

## NOVEL HIERARCHICAL MICRO/NANO MODIFIED SURFACES FOR DENTAL IMPLANTS

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### Abstract

*Present paper presents the modification at nano scale level of the surfaces of Ti6Al4V alloy that were previously modified at micro scale level by acid etching (AE) or by sand blasting with large grit and acid etching (SLA). Continuous, self-ordered nanostructured (nanoporous/nanotubular) oxide layers superimposed onto micro rough topographies were developed by using electrochemical anodization in fluoride based solutions, and optimized process parameters. Novel hierarchical micro/nano modified surfaces, with well developed oxide nanotubes of 40-110 nm in diameter, were synthesis by anodization in 1M H<sub>3</sub>PO<sub>4</sub> + 0.4 wt% HF electrolyte, at anodization potential of 24 V, applied with a potential ramp of 0.08 V/s.*

**Key words:** titanium-based materials, dental implants, SLA modified surface, TiO<sub>2</sub> nanotubes, electrochemical anodization

### 1. Introduction

Dental implants are used for replacing the natural root of the tooth by this allowing the installation of dental prosthesis. The most used materials for dental implants are titanium-based materials, since they provide good mechanical strength, outstanding chemical stability, and excellent biocompatibility [1-4]. Osseointegration is defined as direct contact between living bone and the surface of load-carrying implant, and today is generally acknowledge that the long-term success of dental implants essentially depends on rapid healing with good integration into the jaw bone. The enhancement of osseointegration is a major goal in developing the new types of dental implants. Surface modification proved to be an effective solution and can be performed by many methods: mechanical, chemical, physical, or their combination [5-9].

By modifying implants' surface at the *micro scale level*, micro rough surfaces can be obtained, having large bone-to-implant contact area. Today is a

generally consensus on the fact that the sand blasted (SB) surfaces exhibit stronger bone response than turned implants. Sand blasted and acid etched (SLA) implants have highest amount of bone-to-implant contact, although this surfaces are not the roughest. As a result, the combination of sand blasting followed by acid etching is the technique commonly used for surface modification in recent years. Sand blasted implants are produced by blasting the surfaces by small particles (TiO<sub>2</sub>, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, etc.). The resulting surface topography is usually fragmented, consisting in craters and ridges and some particles embedded in the surface. Sand blasted and acid etched implants (SLA) are first blasted and then etched by acids. The acids commonly used are hydrochloric acid, sulfuric acid, hydrofluoric acid, and nitric acid. Acid attack of the surface of dental implants results in uniform roughness with pits and craters (micropores) of micrometric size, this leading to an increase in surface area. In this micropores osteoblasts and supportive connective tissue can migrate, resulting an enhancement in bioadhesion and an improved

osseointegration process of dental implants [4, 5, 7, 8]. After acid etching, some procedures perform a passivation step, this meaning the immersion in aqueous solution of nitric acid in order to stabilize the titanium oxide layer formed on the surface of the dental implant.

Furthermore, nowadays there is an intense scientific effort on surface modification at nano scale level, since it has been showed that an ordered nanostructured surface of biomedical implants promotes enhanced bone apposition [10-18]. Nanotubular titania (TNT) 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. By using electrochemical anodization technology nanoporous or nanotubular TiO<sub>2</sub> layer can be developed. In anodization cell the material to be modified is placed at the anode, and by using optimized process conditions (electrolyte, current parameters, prior surface preparation, distance anode-cathode, duration) self-arranged, nanotubular titania can be synthesis [19-23]. The growth mechanism of nanotubes is complex and occurs when two processes are in competition: the formation of oxide at the metal-oxide interface and its etching at the oxide-electrolyte interface. The composition of electrolyte is of extreme importance, as in the absence of fluoride ions the oxide layer which is developing is a compact one. The presence of fluoride ions allows the solvation of material as soluble fluoride complexes [TiF<sub>6</sub>]<sup>2-</sup> and by this, its etching. Anodization potential has also a significant importance, allowing the tailoring of nanotubes dimensions.

