

Electrochemical Surface Processing Applied for the Functionalization of Titanium Screw Type Implants

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Abstract

The electrochemical anodization of titanium plates is considered an effective processing method applied to enhance their surface roughness. It is a well-known fact that through the electrochemical anodization of titanium, molecular self-organizing processes can be enabled, and organized micro or nano structures of TiO₂ can be synthesized on its surface. Although this method is not expensive and it is extremely practical, the dependency on a great number of manufacturing parameters require deep understanding and control on the whole fabrication process. Until the moment, a great difficulty has been detected in applying this method at a large scale in areas such as mechanical systems and implantology. For instance, in practice a great difference exists between processing a plate surface and an implant surface. Suitable anodizing conditions result in titania nanotubes layers on pure titanium plates, while the same conditions can only enable the formation of pores on a titanium implant surface. There is a need of a number of theoretical and experimental investigations for a better understanding of the formation of highly organized microstructures on titanium implant surfaces through the electrochemical anodizing method. The present manuscript describes a set of experiments applied for the surface modification of dental screw type titanium implants through the electrochemical anodizing method. Two protocols involving several anodization steps lead to the formation of nanotube-like structures on the implant surface. Further investigations may allow the functionalization of titanium implants surface through the electrochemical synthesis of highly organized nanostructures.

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Introduction

Porous materials have been used since more than two decades ago in surgical implant design, to fabricate replacing devices or augment soft and hard tissues, as coatings on prostheses to accommodate tissue ingrowths for biological fixation, and as scaffolds to facilitate the regeneration of the tissue [1, 2]. It has been reported that porous materials in implants can reduce the stiffness mismatches due to their structure and achieve stable long-term biological fixation due to bone-tissue in-growth into interconnected porosity from the surface to the inside [3]. A porous material allows interpenetration and formation of blood vessels, which is important in order to get the natural bone to grow into the implant. Tissue ingrowths into the pores of the material during the process of repair or regeneration associated with the healing response to surgical implantation provides an interlocking, mechanical attachment of the porous material to the host.

Metallic implants are used in hard tissues replacement. In this category, titanium and its alloys have been widely applied in dental and orthopedic implants manufacturing, as they present many advantages such as excellent biocompatibility, superior mechanical strength, and high corrosion resistance. Although their biomedical performance is quite good comparing to other materials, the problem lies in the interfacial bond between the tissue and the

implant due to the bio-inert nature of metals. For this reason enhancement of the connection between bone and an implant may still be expected in clinical application [4]. Various approaches have been utilized to increase the surface roughness for an increased biocompatibility and functionality of implants and thus promote bone-tissue integration [5-7]. Currently, electrochemical methods are attracting more attention for the lower cost and easier control. These methods aim to modify the surface of metallic implant materials. The chemical reactions are predominantly occurring at the interface between the metal and chemical solution, providing unique properties required in the biological environments. The most common chemical treatments involve acid, hydrogen peroxide (H₂O₂), alkali treatments, sol-gel and anodic oxidation.

Titanium is the most common metal used in hard tissues replacement. The electrochemical anodization of titanium plates is considered an effective processing method applied to enhance their surface roughness and biocompatibility [8-12]. It is a well-known fact that through the electrochemical anodization of titanium, molecular self-organizing processes can be enabled, and organized micro or nanostructures of TiO₂ can be synthesized on its surface. In the class of electrochemically synthesized titanium oxide structures, the most common are the titania nanotubes [13, 14]. As previously stated, the existence of these types of structures on the

titanium surface influences their performance when involved in interphases; a direct relation exists between the synthesis parameters and nanotubes characteristics, as well as between the roughness of the nanotubes layer and its interaction with another substrate [15]. This issue is of particular interest in biological interphases, when a tissue comes in contact with an implant surface.

Although the electrochemical anodization method is inexpensive and extremely practical, the dependency on a great number of manufacturing parameters requires deep understanding and control on the whole fabrication process. Many studies were dedicated to understanding the role of the synthesis parameters on the microstructures formation in the titanium oxide films [16, 17]. The main factors that influence nanotubes synthesis in an anodizing process are: the electrolyte type, the anodizing time, the anodizing voltage and the characteristics of the titanium foil - mainly its initial roughness, purity and geometry.

Research on synthesizing titania nanotubes deals with highly pure titanium, provided by popular suppliers [18, 19]. This type of titanium has a high cost and does not coincide with the medical titanium, which is several times found in alloyed condition. Small differences in the metal's chemical structure may totally alter the anodization results. Researchers present positive perspectives regarding the application of titania nanotubes in commercial sectors. In biomedicine, this substrate is proposed as the base for a drug delivery system. However, in practice this is not yet possible due to technical difficulties in synthesizing highly organized titania nanotubes on different types and geometries of titanium, as for instance on a dental titanium screw type implant. Treatments such as titanium plasma-spraying, grit-blasting, acid-etching, anodization or calcium phosphate coatings have been previously applied on implant surfaces with positive results [20]. On the opposite, the highly organized titania nanotubes are rarely synthesized on titanium implants.

