

THE EFFECT OF ULTRASONIC CLEANING ON MEDICAL GRADE ANODIZED TITANIUM USED FOR DENTAL IMPLANTS

Dragos Vladimir BUDEI, Danut-Ionel VAIREANU*, Eliza BUZAMET, Emanuel AXENTE, Felix SIMA

Department of Inorganic Chemistry, Physical Chemistry & Electrochemistry,
Faculty of Applied Chemistry and Materials Science, University Politehnica of
Bucharest, 1-7 Gh. Polizu Street, 011061, Bucharest, Romania

Abstract

Titanium and titanium alloys of medical grade are preferred for dental implants for their excellent biocompatibility. In order to decrease the rejection percentage of such implants, it was found that electrochemically pretreating the surface by anodization producing self-organized titanium oxide nanotubes arrays will enhance the osteointegration chances of titanium implants. Although ultrasonic cleaning, as part of post-cleaning procedure, is used to get rid of the adsorbed traces of electrolyte, one noticed that, if used in excess, this may also fracture the obtained titanium oxide nanotube arrays. This paper attempts to compare a normal chemical cleaning procedure versus a chemical cleaning procedure used in connection with ultrasonic cleaning, in order to remove the electrolyte traces trapped at the implant surface, after the anodization, to decide whether or not the ultrasonic cleaning is a must and has to be included in the post-anodization procedure.

Key words: surface properties, anodized titanium, titanium oxide nanotubes, ultrasonic cleaning of dental implants

1. Introduction

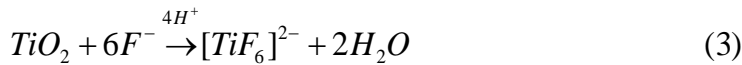
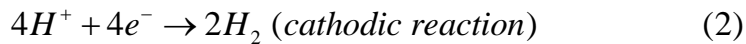
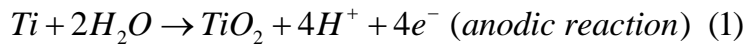
Titanium and titanium alloys are some of the most used metals in the field of medical implants due to their inherent excellent biocompatibility (increased chemical stability, mechanical resistance, absence of toxicity) and some research concerning this field paid increased attention to find out the most suitable treatments to improve the osteointegration of such implants, particularly in restoring the missing dentition [1-6]. One key factor in this direction is the surface modification of implants, either by modifying the roughness of the implant

* Corresponding author. Email address: di_vaireanu@yahoo.co.uk (D.I. Vaireanu)

surface or by functionalizing the surface with various chemical, biochemical or biologically active materials [1], [4-5] [7-9].

The implant surface may be modified by grit-blasting, acid-etching or by a particular electrochemical treatment, namely anodization [7-8], [10]. It was found, however, that the best chances for the attached proteins to interact with cells, may occur when the implant surface was functionalized in the nanometer range, the nanostructured surface improving significantly the osteointegration of titanium implants [11]. Self-organized titanium oxide nanotubes arrays, particularly suitable as basic support for implant fictionalizations may be easily formed, under perfectly controllable conditions, by electrochemical anodization [10-16].

The formation of titanium oxide nanotube arrays by anodization in electrolytes containing fluoride ions may be best described by two competitive processes [12-16], the first one being the anodic formation of TiO_2 (equation 1 and 2), the second one being the chemical dissolution of titanium oxide in the presence of fluoride ions, at the titanium oxide/electrolyte interface (equation 3):



The actual mechanism of titanium oxide nanotube arrays formation and growth by electrochemical anodization can be simplified by dividing it into three stages [12-16]:

I. The formation of an initial barrier layer – a rapid oxide growth takes place on the surfaces of the anodized titanium due to the interaction of the metal (in fact metal ions obtained by anodization) with water. One may notice here a very sharp decrease in current density due to an increased in the total ohmic resistance, as a result of the formation of a compact film of oxide;

II. The formation of uniformly distributed pores - small pits, similar to those produced by pitting corrosion, but at a nanometer level scale, are formed in the oxide film produced by anodization, due to a localized chemical dissolution process, depicted by equation 3, forming a barrier layer at the bottom of the pits, which will lead to an increase in the electrical field intensity across the remaining barrier layer, increasing the current density and resulting in further pore growth;

III. Separation of interconnected pores into nanotubes – a separate region between the formed pores will appear, so that the resulting nanotube formation is a direct consequence of simultaneous formation of oxide due to field assisted oxidation and the process of chemical dissolution in the presence of fluoride ions.