In this context, recently we reported efficient anodization process that leads to the formation of ordered nanotubular TiO<sub>2</sub> layer, superimposed to a micro rough topography resulting by turning, on two phases ( $\alpha+\beta$ ) Ti6Al4V alloy [24]. This has a certain degree of novelty compared with most of studies reporting TNT growth, studies that are made on polished surfaces of pure titanium. The present paper presents successful development of nanotubular titania layers superimposed to micro rough SLA and AE surfaces, results that also have elements of novelty compared to the state of the art.

## 2. Methodology

Present set of experiments was performed on Ti6Al4V alloy samples, having diameter of 16 mm and 3 mm in height. The samples were cut from bar, by using turning on Cincom K16 (Citizen) CNC turning machine.

Sand blasting procedure was performed by using SiO<sub>2</sub> particles with an average dimension of 200-250  $\mu$ m, for 40 seconds, in a Basic Eco (Renfert) sand blasting machine. Acid etching was done by using a combination of HCl 1n and H<sub>2</sub>SO<sub>4</sub> 1n (1:1). The acid etching procedure occurred at 80°C, in a BOV-T25F

(Biobase) furnace, where we kept the samples for a duration of 6 hours. The passivation procedure was done in 30% HNO<sub>3</sub>, at room temperature, for 20 min. After each of preparation step the samples were carefully cleaned in distilled water and alcohol, and dried.

The surfaces' roughness was measured using SJ-310 (Mitutoyo) roughness tester, and the samples' weight was measured using Adam AEA-100G analytical balance with an accuracy of  $\pm 0.1$  mg.

Electrochemical anodization was performed in a custom-built anodization cell with two electrodes configuration, originally designed by us. During the anodization experiments the sample was placed at the anode. A pure copper disk ( $\phi 16 \times 3$  mm), placed at a distance of 15 mm from anode, was used as cathode. The electrolyte was 1M H<sub>3</sub>PO<sub>4</sub> + 0.4 wt% HF, or 1M H<sub>3</sub>PO<sub>4</sub> + 0.5 wt% HF. The end anodization potential (U) was 20 V, or 24 V. The end potential was applied by using potential ramps of 0.08 V/s, or 0.1 V/s. The anodization time was 35 min for all experiments. The current was continuously controlled, monitored and registered during the anodization process by using Nanosource software, originally designed by us.

The scanning electron microscopy analysis was made in a JSM 5200 (JEOL) scanning electron microscope, operated at 25 kV. From each sample the micrographs were collected at 500X, 1500X, 10000X, 20000X, and 35000X magnifications. For better visualization of oxide layers' coverage over the microrough AE, SLA, or SLA and passivated surface we also collected SEM micrographs having samples inclined with a tilt angle of 45°. Open source graphical image processing software (Gimp) was used to measure nanotubes' features (internal diameter, external diameter, wall thickness).

## 3. Results and discussion

The initial surface of the samples resulting after detaching them from bar by CNC turning exhibited a micro rough topography, with regular machining grooves apparent on the surface, and roughness R<sub>a</sub> of  $\sim 1.2$   $\mu$ m.

*SLA surfaces modified at nano scale level.* After sand blasting of the samples their surface morphology become a fragmented one, the roughness increases to R<sub>a</sub>  $\sim 3$   $\mu$ m. By acid etching of the samples, in order to complete SLA procedure, a material removal process occurs, the morphology of the surface becomes smoother, with large valleys and high hills of  $\sim 50$   $\mu$ m, interrupted by micro pores of 5-10  $\mu$ m, and the roughness decreases to R<sub>a</sub>  $\sim 2$   $\mu$ m. These are typical SLA surface, as they are present on many commercial dental implants available today on the market.