In practice, a great difference exists between processing a plate's surface and an implant surface. Suitable anodizing conditions result in titania nanotubes layers on pure titanium plates, while the same conditions can only enable the formation of pores on a titanium implant surface. There is a need of a number of theoretical and experimental investigations for a better understanding of the formation of organized microstructures on titanium implant surfaces through the electrochemical anodizing method. The present work describes a set of experiments applied for the surface modification of dental titanium screw type implants through the electrochemical anodizing method; this research is part of a systematic study with its final target the manufacturing of highly organized micro and nanostructures on titanium or alloyed titanium implant surfaces using well established, standard protocols.

Experimental

Materials

In this study, the control surface was a pure titanium, 1 mm thickness plate provided by Alfa Aesar S.A. Massachusetts. Samples were cut using laser technology (Fig. 1a), cleaned and subjected to electrochemical anodization following the steps described later on, in Section 2.3.

Further on, titanium screw type implants, DENTSLPY FRIADENT, Model XiVe 26 – 146599 S plus Screw Implant with dimensions D 5.5/ L 15 were used for this study. In Fig. 1b, one non-anodized dental implant (left) next to one anodized implant (right), the latter one having the characteristic color as a result of the electrochemical processing.

Cleaning procedure

It is important to mention that in most of the published investigations [21-23] good sandpaper polishing of the metallic

surface is suggested before anodization. This is an easy task when it comes about titanium sheets. However, a screw type implant surface presents spiral geometry, as observed in the micrographs in Fig. 2. For this reason sandpaper polishing is not an appropriate option; therefore, the cleaning procedure for these samples consisted in washing them with distilled water and ethanol.

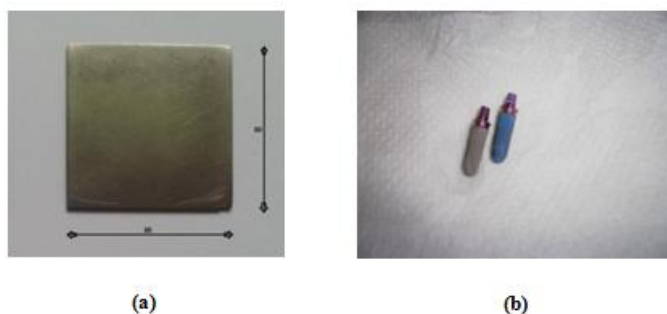


Figure 1: Titanium samples: (a) Titanium plate provided by Alfa Aesar and (b) The virgin (not anodized) dental implant (left), next to the electrochemically anodized dental implant (right)

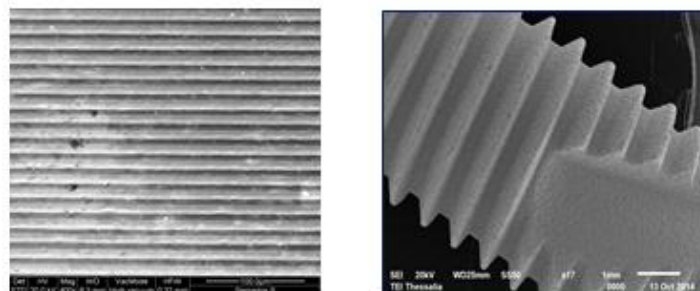


Figure 2: SEM Micrographs of Dental Screw Type Titanium Implants

Anodizing protocol and Sample Analysis

Previously to anodization, samples were prepared as following:

- The sample was polished using sandpaper (where permitted, e.g. flat samples)
- The sample was cleaned with ethanol and distilled water
- The sample was mounted in the electrochemical cell as anode, while the cathode consisted in a graphite bar
- After anodization, the sample was removed from the electrochemical cell and cleaned with ethanol and distilled water.
- The sample was left to dry at room temperature

Table 1: Anodization protocols and involved parameters

Protocol No.	Detailed Protocol	Anodization Time (Hours)	Electric Potential (Volt)	Electrolyte
1 First Screw Type Implants Group	Step 1	8	25	
	Step 2	48	40	0.4% (w/w) in 1:1 (w/w) Water – Glycerol
	Step 3	16	25	
2 Second Screw Type Implants Group	Step 1	8	25	
	Step 2	24	25	

A considerable number of anodization protocols are given in literature. Most commonly known parameters which influence this process are the time, the electric potential and the electrolyte type. The two protocols used in the present study are given in Table 1. The first protocol consisted in a three-step anodization process, while the second protocol involved a two-step anodization. The first anodization step coincided in the two protocols and did not cause any modification to the implants surface. After the first anodization step, screws were separated in two groups and anodized using different electrochemical conditions.

Finally, all samples were analyzed using Energy dispersive X-ray diffraction and SEM device, Model Zeiss SUPRA 35VP, in the absence of any conductive sputtering.