The anodization process is strongly influenced by the proper cleaning (before and after anodization), in the absence of this or in the case of poor cleaning there is a danger that the implants may be rejected for not fulfilling the medical standards, a very costly outcome [17-19]. The explanation for this is that tiny screws, with tight threads, may adsorb and trap reagents used during the anodization process, these reagents becoming unwanted contaminants from the medical point of view, and in the case of fluoride ions being particularly toxic, and such contaminants are difficult to remove using a classical normal cleaning by washing and rinsing.

The use of ultrasonic cleaning was used extensively to get rid of the unwanted residues of electrolyte. If high frequency sound waves are passed through liquids, a cavitation process takes place, tiny bubbles being created on all surfaces, and, at the same time, being rapidly destroyed by implosion, due to the oscillating zones of high and low pressure, transferring the energy to the washed parts and contaminants, which are dislocated from the implants and relocated into the washing liquid.

Although ultrasonic cleaning may offer a real and affordable cleaning solution as part of the titanium anodizing procedure, it was noted that, in some circumstances, ultrasonic cleaning tends to fracture the obtained titanium oxide nanotube arrays.

The aim of this study is to verify if normal chemical cleaning is enough to remove the electrolyte traces trapped at the implant surface after the anodization, and to compare this with a normal ultrasonic cleaning, to decide whether or not the ultrasonic cleaning is a must and has to be included in the post-anodization procedure.

2. Experimental

Reagents

All the reagents used in this study were *p.a.* from Sigma-Aldrich, Merck, and Chimopar. The electrolyte used during the anodization procedure was prepared using distilled water. Titanium used for anodization is 99.9% Ti Grade 4 of medical grade produced by Dynamet USA.

Apparatus and procedure

The equipment used for the titanium implants anodization, the electrolyte composition of the anodization bath and the anodization procedure are subjected to a patent pending procedure. The actual implants were obtained from medical grade 4 titanium produced by Dynamet USA, using a 9-axis Citizen Cincom L20 CNC Swiss Type lathe produced in Japan.

The milled implants were sandblasted using Al₂O₃ (corundum), 70 μm in size, for 30 seconds. The ultrasonic bath used for the ultrasonic cleaning was

Condell 3106, Germany, with an active power of 50 W, operated at a fixed frequency of 35 kHz, and it was provided with an automatic switch off programmable timer. Prior to anodization the implants were cleaned in the ultrasonic bath for 8 minutes @ 40 °C for each stage: twice in distilled water with liquid soap 1%, twice in distilled water, twice in acetone, twice in isopropyl alcohol in order to get rid of the grease (lubricating mineral oil from the milling stage) and any other contaminants which may impurify the anodization bath. A ten times more powerful cleaner, an Elmasonic X-tra 30H Ultrasonic Cleaner Bath, Germany, 35 kHz, 480 W, was used to investigate the effect of excessive ultrasonication. One has collected samples cleaned ultrasonically before the anodization and samples after the anodization cleaned chemically only and cleaned chemically in the ultrasonic bath. Scanning Electron Microscopy (SEM) was used to investigate the surface morphology of the anodized Titanium implants with a FEI Inspect S electron microscope. The measurements were performed at 30 kV acceleration voltages, in high vacuum.

3. Results and discussions

The shape and dimensions of an implant are presented in Figure 1 (one may also see the rod system used for suspending these implant in the anodization bath to avoid a possible anodic dissolution as one has to fully immerse the implant in the bath and at the same time to avoid any anodic dissolution should the contacting rod be made of a different metal). After the anodization, the contacting rod is detached by breaking it from the main body of the implant and the implant is sent for post-anodization cleaning.