By subjecting the samples with SLA modified surfaces to electrochemical anodization in 1M H<sub>3</sub>PO<sub>4</sub> + 0.5 wt% HF, using an end potential U = 20 V, applied with a potential ramp of U<sub>r</sub> = 0.1 V/s, the oxide layer that is developing on the surface is structured at the nano scale level. Figure 1.a presents

SEM micrograph of the nanostructured surface, collected at low magnification of 1500X, showing the oxide layer developed on the previously modified SLA surface. At high magnification of 35000X the

SEM micrograph shows the ordered nanoporous structure of oxide layer, with pore openings of 25-55 nm (fig. 1.b).

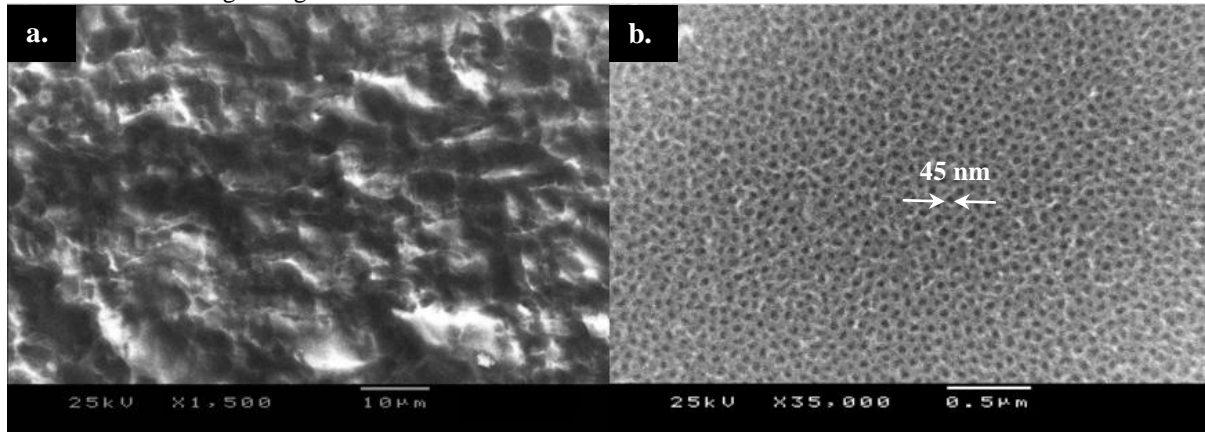


Fig. 1: SEM micrographs of TiO<sub>2</sub> nanostructured (nanoporous) layer developed on SLA surface; a – 1500x magnification; b - 35000X magnification

By optimizing the electrochemical anodization process parameters, which means the addition of 0.4 wt. % HF in 1M H<sub>3</sub>PO<sub>4</sub>, U = 24 V, U<sub>r</sub> = 0.08 V/s, the TiO<sub>2</sub> layer that is developing on the SLA surface has a self-ordered nanotubular morphology. This nanotubular layer is a continuous one and is superimposed on SLA micro rough surface, as the SEM micrograph, collected at a magnification of 1500X and a tilt angle of 45° (fig. 2.a) shows. The inset of the fig. 2.a taken at a higher magnification (10000X) shows in greater detail the continuity of the

oxide layer, and one can also observe, even the magnification is not high enough to distinguish with accuracy, that the layer is not a compact one, being structured also at nano scale level. SEM micrograph taken at a magnification of 35000X, top view, clearly demonstrates the nanotubular morphology of the titania layer (fig. 2.b). The diameter of nanotubes is in 50-110 nm range, the majority presenting a diameter of ~75 nm.

