Surface modification to develop hierarchical micro/nano topography on titanium based medical implants

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Abstract. Self-organized nanostructured TiO₂ layers were developed on micro rough planar, cylindrical, and threaded surfaces of Ti6Al4V alloy by electrochemical anodization (EA) performed in phosphate-fluoride solution (1M H₃PO₄ with different HF additions) by using different process parameters (electrolyte concentration, anodization potential U, potential ramp Uᵣ, and sample rotational speed n). Optical microscopy and scanning electron microscopy (SEM) was used to evaluate the morphology of the oxide layers. Nanostructured oxide layers with nanotubes/nanopores internal diameter in 25-110 nm range were developed on surfaces with an initial micro rough topography (Rₐ = 0.5-2 µm, resulting by CNC turning or by sand blasting and acid etching - SLA). For planar surfaces, the optimal EA process parameters in our custom-built anodization cell are: 0.5 wt.% HF addition in electrolyte, U = 20 V, and Uᵣ = 0.1 V/s - for turned surfaces, and 0.4 wt.% HF addition in electrolyte, U = 24 V, and Uᵣ = 0.08 V/s - for SLA surfaces. For cylindrical surfaces the nanotubes were superimposed on micro rough surface by using 0.4 wt.% HF addition in electrolyte, U = 24 V, and Uᵣ = 0.08 V/s. On threaded surfaces continuous nanoporous oxide layer covering all geometrical features - frontal apex, spiral channels, major diameter, minor diameter, thread flanks - was developed by using 0.4 wt.% HF addition in electrolyte, U = 24 V, Uᵣ = 0.08 V/s, and n = 8 rev/min.

1. Introduction

Nanoengineered titanium-based surfaces for medical applications such as dental/bone implants have gained recently considerable interest due to their increased osseointegration and the possibility to be tailored in order to achieve specific properties.

Among different kind of nanostructures that can be developed, self-arranged TiO₂ (titania) nanopores/nanotubes are of particular interest for bio active implants with functionalized surfaces to perform as carriers for drug delivery: growth factors, anti inflammatory, anti bacterial, and anti cancer agents. This interest is due to the fact that the technology available to fabricate the titania nanotubes (TNT) is relatively simple and cost effective. By using electrochemical anodization (EA) and finding the optimized process parameters the TNT can be tailored and precisely controlled in regard of their diameters and length. Nanotubular titania with tube openings of 15-100 nm can promote bone cell
function mainly due to increase surface roughness/energy, incorporating of fluoride ions, and the ability to mechanically stimulate cells.

Surface modification at micro scale level in order to develop micro topographies was proved to improve the bone to implant contact (BIC) through mechanical interlocking and the promotion of osteoblasts cells functions. As a consequence, certain micro scale modified surfaces, such as SLA (sand blasted with large grits and acid etched), are now common for commercial implants products, being extensively utilized with good clinical results. Processing the surface by sand blasting followed by acid etching leads to the formation of a topography with uniform roughness with pits and craters (micropores) of micrometric size, with an increased surface area. In these micropores osteoblasts and supportive connective tissue can migrate, resulting in enhancement of bio adhesion and an improved osseointegration process of medical implants.

In the literature there are many reports on nanotubular TiO₂ synthesis on planar, extra polished surfaces. The idea of combining micro and nano topographies emerged recently, in their studies the authors emphasizing that “The optimal implant surface may be a combination of both micro- and nanorough surface features” [1] and “TNTs may be able to be superimposed on existing micro-rough surfaces, in order to achieve synergistic outcomes by combining the unique features of TNTs with the established clinical success of micro-rough surfaces” [2]. This approach is extremely valuable having in mind that medical implants - dental implants, or orthopedic implants for fracture fixation (screw, plates) or joint replacement - present various shapes, cylindrical, conical, and threaded, and complex geometries with curves, edges and grooves. On this macro geometry, the micro topography is usually micro rough, due to the processing methods (turning, grinding, sand blasting, SLA). TNTs synthesis on complex micro rough surfaces is a challenge that is not yet properly addressed. The methods to produce uniform, hierarchical micro/nano structures that can mimic the structure of extra cellular matrix remains challenging and several studies focused on this issue reported successful results in the latest years [3-13].

In the present work we report the development of hybrid micro/nano structured surfaces of two phase Ti6Al4V titanium alloy, on planar, cylindrical and threaded macro shapes, by using electrochemical anodization method.

2. Methodology
Planar, cylindrical and threaded specimens were prepared by using titanium-based Ti6Al4V alloy.

Planar specimens were cut from round hot forged titanium alloy bar on a Cincom K16 (Citizen) CNC turning machine, their final form being of a φ16 x 3 mm disc. Cylindrical specimens dimensions were φ3.8 x 20 mm. Threaded specimens were commercial dental implants MIS M4 (MIS Implants Technologies) φ14.2 x 13 mm.