Results and Discussion

In the frame of the present study two types of titanium geometries: (i) *titanium plates* and (ii) *screw type titanium implants* were subjected to electrochemical anodization. The purpose of the investigation was to study the microstructure of the oxide layer formed on the samples as a result of their processing surface.

Metal oxide surfaces are prime examples of the close relationship between structure and reactivity, as local non-stoichiometries or geometric defects directly affect the structure. Because of the mixed ionic and covalent bonding in metal oxide systems, the surface structure has an even stronger influence on local surface chemistry as compared to metals or elemental semiconductors. A great amount of work has been performed on TiO_2 over the years, and allowed to an understanding that is unprecedented for a metal oxide surface [24]. The interest on titanium dioxide increased even more with nanotechnology development, due to the highly organized nanostructures which form on its surface under controlled electrochemical conditions of the anodization. However, the characteristics of the initial titanium, such as purity, density, porosity and others influence in a great extent the thickness and properties of the titanium dioxide layer. For this reason, the EDX analysis of the samples involved in the present investigation was considered necessary; results are presented in *Section EDX analysis*, while the anodization results are presented in *Section SEM Analysis of the Titanium Plates*.

EDX Analysis

A very important factor involved in the synthesis of titania based microstructures is the titanium bulk and surface level of purity. The formation of a homogeneous titanium dioxide layer on pure titanium sheets is an easy task, while in the case of alloyed titanium this process is strongly affected by the presence of other atoms than titanium. As observed, EDX Analyses (Figs. 3a and 3b) demonstrated that both the plates and the dental implants used in the present study are made of pure titanium.

SEM Analysis of the Titanium Plates

The titanium plates were anodized using the conditions described in Table 1, *Protocol No. 1 - Step 1* - 8 hours anodization time, at 25 volts in an electrolyte containing 1wt% HF in 1:1 (w/w) glycerol-water solution. A balance of time, anodization voltage and electrolyte lead to the formation of highly organized titanium dioxide nanotubes (Fig. 4) of approximately 100 nm diameter. Results are highly repeatable. These types of nanostructures were previously studied by the authors in an attempt to understand the optimum combination of parameters involved in their synthesis [15, 25].

SEM Analysis of the Titanium Screw Type Implants

Surface polishing is an important factor in a controlled anodization process; a polished surface assures a uniform

corrosion, leading to organized pits formation, fairly distributed on the sample surface. In this study, the control samples, the titanium plates respectively, were polished before anodization. Polishing of titanium implants was not possible, as their geometry is too complicated. In the SEM images in Fig. 5 one can observe that the surface topography of the titanium implants was porous, as provided by the supplier.

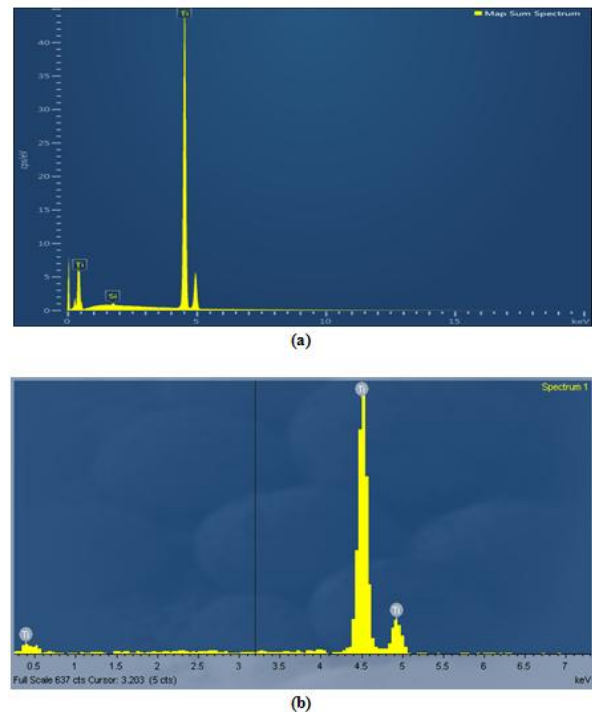


Figure 3: EDX Analyses of (a) Titanium plates made of pure Ti (traces of Si can be observed after sandpaper polishing) and (b) Screw type implant made of pure Ti.

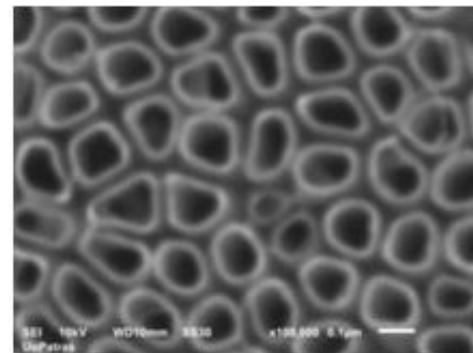


Figure 4: SEM micrographs of the synthesized highly organized titanium dioxide nanotubes.