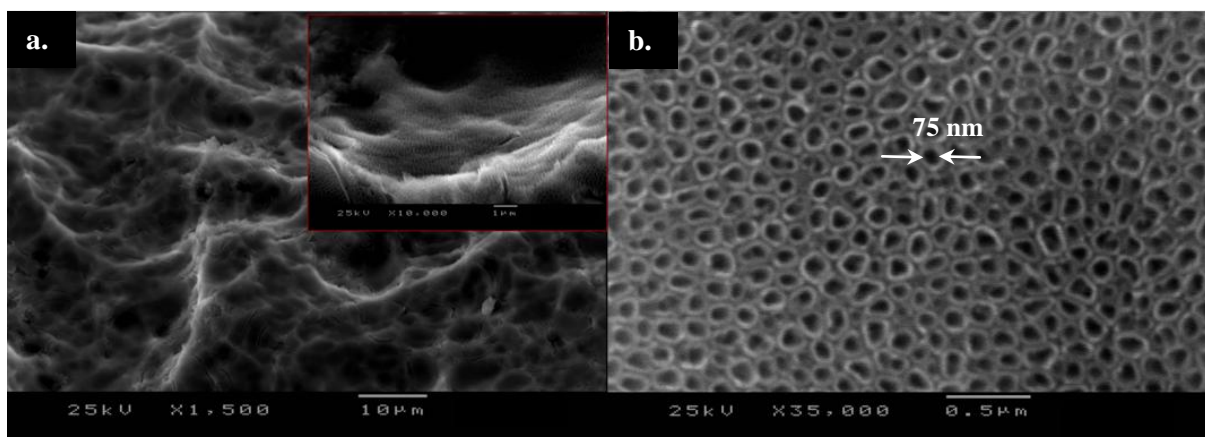


Fig. 2: SEM micrographs of TiO<sub>2</sub> nanostructured (nanotubular) layer developed on SLA surface; a – 1500X magnification (inset – 10000X magnification); b - 35000X magnification

The optimized process parameters were used by us for electrochemical anodization of surfaces that were initially subjected to SLA procedure, followed by a passivation step. Figure 3 presents the results of our experiments showing the development of a continuous, self-arranged nanotubular TiO<sub>2</sub> layer, with nanotubes diameter of 40-110 nm, the majority having ~70 nm.

AE surfaces modified at nano scale level. The initial morphology of acid etched surfaces is a micro rough one, exhibiting a roughness of R<sub>a</sub> ~ 1.2 µm. By subjecting this surface to electrochemical anodization in optimized conditions for our setup (1M H<sub>3</sub>PO<sub>4</sub> + 0.4 wt% HF, U = 24 V, U<sub>r</sub> = 0.08 V/s) the initial AE micro rough surface becomes covered with a nanostructured titania layer as fig. 4.a and its inset

shows. Top view SEM micrograph taken at high magnification shows the nanotubular morphology of this nanostructured layer (fig. 4.b). The nanotubes'

diameter is in 40-110 nm range, the most of them having a tube opening of 80 nm.