The micro rough turned surface of planar samples was modified by sand blasting with SiO₂ grits using a Basic Eco (Renfert) sand blasting machine. SLA process step was completed by acid etching the specimens in an acid solution of HCl 1n and H₂SO₄ 1n (1:1). The samples were put in a BOV-T25F (Biobase) furnace, at 80°C for 12 hours.

Electrochemical anodization (EA) was performed in a custom built anodization setup, consisting in: anodization bath, specimen and cathode holding system having the possibility of sample rotation, DC power supply and instrumentation for process parameters monitoring. The setup is assisted by dedicated Nanosource software application developed by us to control and monitor the process parameters, allowing also their real time visualization and registration for further analyses. The specimens were placed at the anode of the anodization cell and a pure copper cathode was placed at a distance of 15 mm. An aqueous solution of 1M H₃PO₄ with 0.4 or 0.5 wt% HF was the electrolyte. The end potential \( U \) of 20 V or 24 V, applied with an initial potential ramp \( U_r \) of 0.08 V/S or 0.1 V/s, was provided by a programmable dual range DC power supply 9184B (BK Precision). For threaded specimens rotational speed \( n \) in the range of 4-10 rev/min was applied. The duration of the experiments results from adding the duration of potentiodynamic stage, were the potential rises from 0 to the end potential, to the duration of potentiostatic stage, which was of 30 min for all experiments.
The roughness of the surfaces was measured by using SJ-310 (Mitutoyo) roughness tester. Optical microscopy was performed on 383MET (Optika) optical microscope assisted by D3400 (Nikon) DSLR camera and open source digiCamControl software. Electron microscopy was performed on JSM 5200 (JEOL) scanning electron microscope, operated at 25 kV. Open source ImageJ and Gimp software were used for nanostructures’ dimensions evaluation.

3. Results and discussion
Ti6Al4V titanium alloy is a dual phase one consisting in hexagonal closed-packed α phase and body-centered cubic β phase.

In figure 1.a the optical microstructure of the alloy is revealed on mechanical polished surface etched by using Kroll reagent, showing dark α (hcp) phase and bright β (bcc). On SEM micrographs the bi phase structure can be visualized with more accuracy (figure 1.b). By subjecting the polished (Ra = 0.01 μm) samples to EA, TiO2 layer is developing on the surface, as figure 1.c collected at magnification of 1500X shows. Higher magnification SEM micrograph (10000X) show well structured nanotubes of 50-90 nm in diameter developed on α phase (figure 1.d). On β phase the nanotubes are different in diameter and height, due to the fact that there are different oxidation and oxide dissolution rates depending on the substrate on which the oxide is developing. The results show that on polished surfaces the microstructure of the specimens’ material has an important effect.

EA of micro rough planar turned surfaces (Ra = 1 - 2 μm) in 1M H3PO4 + 0.5 wt.% HF, U = 20 V, and Ur = 0.1 V/s leads to the formation of self arranged TiO2 nanotubes with internal diameter of 25-100 nm and heights of 300-500 nm. Optical and SEM micrographs presented in figures 2.a and 2.b show the micro rough topography of initial surface as a result of machining process by turning. On this micro scale topography, a nano scale structured oxide layer is developing due to EA, the layer covers all features of the surface, as figure 2.c taken at low magnification (1500X) shows. SEM micrographs taken at high magnifications (10000X and 20000X) presented in figures 2.d, 2.e show top views and a cross section view taken on an area were the oxide layer was detached from the surface by deliberately applying mechanical stress (figure 2.f). Experiments made with previously used electrolyte, not with fresh prepared one, using the same type of initial surface and the same process parameters lead to the formation of nanotubes on the micro rough surface, but their shape, uniformity and arrangement are different in comparison with those prepared with fresh electrolyte, as figure 2.g shows.

Figure 3 presents our results on hierarchical micro/nano topography development on sand blasted and acid etched surfaces (Ra = 1 - 2 μm), by EA in 1M H3PO4 + 0.4 wt.% HF, U = 24 V, and Ur = 0.08 V/s. Optical and SEM micrographs presented in figures 3.a and 3.b show the topography of initial surface consisting in smooth valleys and craters with micropores opened in their surfaces. On this micro scale topography, a nano scale structured oxide layer is developing due to EA, the layer covers all features of the surface, as figure 3.c taken at low magnification (1500X) shows. SEM micrographs collected at high magnifications (10000X and 20000X) presented in figures 3.d, 3.e, and 3.f, show top views and a tilted view of nanotubular oxide of diameters on 50-110 nm range superimposed onto micro rough topography, proving the development of hierarchical micro/nano topography.
Figure 2. Nanotubular TiO₂ developed on planar turned micro rough surface; initial surface (a – optical micrograph, b – SEM micrograph) and modified micro/nano structured surface (c, d, e, f – in fresh electrolyte, g – in used electrolyte)

