Controlling morphological parameters of a nanotubular TiO$_2$ coating layer prepared by anodic oxidation

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Abstract

A promising modification route to improve osseointegration of dental and medical titanium devices is a nanostructured titanium oxide coating layer in the form of self-ordered vertically aligned nanotubes (or nanotubular TiO$_2$). In this work, we report a detailed investigation of nanotubular TiO$_2$ coating layer on metallic Ti substrate prepared by anodic oxidation. The main goal was to determine an optimized and reproducible route to produce a nanotubular TiO$_2$ layer with homogenous morphology, narrow distribution and accurate control of the nanotube diameter. The influence of electrolyte temperature, anodizing time and applied voltage were studied, comparing three different electrolytes: 1.5 wt% HF, 0.5 wt% HF, and 0.5 wt% HF + 1 mol l$^{-1}$ H$_3$PO$_4$. Samples were analyzed by SEM, EDS, FIB, and XPS techniques. The most favorable result was achieved by using 0.5 wt% HF + 1 mol l$^{-1}$ H$_3$PO$_4$ electrolyte, for anodizing time of about 90 min, temperature of 20 °C, and anodizing potential from 1 to 25 V. Using these parameters, a uniform self-organized nanotubular TiO$_2$ layer was prepared with a fine control of the nanotube diameter value over a wide range (10 to 100 nm).

1. Introduction

Titanium and its biomedical alloys have been extensively used in implantology due to their favorable characteristics such as fatigue and corrosion resistance, biocompatibility, low density and relatively low modulus of elasticity. The reported long-term clinical success for titanium and its alloys has made titanium the standard material for the fabrication of dental implants [1, 2]. Metallic titanium and its alloys oxidize immediately upon exposure to air. However, at ambient temperatures, the formation of a passive oxide coating protects the bulk metal from further oxidation. This layer is biologically inert, which impairs osseointegration because it induces the formation of a fibrous tissue between bone and implant, which may cause implant loss [3, 4]. To avoid implant encapsulation and increase the effectiveness of the osseointegration process, modifications are usually introduced on the implant surface. Common surface modifications can be made through coatings with materials with osteoinductive characteristics such as hydroxyapatite or other calcium phosphate compounds, or with morphological modifications such as blasting (which will produce a micrometer roughness) or anodic oxidation [1, 5]. Anodic oxidation or anodizing is a promising modification used to produce a nanostructured titanium oxide (TiO$_2$) coating layer in the form of self-ordered vertically aligned nanotubes (or nanotubular TiO$_2$) on titanium implant devices [6].

Zwilling et al, in a pioneering study, has produced nanotubular TiO$_2$ arrays on metallic titanium via anodic oxidation in a chromic acid electrolyte containing hydrofluoric acid [7]. Thereafter, anodizing has become a well-known method for the production of nanotubular TiO$_2$ [6, 8]. This is an attractive procedure due to its ease of implementation and low cost. Besides that, it enables to control the main properties of nanostructured TiO$_2$. 
overlayer (i.e. morphology, thickness and internal pore diameter) by tuning the anodizing variables such as applied potential and electrolyte composition.

The mechanism of nanotubular titanium oxide formation by the anodization of Ti metal has previously been detailed [9, 10] and it will be briefly discussed here. The anodizing procedure is typically carried out in a two-electrode configuration with clean metallic titanium at the anode. Once a sufficient large potential is applied (about 1 V), two processes start to occur at the anode: (i) the oxidation of the metallic Ti to Ti$^{4+}$ and (ii) the diffusion of O$^{2-}$, formed by deprotonation of water present in the electrolyte, toward the surface of the metal, as describe by equation (1).

$$\text{Ti} + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4\text{H}^+ + 4\text{e}^- \quad (1)$$

The result is the formation of a thin layer of titanium oxide on the exposed metal surface. Oxide dissolution occurs at the oxide/electrolyte interface because Ti–O bonds are weakened due to polarization. In the presence of fluoride ions, localized dissolution of titanium oxide takes place, forming water-soluble [TiF$_6$]$^{2-}$ complexes that initiates the nanotube formation, as describe by equation (2).

$$\text{TiO}_2 + 6\text{F}^- + 4\text{H}^+ \rightarrow [\text{TiF}_6]^{2-} + 2\text{H}_2\text{O} \quad (2)$$

The O$^{2-}$ ions remain diffusing through the TiO$_2$ layer and reacts with the metal to produce fresh oxide at the bottom of the nanotubes. The rate of oxide growth at the metal-oxide interface and the rate of oxide dissolution at the oxide-electrolyte interface equalizes, thus the thickness of the oxide layer at the base of the nanotube essentially remains unchanged as it moves further into the metal making the pore deeper [11, 12].