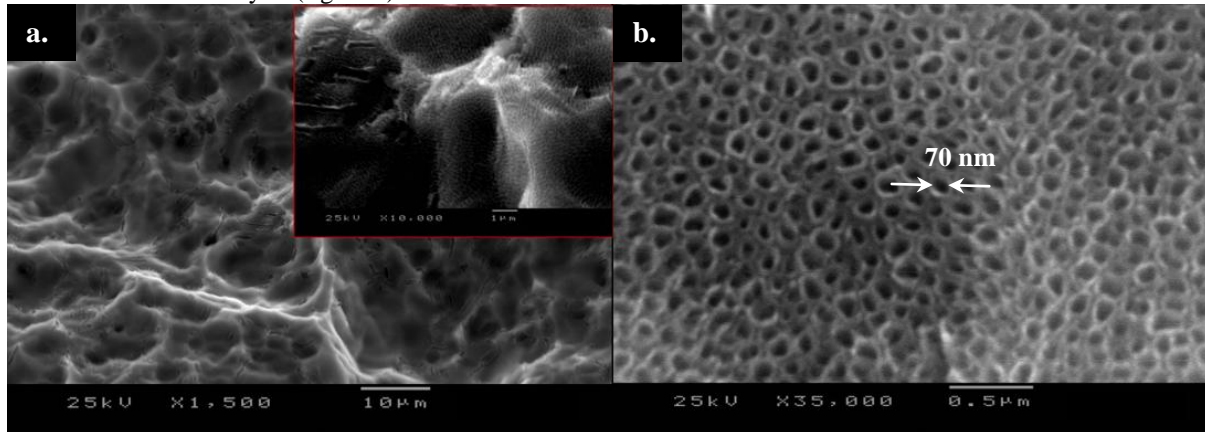


Fig. 3: SEM micrographs of TiO<sub>2</sub> nanostructured (nanotubular) layer developed on SLA followed by passivation surface; a – 1500X magnification (inset – 10000X magnification); b - 35000X magnification

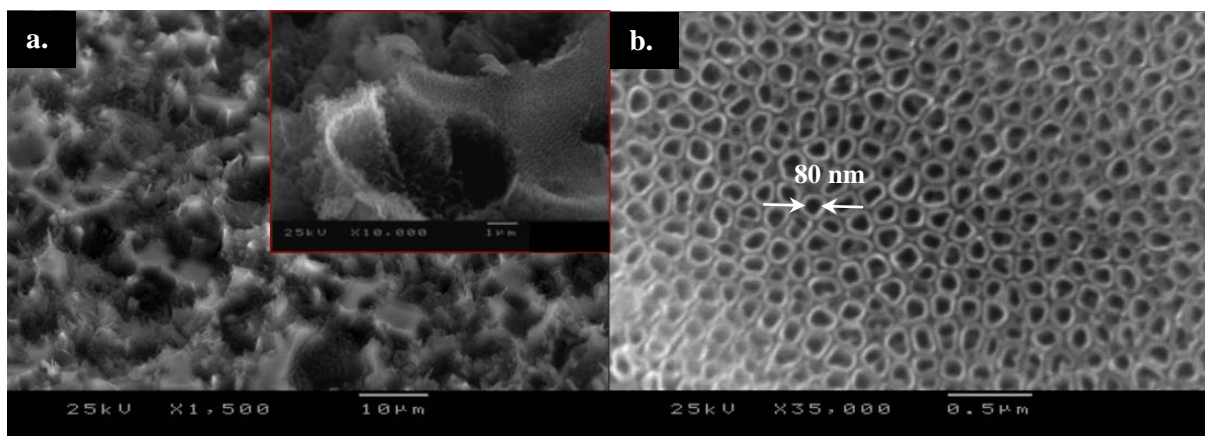


Fig. 4: SEM micrographs of TiO<sub>2</sub> nanostructured (nanotubular) layer developed on AE surface; a – 1500X magnification (inset – 10000X magnification); b - 35000X magnification

#### 4. Conclusions

Present research demonstrates the successful synthesis of hierarchical micro/nano modified surfaces consisting in nanostructured TiO<sub>2</sub> layer superimposed on micro rough sand blasted and acid etched (SLA) or acid etched (AE) surfaces of two phases ( $\alpha+\beta$ ) Ti6Al4V alloy.

By using electrochemical anodization in 1M H<sub>3</sub>PO<sub>4</sub> + 0.5 wt% HF electrolyte, anodization potential of 20 V, and potential ramp of 0.1 V/s the morphology of nanostructured layer is a nanoporous one, with nanopores' openings in 25-55 nm range. By optimizing anodization process parameters (1M H<sub>3</sub>PO<sub>4</sub> + 0.4 wt% HF electrolyte, anodization potential of 24 V, potential ramp of 0.08 V/s) the nanostructured layers become nanotubular ones, and are developing as continuous, self-ordered layers superimposed on SLA or AE surfaces. The diameter of nanotubes is in 40-110 nm range, most of them being of 70-80 nm.

These results have elements of novelty compared

with the state of the art, where the most results on titania nanotubular layer development are reported as carried out on pure titanium extra polished surfaces.

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