Figure 3. Nanotubular TiO₂ developed on planar micro rough SLA surface; initial SLA surface (a – optical micrograph, b – SEM micrograph), modified micro/nano structured surface (c, d, e, f); compact TiO₂ on planar micro rough sand blasted surface: g - initial surface, h – modified surface
By using the same process parameters to modify sand blasted surfaces \( (R_a = 2 - 3 \, \mu m) \), due to their highly fragmented topography (figure 3.g) the conditions of self formation of nanotubes are not achieved, as a result the oxide layer is a compact one (figure 3.h).

Fluoride ions are essential on oxide layer growth in the form of nanoporous/nanotubular structure, and their migration through the anodic film is driven by electric field. By this reason, the experimental anodization setup used on TiO\(_2\) nanostructures’ synthesis on cylindrical and threaded surfaces was designed to enhance the electrical field lines distribution and a proper electrolyte (1 in figures 4.a and 5.a) circulation. As a result, in the case of cylindrical surfaces our solution was to use a pure copper cathode foil which was shaped in an annular form where slits were cut (3 in figure 4.a). Regarding the anodization of threaded specimens we used a planar pure copper foil cathode (3) and the sample (2) was rotated with different rotational speeds \( n \) [rev/min] (figure 5.a).

The results on hierarchical micro/nano topography development on turned cylindrical surfaces exhibiting a roughness of \( R_a = 1 \, \mu m \) (figure 4.b), by EA in 1M H\(_3\)PO\(_4\) + 0.4 wt.% HF, \( U = 24 \, V \), and \( U_r = 0.08 \, V/s \) are presented in figures 4.c and 4.d. SEM micrographs show the oxide layer covering all features of the surface, as figure 4.c taken at low magnification (1500X) proves, and top view of self arranged nanotubes of diameters on 25-110 nm range superimposed on micro rough topography, as figure 4.d taken at high magnification (20000X) proves.

By subjecting the threaded surfaces manufactured by CNC turning (Ra = 0.5-1 \, \mu m) to modification by anodization a hierarchical macro/micro/nano topography is developing. The macro scale shape of the thread and its surface micro scale topography is shown by SEM image of the specimen collected at magnification of 200X (figure 5.b) before anodization procedure. After EA in 1M H\(_3\)PO\(_4\) + 0.4 wt.% HF, \( U = 24 \, V \), \( U_r = 0.08 \, V/s \), and rotating the specimen with \( n = 8 \) rev/min, a nanostructured porous oxide layer covers the threaded surface, as figure 5.c collected at magnification of 1500X shows. High magnification (20000X) SEM image, presented in figure 5.d, shows a nanoporous structure of the oxide, with openings of 25-80 nm. The structure did not evolve in a nanotubular one, and completely expanded nanotubular structure was not achieved by our experiments. We supposed that this was due to the fact that the anodization duration was not long enough and we performed longer experiments.
(120 min). After 35 minutes of anodization, the current began to rise from the steady state in which the nanostructure is developing where it was \( I = 1.6 \) mA, to \( I = 10 \) mA, and the SEM analysis shows the development of a puzzled surface with areas of fragmented compact oxide layer and areas where the oxide was expelled from the surface. By this we conclude that not anodization duration is the process parameter that prevents the nanotubes formation. Further analysis and experimental work is planned for the nearest future to develop well defined nanotubular TiO\(_2\) layers on threaded surfaces.

4. Conclusions
Hierarchical dual scale structures were synthesis on titanium-based Ti6Al4V alloy by electrochemical anodization in phosphate-fluoride solution.

Well developed, self arranged nanotubular TiO\(_2\) layers with tube openings of 25-110 nm were synthesis on micro rough (\( R_a = 1 - 2 \) \( \mu \)m) planar and cylindrical surfaces. On threaded specimens we combine macro/micro/nano scale topographies by superimposing 25-80 nm nanoporous TiO\(_2\) layer onto micro rough (\( R_a = 0.5 - 1 \) \( \mu \)m) surface of threaded macro-scale geometry of the implants.

The modified surfaces combine nano-scale tubes/pores developed by EA superimposed on rough micro-scale topography prepared by turning or by SLA (sand blasting and acid etching). This approach can be valuable for enhancement of medical implants osseointegration - due to the increased protein and cell attachment, and osteoblasts proliferation and differentiation effects of modified surfaces – leading to the reduction of the risk of implants failure.

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