It is well acknowledged that titanium covered with a nanotubular TiO$_2$ overlayer presents a large potential for clinical applications mainly due to its exceptional biocompatibility. There are many works reporting an increase in cell adhesion and proliferation in the presence of nanostructured surface compared to smooth titanium surface. However, there is no consensus about which nanotube diameter is more effective for cell response [6, 13–16].

Since Bauer et al [17] showed the dependence of tube diameter with applied voltage during anodizing process, authors have been studying the in vitro effects of nanotubes of different diameters and the results are controversial. One group has related the best biological performance with nanotubular titania layer with an internal nanotube diameter smaller than 30 nm [18–21]. Conversely, other authors have reported an increasing on the biological performance for nanotubular titania surfaces with nanotube diameter around 100 nm [22, 23].

The cellular behavior on a nanotubular TiO$_2$ surface is a matter of great interest and have been intensively investigated, especially in comparison with a smooth or a blasted surface, aiming to use in implantology [21, 23–25]. The vast majority of the reports had shown favorable results for a nanotubular TiO$_2$ surface. However, there is still no consensus on what would be the most appropriate TiO$_2$ nanopore diameter to use in order to improve the osseointegration character of Ti implant devices, requiring further studies on this subject. Regardless of the nanotube diameter best suited for the cell response, the production of a nanotubular titania coating on titanium with a narrow distribution of nanotube diameter and well controlled thickness is a key issue for a detailed study of its biological performance.

Tailoring and controlling the anodic oxidation preparation route for large-scale production is not an easy task due to the large number of thermodynamic parameters associated to the process. While the process duration, potential, temperature and fluoride concentration are the main parameters that control the nanostructured titania layer thickness, diameter, and growth rate, different electrolyte features including pH, viscosity, conductivity, and organic additives can affect the process, leading to the formation of a nanotubular coating layer with undesired morphology or even to the non-formation of a nanostructured oxide layer [5, 8, 12]. In general, the most commonly used electrolytes for titanium anodization can be divided into two groups: organic, such as glycerol [26] and ethylene glycol [24]; and inorganic, such as HF [27], HF + H$_3$PO$_4$ [17], NH$_4$F + (NH$_4$)$_2$SO$_4$ [28], H$_2$SO$_4$ + HF [29].

Here we present a detailed investigation of the preparation of nanotubular TiO$_2$ surface coating obtained by anodic oxidation of metallic Ti substrates. The influence of electrolyte temperature, anodizing time and applied voltage were studied, comparing three different electrolytes: 1.5 wt% HF, 0.5 wt% HF, and 0.5 wt% HF + 1 mol l$^{-1}$ H$_3$PO$_4$. These electrolytes were chosen due to previous results that have demonstrated reproducibility [17, 18, 27, 30]. In addition, we also evaluated the effect of the presence of H$_3$PO$_4$ on morphology of TiO$_2$ nanotubes as compared to pure HF electrolytes. The aim of this work was to establish the most favorable condition for obtaining a uniform layer of titanium oxide nanotube on metallic Ti substrate by anodic oxidation, with homogenous morphology, narrow distribution and accurate control of nanotube diameter.
Table 1. Summary of sample preparation parameters (electrolyte, anodizing voltage, time and temperature).

| Electrolyte             | Voltage (V) | Time (min) | Temperature (°C) |
|-------------------------|-------------|------------|------------------|
| HF 1.5 wt%              | 20          | 8, 10, 30, 60 | 18, 24          |
|                         |             | 10, 30, 60 | 12               |
| HF 0.5 wt%              | 20          | 10, 30, 60 | 12, 18, 24      |
| HF 0.5 wt% + H₃PO₄ 1 mol l⁻¹ | 25         | 10, 30, 60 | 20               |
|                         |             | 90         | 10, 15, 20, 24  |

2. Material and methods

2.1. Sample preparation

Ti substrates were obtained by machine cutting of a circular rod made of commercially pure titanium grade IV (ASTM F67) in form of discs with 12.7 mm of diameter and 2.0 mm thick. After machine cutting, titanium substrates were cleaned as described here. Firstly, Ti discs were subjected to a degreasing bath, washed using warm water (>80 °C) and biodegradable detergent in ultrasonic bath cleaner. Then, discs were chemical cleaned using sodium hydroxide (NaOH), rinsed with deionized water (dH₂O), immersed in aqueous solution of hydrofluoric and nitric acids for 5 min and rinsed again with dH₂O in ultrasonic bath cleaner. Finally, discs were dried in an oven at 70 °C by 20 min. Immediately before anodizing process, titanium substrates were cleaned using acetone (CH₃COCH₃ – 99.5%, Anidrol) and deionized water, and, with the purpose of removing a natural layer of TiO₂, discs were immersed in a solution containing 2 v% HF + 3 v% HNO₃ 65%, Vetec, for 5 min and rinsed with dH₂O. Millipore Milli-Q system.