Scanning electron microscopy (SEM) was used to characterize the anodized titanium. One has measured the inner diameters and the wall thickness of titanium oxide nanotubes arrays produced by anodization (see Table 1), and it was found that their dimensions are well within the results reported in the literature [7], [10-11] [13-17].



Fig. 1. Samples of the mechanically milled titanium implants with **a)** (before) anodization) and without **b)** the suspending rod (after anodization) (2 mm diameter, 4 mm length)

Table 1

Dimensional characteristics of titanium oxide nanotubes produced by anodization

No.		Inner diameter, nm	Wall thickness, nm
1	Min	25	7
2	Max	104	8

In Figure 2 is presented a sandblasted implant before the anodization procedure, chemically cleaned @ 40 °C in conjunction with ultrasonic cleaning. The surface morphology is a smooth one, corresponding to that of an object produced by milling.

In the absence of ultrasonication, one may see crystals of fluoride salts and other solid contaminants trapped within the titanium oxide nanostructures (Figure 3) showing that a classical chemical cleaning with distilled water and alcohol is not enough for a thorough cleaning. In contrast with this, ultrasonically assisted chemical cleaning managed to get rid of these unwanted contaminants (Figure 4).

The use of excessive ultrasonic cleaning tends to fracture and level the titanium oxide nanostructure, leading to a rather planar honeycomb based nanostructure (Figure 5 versus Figure 6).

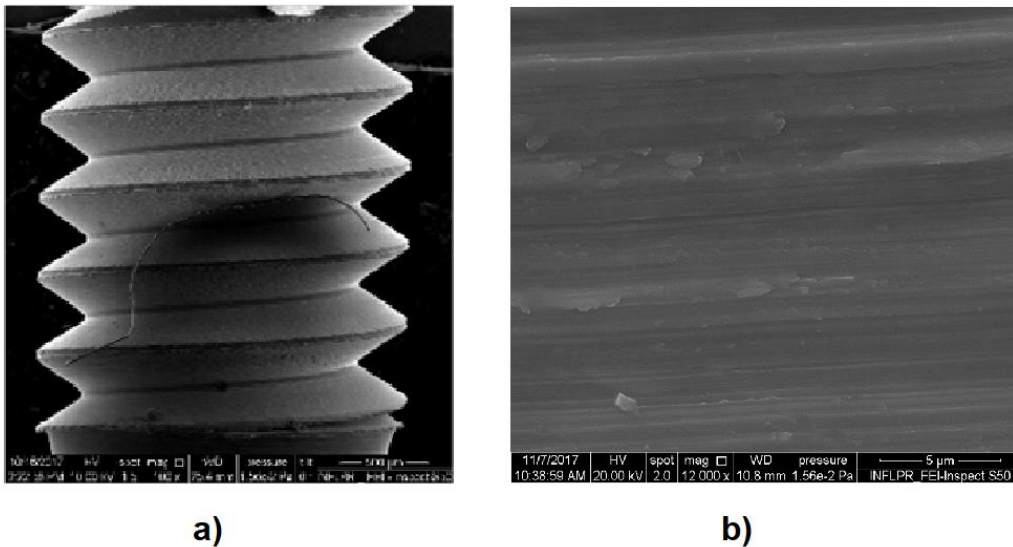


Fig. 2. a) Low (200x magnification) and **b)** high (12000x) magnification SEM picture of the implant before anodization, chemically cleaned @ 40 °C in conjunction with ultrasonic cleaning (2 times in distilled water with liquid soap 1%, 2 times in distilled water, 2 times in acetone, 2 times in isopropyl alcohol), 8 minutes/stage, the ultrasonic bath characteristics: 50 W, 35kHz