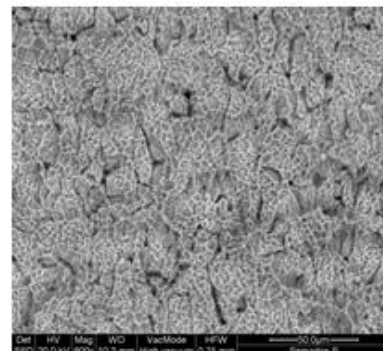


Figure 5: SEM micrographs of the titanium implant surface as provided by the supplier.

Both titanium plates and titanium implants were firstly anodized under the conditions presented in Table 1, *Protocol No.1 - Step 1 - 8 hours anodization time, at 25 volts in an electrolyte containing 1 wt % HF in 1:1 (w/w) glycerol-water solution*. These conditions did not enable a self-structuring effect on the implant surface. No increased roughness or molecular self-organization has been observed. As a consequence, the anodization conditions needed to be shifted in order to get more intense corrosion. Interplay between anodization time and voltage is often the key to getting highly organized metal oxide surfaces. Thus, implants were separated in two groups which were subjected to: (i) a time dependent activation and (ii) a voltage dependent activation of their surface structuring. Some complementary anodization steps were applied to the two implants groups to observe the effect of an increased anodization time and voltage on their surface topography. *Protocol No.1 - Step 2* involved both an extended anodization time (48 hours) and an increased electric potential (40 volts). This protocol proved to be highly corrosive; for this reason the second implants group was subjected to a reduced anodization time and lower electric potential (*Protocol No.2 - Step 2: 24 hours, 25 volts*). In the SEM images in Table 2 one may observe the effect of the two different protocols applied to the implants and compare them with the control surface. As previously mentioned, the conditions in *Step 2 - Protocol 1* were highly corrosive and significantly deteriorated the implant, modifying its initial dimensions and geometry, as seen in Table 2, Column 2. On the other hand, the conditions in *Step 2 - Protocol 2* had no significant effect on the implant surface and did not modify its dimensions or geometry (Table 2, Column 3). A magnified SEM analysis of the samples in Table 2, Column 2 revealed the formation of crystalline-shaped regions on the sample surface (Fig. 6). These regions were not uniformly distributed on the metal surface. For this reason their further investigation was considered unnecessary. The samples in this group were subjected to a third anodization step, described in Table 1, *Protocol 1 - Step 3*. In this third step, the following conditions were used: the anodization time was of 16 hours and the anodization electric potential was 25 volts. It has been taken into consideration the fact that the previous anodization step (*Protocol 1 - Step 2*) aggressively corroded the implant and created a more uniform surface with less pronounced spiral geometry, as observed in Table 2, Column 2. After the third anodization step, the implant surface was rough and discontinuous. Despite that, the formation of uniformly distributed nanotube-like pores was observed at a higher magnification (Fig. 7). These pores were formed on the implant surface after a three step anodization; as seen, they present well defined circular shape and are observable at the same magnitudes as the titania nanotubes. Common pores are usually synthesized at a microscopic level and they are less regular. Usually, common pores are spread on the entire surface of a sample and no distance exists between them. The nanotube-like pores in Fig. 7 are spread on the entire analyzed area, at equal distances between each other. They can be considered precursor structures of the nanotubes.

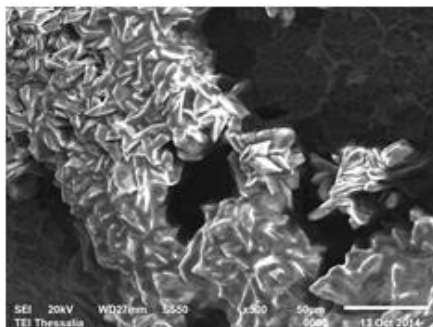


Figure 6: SEM images of crystalline-shaped regions on the screw surface after two-steps anodization, described in Table 1, *Protocol 1 - Steps 1 and 2*.

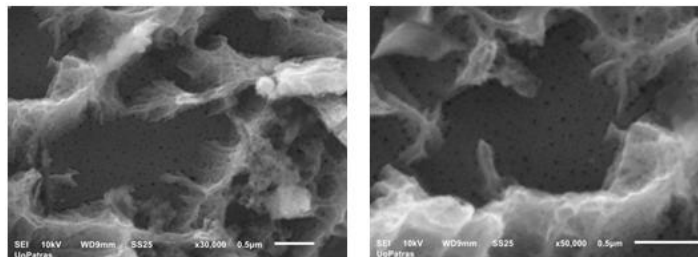
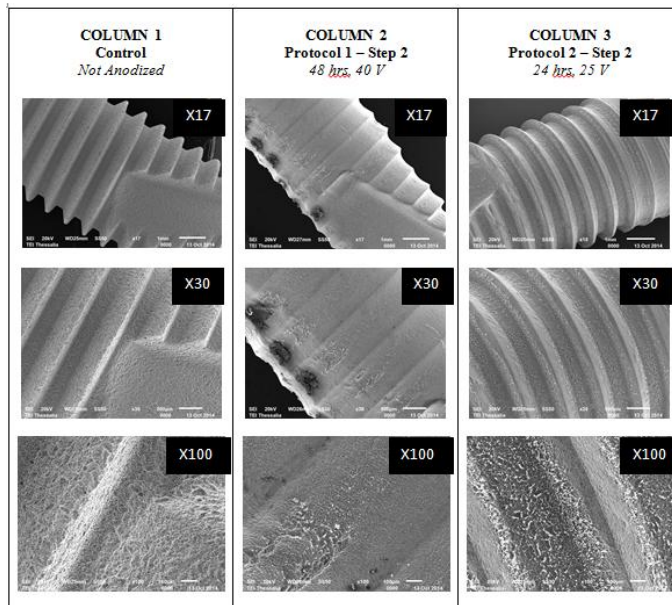


