U=20 V, in 1M H₃PO₄ + 0.3 wt% HF the nanostructures (figure 3a) present internal diameters (Dᵢ) ranging from 40-90 nm and external diameters (Dₑ) of 70-130 nm. The majority of nanotubes have Dᵢ=70 nm and Dₑ=100 nm.

Sample 63, developed at U=20 V, in 1M H₃PO₄ + 0.5 wt% HF, presents nanotubes (figure 3b) with internal diameters in 50-100 nm range and external diameters of 90-160 nm. The majority of nanotubes have Dᵢ=80 nm and Dₑ=120 nm.

By analyzing the surfaces’ morphology at lower magnifications (SEM not shown here) we found that the oxide coverage of the surface is better in the case of the 1M H₃PO₄ + 0.5 wt% HF electrolyte, compared with 1M H₃PO₄ + 0.3 wt% HF electrolyte. This is explainable by the fact that on the surface is growing a compact oxide layer when using only phosphoric acid solution. The addition of hydrofluoric acid is the key factor in achieving the necessary conditions of the complex process of nanotubes development by anodizing process in phosphate-fluoride solutions.

Other parameter of anodization process which is reported to have an important influence on surface morphology is anodization potential. In order to elucidate its effect we performed our experiments in 1M H₃PO₄ + 0.5 wt% HF electrolyte, which we found to be the most beneficial in terms of Ti₆Al₄V surface coverage, using different anodization potentials (10 V, 15 V, and 20 V) for potentiostatic stage of our anodization process (see Table 1). The SEM micrographs presented in figures 4 and 5 show the development of ordered TiO₂ nanotubes on all surfaces. The results of nanostructures measurements (made by using Gimp graphical image processing software and presented in Table 1) show a strong influence of anodization potential on nanotubes diameters.

At U=10 V the nanostructures (figure 4a) present internal diameters ranging from 25-45 nm and external diameters of 50-90 nm. The majority of nanostructures have Dᵢ=30 nm and Dₑ=60 nm.

By anodization at U=15 V the nanostructures have slightly bigger dimensions (figure 4b). Internal diameters are ranging from 30-50 nm and external diameters from 60-100 nm, with the majority of nanostructures having Dᵢ=40 nm and Dₑ=70 nm.

Using a higher anodization potential of U=20 V, the dimensions of nanostructures are clearly bigger compared to those developed at 15V and 10V. As figures 5a (collected at a magnification of 35000X) and 5b (collected at 100000X magnification) show, internal diameters are in 50-100 nm range and external diameters in 90-160 nm range. The majority of nanostructures have Dᵢ=80 nm and Dₑ=120 nm.

The thickness of nanostructured oxide layer developed in 1M H₃PO₄ + 0.5 wt% HF electrolyte at U=20 V and an anodization time of 2 hours is in 200-250 nm range (figure 6).
Our results show the best nanotubes separation in the case of the modified surfaces developed at 20 V anodization potential. All samples developed by anodization in 1M H₃PO₄ + 0.5 wt% HF electrolyte, at U=20 V, applied with a potential ramp of 0.1 V/s, and then maintained constant until reaching the total time of the process of 2 hours, presents self-ordered TiO₂ nanotubes, with high uniformity on large areas of the surface. By our present research we demonstrate the possibility of formation of a nanostructured, ordered oxide layer on the surface of two phase Ti₆Al₄V (α + β) alloy.

4. Conclusions
In the present set of experiments we have successfully developed ordered nanostructured TiO₂ layer on the surface of Ti₆Al₄V alloy for biomedical applications (orthopaedic and dental implants) by using electrochemical anodization in H₃PO₄/HF electrolytes. Our results show that the ordered oxide nanotubes grow on large areas on the samples surface, on both phases of (α + β) Ti₆Al₄V titanium alloy, with some differences in size (diameter and height) and uniformity, depending, probably, on the initial microstructure and/or the processes that occur in the initial potentiodynamic stage of anodization. More research in order to elucidate the causes of these differences is planned in the nearest future.
Regarding the influence of electrolyte composition on surface morphology we found that in phosphate based solutions (1M H₃PO₄) an addition of 0.5 wt% HF provides the best conditions for nanotubes development on entire surface of Ti6Al4V alloy.

Our results on the influence of anodization potential on surface morphology show the ordered nanostructures development in 1M H₃PO₄ + 0.5 wt% HF electrolyte at 10 V, 15 V, and 20 V. The potential has an important effect on nanotubes diameter. At 10 V and 15 V potentials we measured nanotubes internal diameter of ~30-40 (±10) nm and by using 20 V potential the nanotubes internal diameter was ~70-80 (±20) nm. In our anodization cell, at 20 V potential and a process time of 2 hours, the thickness of the developed nanostructured oxide layer is 200-250 nm.

Based on present results, future research is planned by us in order to further analyze and elucidate the complex and interdependent influence of surface microstructure, surface preparation prior to anodization, potential applying ramp in the potentiodynamic stage of the anodization, current in the potentiostatic stage of the anodization, and anodization time on the uniform development of highly ordered nanotubular oxide structures on two phase titanium alloy Ti6Al4V using electrochemical anodization in H₃PO₄/HF electrolytes.

Acknowledgments

The Ti6Al4V titanium alloy bar for substrates preparation was supplied by SC Procam SRL, Tirgu Mures. The authors thank Anca Mazare and Biro Dominic for their helpful discussions, Andrei Serban Gaz and Nicolae Chirila for their help with chemical solutions formulation and preparation, and Petrica Morar for his help with electrical set-up of anodization cell. Dissemination of the results of present research work is partially supported by Petru Maior University research centre Advanced Technologies of Design and Assisted Manufacturing (TAPFA).

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