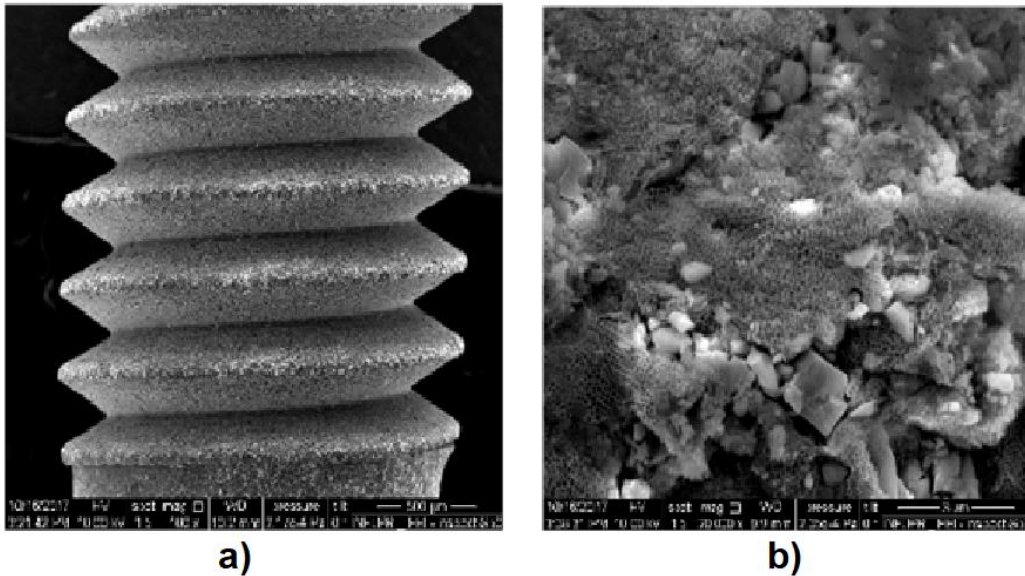


Fig. 3. Chemical cleaning. Low **a)** 200x magnification and high **b)** 20000x magnification SEM picture of anodized titanium surface, chemically cleaned only @ 40°C (twice in distilled water, once in isopropyl alcohol)

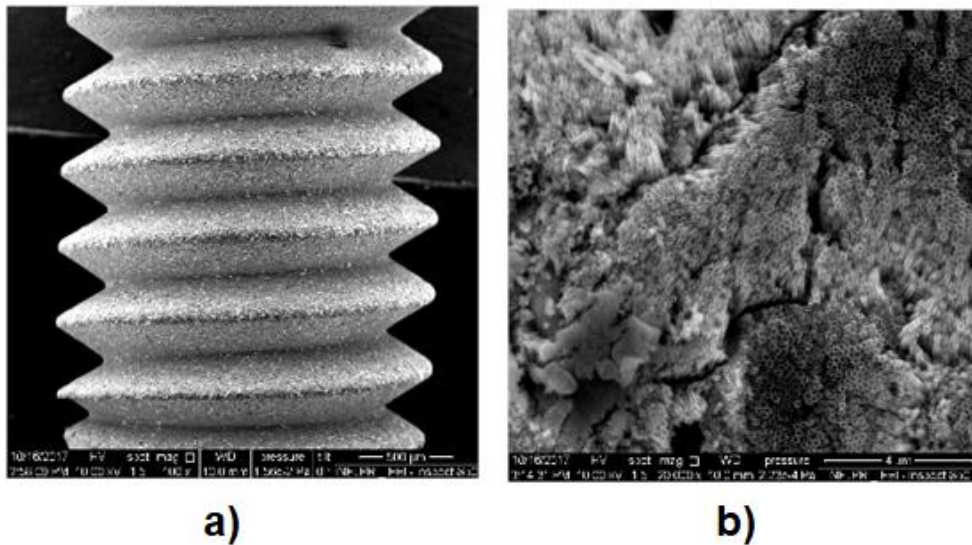


Fig. 4. Chemical cleaning used in conjunction with ultrasonic cleaning. Low **a)** 200x magnification and high **b)** 20000x magnification SEM picture of anodized titanium surface, chemically cleaned @ 40 °C in conjunction with ultrasonic cleaning (2 times in distilled water, 1 time in isopropyl alcohol). Each stage lasted 3 minutes, the ultrasonic bath characteristics: 50 W, 35kHz