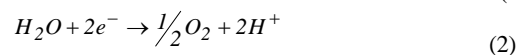
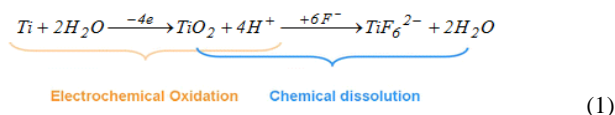
Figure 7: SEM image: Pores with nanotubes-like structure formed on the screw type implant surface after three-step anodization, described in Table 1, *Protocol 1 - Steps 1,2,3*.

Table 2: SEM micrographs of the non-anodized implant (Column 1) and implants anodized in different conditions (Columns 2 and 3), at various magnifications.



The formation of the nanostructures in Fig. 7 may be attributed to the second and third anodization steps in *Protocol 1*. An attempt to understand what lead to their formation is given below.

The formation of highly organized microstructures on the titanium surface can be enabled through the electrochemical oxidation of titanium. This process of oxidation into amorphous TiO_2 is followed by the chemical dissolution of the oxide into soluble titanium fluoride species (TiF_6^{2-}) as shown in **Relations (1) and (2)**:



It was established that field - enhanced oxidation occurs at the metal-oxide interface while the field enhanced dissolution of TiO_2 as $[\text{TiF}_6]^{2-}$ occurs at the oxide- electrolyte interface. Pores will grow when the oxidation and dissolution rates come to a steady state. A constant thickness of the titanium dioxide layer leads to the formation of highly organized microstructures due to a uniform flow of ions into the electrolyte through phenomena which take place at the material - electrolyte interface. The thickness of the anodic film is essentially the result of the steady state between the pore formation and the dissolution of the anodic film in the acidic

electrolyte [26]. One of the roles of the dissolution of oxide occurring due to local acidity is to determine the progressive growth of pore/nanotube length.

These standard processes, together with a chosen combination of parameters that affect the anodization (the substrate purity and geometry, the distance between electrodes, the applied voltage, the initial current, the voltage sweep rate, the concentration of F^- , the viscosity of the electrolyte, the temperature, and the anodizing time) lead to the synthesis of microstructures on the metal surface. A different parameter combination may result in micro or nanostructures with different shape, height, diameter length and surface density. The physics of the entire phenomenon can be explained using three basic theories:

1. Nernst diffusion layer: This is a virtual layer, within which the gradient of the ion concentration is constant and equal to the true gradient at the electrode–electrolyte interface. The thickness of the Nernst diffusion layer may be measured on the graph “ion concentration vs. distance from the electrode surface” and varies within the range 0.1–0.001 mm depending on the intensity of convection caused by agitation of the electrodes or electrolyte.
2. The two Fick’s laws: Diffusion is the mechanism by which components of a mixture are transported around the mixture by means of random molecular movements. The flow of mass by diffusion (i.e., the flux), across a plane, is proportional to the concentration gradient of the diffusant across that plane. According to First Fick’s law, the diffusion of the ions through the layers controls the material transfer and the deposition rate. Fick’s second law predicts how diffusion causes the concentration to change with time; more precisely it states that the time rate of concentration change is related to the second derivative of the concentration gradient through the diffusion coefficient.

To understand the effect of the anodization when applied to titanium anodes, one shall analyze (i) the factors related to the metal structure; (ii) the given anodization parameters and (iii) the flow of ions into the electrolyte. However, all these are interdependent and their interpretation must always be interconnected. An attempt to achieve the understanding of the anodization effect when applied to dental titanium screw type implants is presented in the sequence.

(1) Factors related to the metal structure

An appropriate combination of the anodization parameters applied on well gridded, cleaned, pure titanium plates enable the formation of a titanium dioxide nanotubes layer. As previously mentioned, the titanium purity is important; the presence of atoms of a different chemical nature will disturb the dioxide self-organizing process. Highly organized microstructures are hardly obtained on alloyed titanium. For the present study, titanium purity was clarified through EDX analysis. Both the flat samples and the dental implants were made of pure titanium. The conditions described in Table 1, *Protocol 1 - Step 1* were used to anodize the flat titanium and the dental implants. SEM analysis showed different results for the two types of samples. This is due to the different geometry and surface structure existing between them. A flat surface allows a homogeneous distribution of the ions on the sample surface. Under constant electric potential (25V) and for a specific anodization time (8 hours) the electrochemical reactions will lead to the formation of highly organized nanostructures due to the balance of processes assured by fairly distributed ions fluxes. This protocol was therefore adapted for a certain titanium type, respectively a flat titanium surface. When applied on circular samples with a porous surface, the protocol has different anodization effect. The discontinuity of the titanium electrode surface affects the ions flow in the electrolyte and determines the

formation of ion concentration picks. According to Nernst diffusion layer, ions flow in the electrolyte shall be constant and equal to the true gradient at the electrode–electrolyte interface. This is not valid in practice, when titanium samples having complicated geometries are involved. In this case, the protocol has to be adapted to the needs of the sample.

In this study, a carefully selected electrolyte has been used in all experiments: 1 wt % HF in 1:1 (w/w) glycerol-water solution. Its consistency allows for a gradual and organized synthesis of the titanium microstructures due to the water-glycerol combined action which confers an appropriate and constant ions speed due through the viscous nature of the glycerol, and good conductivity for ions transport through the water. Two other main parameters are considered basic: the electric potential and the anodization time, respectively. It is well known that these two parameters are interchangeable. It was also experimentally observed that a longer anodization time shall be associated to thicker samples, while the increased electric potential, which leads to more intense processes, has to be applied in the case of porous titanium. The dental titanium implants are thick and their surface is porous; for this reason an increase in both electric potential and anodization time was applied in *Protocol 1 - Step 2*. Thus, the electric potential was shifted from 25 to 40 V and the anodization time was prolonged to 48 hours instead of 8 hours. Although some crystalline – shaped microstructures were synthesized on the implant surface, the results were considered insignificant due to the fact that these weren’t fairly distributed on the entire area. This anodization treatment was considered extremely aggressive and therefore inappropriate. However, a third anodization step was applied to the first implants group (*Protocol 1 - Step 3*). The choice to further process the first implants group was related to the fact that the sample surface was modified and presented a more uniform geometry. Thus, geometry role in the whole fabrication process could be tested. A 25 volts electric potential was applied for 16 hours. The structure of the sample surface favored the formation of nanotubes-like structures with well-defined shaped, uniformly spread on the metal surface.

The second implants group was anodized under the conditions described in *Protocol 2 - Step 2* (25 V and 24 hours anodization time). These conditions were considered less aggressive. However, no significant self-organization of the titanium implant surface was observed, while the implant maintained its initial dimensions.

(2) Anodization Parameters

Anodization parameters refer to aspects such as the choice of the two electrodes and the distance in between them, the electrolyte, the anodization temperature etc. In this study, for reasons already mentioned, a viscous electrolyte which incorporated an organic phase (glycerol) has been used: 0.4% (w/w) in 1:1 (w/w) Water – Glycerol. The hydrofluoric content was reduced as much as possible, while the water content was added to enhance conductivity. The distance between the two electrodes, the titanium plate/ implant and the graphite bar was of maximum 2 cm. The anodization temperature was always the room temperature. The anodization time and the electric potential were chosen based on previously reported investigations and on experimental observations.

(3) The flow of ions

After the initiation of the anodization, ions are projected in all directions into the electrolyte and time is needed until they reach a constant speed after fluxes are established. In ideal conditions, according to Nernst diffusion layer, the gradient of the ion concentration is constant and equal to the true gradient at the electrode–electrolyte interface and its thickness is reduced with the increased distance from the electrode surface. In practice, the gradient of the ions concentration is highly dependent on the

electrolyte homogeneity and affected by impurities in the electrolyte, by the sample geometry and its surface structure and by a serious of other factors. The gradient of ions concentration at the *implant electrode – electrolyte interface* is not constant because of the irregularities of the implant surface. On a flat surface, pits are uniformly formed on the metal surface during corrosion. The progressive growth of the microstructures resulting from pits takes place at constant voltage, as long as it does not overpass a specific threshold. High voltages and intense processes result in the formation of pores with undefined shape. On the opposite, an appropriate electric potential leads to the gradual, organized formation of microstructures with different shapes and dimensions such as micro crystallites or nanotubes.