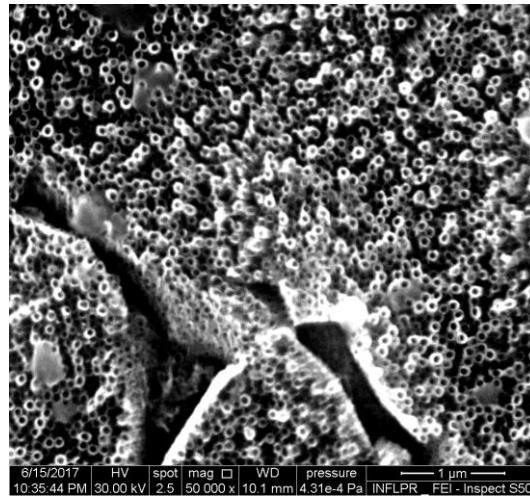


Fig. 5. SEM image of an anodized implant subjected to a chemical cleaning @40 °C used in connection with a soft ultrasonic cleaning procedure (3 minutes, 50 W, 35kHz, and: twice in distilled water and once in isopropyl alcohol)

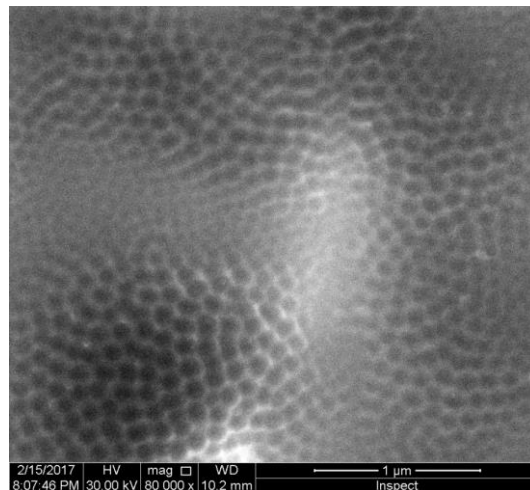


Fig. 6. The effect of extensive ultrasonication
SEM image of an anodized implant, 80000x magnification, subjected to an increased power (9.6 times) excessive ultrasonic cleaning procedure (2 minutes, 480 W, 35kHz, and 40 C: twice in distilled water and once in isopropyl alcohol)

4. Conclusions

The use of ultrasonication chemical cleaning, as a post-anodization cleaning phase, is a very useful *sine qua non* stage during the production of the anodized dental implants, obtained in fluoride based electrolytes, as chemical cleaning by itself is not enough to remove the electrolyte traces and other contaminant trapped at the implant surface.

One should however use it carefully, and initial verifications are compulsory, as an excessive ultrasonic cleaning tends to destroy and level the fragile titanium oxide nanostructure.

This disadvantage may be used as a control lever should one desire to obtain a more planar titanium oxide nanostructure required in some instances for particular fictionalizations with biological active materials.

Acknowledgements

This research was supported by Dentix Millennium SRL through the project “Dental implants surface functionalization for improved osseointegration – an innovative method” (“Metodă inovativă pentru funcționalizarea suprafețelor implanturilor dentare cu scopul îmbunătățirii osteointegrării”) code MySMIS 104809, contract no. ANCSI 73/8.09.2016.

REFERENCES

- [1]. Yanko, V. M., Surface treatment of titanium components with the aim of improving operating properties, *Chem. Pet. Eng.* 49, 7, (2013), 44 – 45.
- [2]. Geetha, M., Singh, A.K., Asokamani, R.A. Gogia, K., Ti based biomaterials, the ultimate choice for orthopaedic implants—a review, *Prog. Mater. Sci.*, 54, 3, (2009), 397-425.
- [3]. Alhag, M., Renvert, S., Polyzois, I., Claffey, N., Re-osseointegration on rough implant surfaces previously coated with bacterial biofilm: an experimental study in the dog. *Clin Oral Implants Res.* 19, (2008), 182-187.
- [4]. Schwarz, F., Sahm, N., Iglhaut, G., Becker, J., Impact of the method of surface debridement and decontamination on the clinical outcome following combined surgical therapy of peri-implantitis: a randomized controlled clinical study, *J. Clin. Periodontol.* 38, 3 (2011), 276-284.
- [5]. Ungvari, K., Pelsoczi, I.K., Kormos, B., Oszko, A., Rakonczay, Z., Kemeny, L., Radnai, M., Nagy, K., Fazekas, A., Turzo, K., Effects on titanium implant surfaces of chemical agents used for the treatment of peri-implantitis. *J. Biomed. Mater Res. B Appl. Biomater.*, 94, (2010), 222-229.
- [6]. Elias, C.N., Meirelles, L., Improving osseointegration of dental implants, *Expert Rev Med Devices*, 7, (2010), 241-256.
- [7]. Nishimoto, S.K., Nishimoto, M., Park, S.W., Lee, K.M., Kim, H.S., Koh, J.T., Ong, J.L., Liu, Y., Yang, Y., The effect of titanium surface roughening on protein absorption, cell attachment, and cell spreading, *Int. J. Oral. Maxillofac. Implants*, 23, (2008), 675-680.
- [8]. Pae, A., Kim, S.S., Kim, H.S., Woo, Y.H., Osteoblast-like cell attachment and proliferation on turned, blasted, and anodized titanium surfaces, *Int. J. Oral Maxillofac. Implants*, 26, (2011), 475-481.
- [9]. Piattelli, M., Scarano, A., Paolantonio, M., Iezzi, G., Petrone, G., Piattelli, A., Bone response to machined and resorbable blast material titanium implants: an experimental study in rabbits, *J. Oral Implantol.*, 28, (2002), 2-8.
- [10]. van Vuuren, D., Laubscher, R., Surface friction behaviour of anodized commercially pure titanium screw assemblies, *Procedia CIRP* 45, (2016), 251-254.
- [11]. Salou, L., Hoornaert, A., Louarn, G., Layrolle, P., Enhanced osseointegration of titanium implants with nanostructured surfaces: An experimental study in rabbits, *Acta Biomaterialia*, 11, (2015), 494-502.

- [12]. Mor, G. K., Varghese, O. K., Paulose, M., Shankar, K., Grimes, C. A. A review on highly ordered, vertically oriented TiO₂ nanotube arrays: fabrication, material properties, and solar energy applications, *Solar Energy Materials and Solar Cells*, 90, (2006), 2011-2075.
- [13]. Crawford, G. A., Chawla, N., Das, K., Bose, S., Bandyopadhyay, A. Microstructure and deformation behavior of biocompatible TiO₂ nanotubes on titanium substrate, *Acta Biomaterialia* 3, (2007), 359-367.
- [14]. Sobieszczyk, S. Self-organized nanotubular oxide layers on Ti and Ti alloys, *Advances in Materials Sciences*, 9, (2009), 25-41.
- [15]. Macak, J. M., Tsuchiya, H., Ghicov, A., Yasuda, K., Hahn, R., Bauer, S., Schmuki, P., TiO₂ nanotubes: self - organized electrochemical formation, properties and Applications, *Current Opinion in Solid State & Materials Science*, 11, (2007), 3-18.
- [16]. Macak, J. M., Sirotna, K., Schmuki, P., Self-organized porous titanium oxide prepared in Na₂SO₄/NaF electrolytes, *Electrochimica Acta*, 50, (2005), 3679-3684.
- [17]. Lee, T. C., Mazlan, M. H. H., Abbas, M. I., Abdullah, H., Idris, M.I., Effect of Ultrasonic Amplitude on Surface Properties of Anodized Titanium for Biomedical Application, *Materials Science Forum*, 840, (2016), 160-164.
- [18]. Kawashima, H., Sato, S., Kishida, M., Yagi, H., Matsumoto, K., Ito, K., Treatment of titanium dental implants with three piezoelectric ultrasonic scalers: an in vivo study, *J. Periodontol.*, 78, (2007), 1689-1694.
- [19]. Sato, S, Kishida, M., Ito, K., The comparative effect of ultrasonic scalers on titanium surfaces: an in vitro study, *J. Periodontol.*, 75, (2004), 1269-1273.