Ions diffusion is not determined only by the initial electric potential. According to second Fick's law this is a time dependent process. The growth of nanotubes, for instance, is related to the diffusion of F^- ions through the oxide layer and effusion of $[TiF_6]^{2-}$. Grain boundaries and dislocations play the leading role in accelerating reaction rate and ion diffusion coefficient during the entire anodization process. During the first anodization moments ions are projected in the electrolyte through chaotic movements, immediately after the current supply is on; as time passes, their direction is established and their speed becomes constant. The anodization process takes a different course for the two types of titanium geometries when the hydrofluoric species reach the sample surface. Ions flow is constant when a regular, non-porous and flat titanium surface is involved in the experiment, which is not the case of titanium implants. Anodization can be considered a cyclic event; ions are moving towards the two electrode surfaces guided by self-organized processes. Their corrosive action on the titanium surface can be delayed by an irregular geometry and by initial porosity of the sample. In this case, the dioxide layer formation is also disturbed, while its thickness is not uniform on the sample surface. Self-organization of titanium dioxide nanotubes refers to the dependency of the entire process on a number of parameters which are ideally combined to lead to the synthesis of these perfect structures. The dioxide thickness is one of the main parameters with influence on nanotubes formation. Nanotubes are instantly shaped in the dioxide layer in the first moments of the anodization and their height is gradually increasing while they are growing in parallel, as time is given to the process. Roughness and inhomogeneity of the substrate determine the formation of local concentration gradients and thus non uniform corrosion. Titanium implants surface processing through the electrochemical anodization method still remains a challenge in research, with great perspectives in dental applications.

Conclusions

Surface processing of the metallic implants can be a solution to *tissue – implant* interfacial problem in implantation surgeries. Patents were released on the subject of the electrochemical processing of titanium flat surfaces; although it is affirmed that this is the solution for titanium implants surface functionalization, there are doubts regarding the anodization protocols. The present investigation has been undertaken to study the surface structure of dental titanium implants after their electrochemical processing. In this study, it was shown that the controlled corrosion of a titanium implant allows the subsequent formation of nanotube-like pores on its surface.

The anodization depends in a great extent on the geometry and structure of the involved surfaces; protocols that lead to the formation of titanium dioxide nanotubes on flat titanium surfaces provided by well-known suppliers, do not have the same effect on titanium implants. This is mainly due to the geometry of the implant, which changes the priority, intensity and interconnection of the electrochemical processes. Each implant type has to be

studied on its own, while protocols should be carefully adapted to its internal and external structure. In the present investigation pure titanium plates and dental titanium screw type implants were anodized to perform a comparative study of the electrochemical parameters effect on the different sample geometries. The samples purity was analyzed using EDX. The surface topography of each sample before and after anodization was analyzed using a SEM device.

The following conclusions came out from the present study:

- a. Three main parameter categories are responsible for the electrochemical anodization effect on a titanium surface: (i) the factors related to the metal structure; (ii) the given anodization conditions and (iii) the flow of ions into the electrolyte.
- b. Titanium purity and geometry are essential to obtain self-organization on the titanium surface as a result of electrochemical anodization; highly organized nanotubes layers can be obtained on flat titanium and have been often reported in literature. Anyway, protocols for getting nanotubes layers on flat titanium do not fit to an implant surface, showing that the metal structure and geometry are very important parameters in the anodization process.
- c. Interplay of the voltage and anodization time has been applied to observe the effect of these two anodization parameters on the surface modification of dental titanium implants. The first anodization step did not cause changes to the screw surface. A more intense treatment has been used involving an extended anodization time and increased electric potential. This lead to the corrosion of the implants and the modification of their initial dimensions. A third anodization step has been applied to the already corroded implants; this determined the formation of nanotube-like structures on the implant surface. However, it must be underlined that the implant geometry and dimension were considerably modified.

Titanium dioxide nanotubes can be easy synthesized on titanium plates with extra-polished surfaces, provided by well-known suppliers, while their synthesis on titanium implants requires adapted protocols. The protocols to synthesizing such highly organized nanostructures on dental implants can be established after a deep understanding of the anodization processes when applied to different surface geometries. Further investigations are needed to establish the extent of sample geometry, internal structure and surface topography effect on the entire process.

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References

1. Buser D (1991) Influence of surface characteristics on bone integration of titanium implants. A histomorphometric study in miniature pigs. *Journal of Biomedical Materials Research* 25(7):889–902.
2. Desai T.A. et al (1999) Nanopore Technology for Biomedical Applications. *Biomedical Microdevices* 2:1, 11±40.
3. Kienapfel H, Sprey C, Wilke A, Griss P (1999) Implant fixation by bone ingrowth. *The Journal of Arthroplasty* 14(3):355–368.
4. Shih Y-H, Lin C-T, Liu C-M, Chen C-C, Chen C-S, Ou K-L (2007) Effect of nano-titanium hydride on formation of multi-

- nanoporous TiO₂ film on Ti. *Applied Surface Science* 253:3678–3682.
5. Fujibayashi S, Nakamura T, Nishiguchi S, Tamura J, Uchida M, Kim HM, Kokubo T (2001) Bioactive titanium: Effect of sodium removal on the bone-bonding ability of bioactive titanium prepared by alkali and heat treatment. *J. Biomed. Mater. Res.* 56(4):562-570.
 6. [Goldberg JR, Gilbert JL (2004) The electrochemical and mechanical behavior of passivated and TiN/AlN-coated CoCrMo and Ti6Al4V alloys. *Biomaterials* 25(5):851-864. doi:10.1016/S0142-9612(03)00606-9.
 7. Sul YT, Johansson CB, Jeong Y, Albrektsson T (2001) The electrochemical oxide growth behaviour on titanium in acid and alkaline electrolytes. *Med. Eng. Phys.* 23(5):329-346. doi:10.1016/S1350-4533(01)00050-9.
 8. Ghafar A, Chong C, Seung HY, Jong MK, Sung OC (2011) Fabrication of complete titania nanoporous structures via electrochemical anodization of Ti. *Nanoscale Research Letters* 1 6:332.
 9. Gao L, Feng B, Wang J, Lu X, Liu D, Qu S, Weng J (2009) Micro/Nanostructural Porous Surface on Titanium and Bioactivity. *Journal of Biomedical Materials Research Part B: Applied Biomaterials* Volume 89B(2): 335–341. doi: 10.1002/jbm.b.31221.
 10. Manole CC, Pirvu C, Demetrescu I (2009) TiO₂: From Nanotubes to Nanopores by Changing the Anodizing Voltage in Floride-Glycerol Electrolyte. *Key Engineering Materials* 415:5-8.
 11. Manole CC, Pirvu C (2010) Surface and electrochemical analysis for the understanding of TiO₂ nanopores/nanotubes changes in post-elaboration treatment. *Surface and Interface Analysis* 43(7):1022–1029. doi: 10.1002/sia.3685 .
 12. Ungureanu C (2016) Enhancing antimicrobial activity of TiO₂/Ti by torularhodin bioinspired surface modification. *Bioelectrochemistry* 107:14–24.
 13. Cai Q, Paulose M, Varghese OK, Grimes CA (2004) The effect of electrolyte composition on the fabrication of self-organized titanium oxide nanotube arrays by anodic oxidation. *J. Mater. Res.* 20(1):230-236. doi: 10.1557/JMR.2005.0020.
 14. Wang J, Lin Z (2008) Freestanding TiO₂ Nanotube Arrays with Ultrahigh Aspect Ratio via Electrochemical Anodization. *Chem. Mater.* 20 (4): 1257–1261. doi: 0.1021/cm7028917.
 15. Portan DV, Papaefthymiou K., Arvanita E, Jiga G, Papanicolaou GC (2012) A combined statistical and microscopic analysis of TiO₂ nanotubes synthesized under different electrochemical anodizing conditions. *Journal of Materials Science* 47(11): 4696-4705. doi 10.1007/s10853-012-6338-x.
 16. Yao C, Webster TJ (2006) Anodization: A Promising Nano-Modification Technique of Titanium Implants for Orthopedic Applications. *Journal of Nanoscience and Nanotechnology* 6(9-10): 2682-2692.
 17. Xiaoye H et al (2009) Single-Crystalline Anatase TiO₂ Dots Assembled Micro-Sphere and Their Photocatalytic Activity. *Cryst. Growth Des.* 9(5):2324–2328. doi: 10.1021/cg801181y.
 18. Macak JM (2005) Self-organized nanotubular oxide layers on Ti-6Al-7Nb and Ti-6Al-4V formed by anodization in NH₄F solutions. *Journal of Biomedical Materials Research Part A* 75A(4):928–933. doi: 10.1002/jbm.a.30501.
 19. Das K, Bose S, Bandyopadhyay A (2007) Surface modifications and cell–materials interactions with anodized T. *Acta Biomaterialia* 3(4):573–585. doi: 10.1016/j.actbio.2006.12.003.
 20. Gu´ehennec LL, Soueidan A, Layrolle P, Amouriq Y (2007) Surface treatments of titanium dental implants for rapid osseointegration. *Dental Materials* 23(3):844–854.
 21. Chen ZX, Takao Y, Wang WX, Matsubara T , Ren LM (2009) Surface characteristics and in vitro biocompatibility of titanium anodized in a phosphoric acid solution at different voltages. *Biomed. Mater.* 4: 065-003.
 22. Lee IG et al (2008) Influence of electrolyte temperature on pure titanium modified by electrochemical treatment for implant. *Surf. Interface Anal.* 40:1538–1544.
 23. Pavón J et al (2013) Anodic oxidation of titanium for implants and prosthesis: processing, characterization and potential improvement of osteointegration, V Latin American Congress on Biomedical Engineering CLAIB 2011 May 16-21, 2011, Habana, Cuba IFMBE Proceedings (2013) 33:176-179.
 24. Diebold U (2003) The surface science of titanium dioxide. *J. Surface Science Reports* 48:53-229.
 25. Portan DV, Papanicolaou GC, Jiga G, Caposi M (2012) A novel experimental method for obtaining multi-layered TiO₂ nanotubes through electrochemical anodizing. *J ApplElectrochem* 42:1013-1024.
 26. Xiaofeng Y, Yongxiang L, Wojtek W, Sasikaran K, Kourosh K (2008) Fabrication of nanostructured TiO₂ by anodization: A comparison between electrolytes and substrates. *Sensors and Actuators B* 130:25–31.