The anodizing setup consisted of a homemade electrochemical cell, composed of two electrodes, an adjustable DC power supply (Agilent 6634B) and a monitoring system developed on LabVIEW platform that allows storing the main electrochemical parameters (applied potential, current, and electrolyte temperature) and setting the anodizing duration.

The titanium sample is set as the anode, with 0.994 cm² of area exposed to anodizing electrolytes and the stainless-steel mesh set as the cathode. The distance between anode and cathode is about 2.5 cm. All the anodizing procedures were performed in the potentiostatic mode.

Here, three different electrolyte solutions were tested: 1.5 wt% HF (pH 2.6), 0.5 wt% HF (pH 3.0), and 0.5 wt% HF + 1 mol l⁻¹ H₃PO₄ (pH 1.8), for simplicity also referred as HF + H₃PO₄. In all, about 300 samples were produced: 60 samples for 1.5% HF; 120 samples for 0.5% HF and 120 samples for 0.5% HF + 1 mol l⁻¹ H₃PO₄ electrolyte. The manufacturers and the purity of used reagents are, respectively, HF: Anidrol, 40%; H₃PO₄, Vetec, 85%.

A summary of sample preparation parameters to evaluate the effect of anodizing time and temperature on the nanotubular TiO₂ coating layer obtained by anodic oxidation is presented in table 1. For HF 1.5 wt% electrolyte, a set of samples were prepared at 18 °C and anodizing time of 8 min in order to compare with the results presented by Gong et al [27].

The influence of anodizing voltage on the nanotube diameter was explored by fixing time and temperature (60 min and 12 °C for HF 0.5% electrolyte and 90 min and 20 °C for HF + H₃PO₄ electrolyte, respectively) and varying anodizing voltage in the range from 1 to 25 V.

After anodizing, each sample was washed in dH₂O, dried rapidly with a heat blower and then placed in an oven at 100 °C for 30 min in order to achieve complete drying. Once ready, the samples were stored in desiccator.

2.2. Sample characterization

Prepared samples were characterized by Scanning Electron Microscopy (SEM), Energy-dispersive x-ray Spectroscopy (EDS), Focused Ion Beam (FIB), and x-ray Photoelectron Spectroscopy (XPS). For SEM, EDS, and XPS analyzes, samples were removed from the desiccator and fixed with carbon tape in 12.7 mm diameter stubs.

SEM/EDS analyzes were performed in a SEM-FEG microscope (SIGMA-VP, brand Carl Zeiss, CDTN). From the SEM micrographs, the average diameter of the TiO₂ nanotubes was determined using the Quantikov [31] software. About 10 samples of each anodizing voltage were used to estimate the average nanotube diameters.

A FIB/SEM microscope (Quanta FEG 3D FEI, CM/UFMG) was used to obtain cross sections of titanium samples after nanotubular TiO₂ surface preparation. A beam of Ga⁺ ions, with energy of 30 keV and current of
0.5 nA, swept a delimited region in sample in order to excavate a wedge-shaped surface pit (nominal dimensions of 7 × 5 × 2 μm).

In order to evaluate the surface chemical composition after nanotubular TiO$_2$ coating layer preparation, samples were investigated by XPS (Phoibos 150, Specs). XPS is a surface sensitive technique that provides information about chemical state of constituting species. Here, the differences in the chemical state of O, F and Ti species were evaluated for the three different preparation routes. The results were analyzed in detail and correlated with the observed surface morphology of the TiO$_2$ nanotubular coatings. Titanium samples were pretreated by Ar$^{+}$ sputtering for 10 min (0.8 keV ion energy), in order to remove surface contamination, especially carbon. The experimental XPS spectra were analyzed using CasaXPS software. High-resolution spectra were deconvoluted with Gaussian–Lorentzian mixed function, with peak intensity ratio of 30/70.

3. Results and discussion

3.1. 1.5 wt% HF electrolyte
Gong et al [27] have reported the formation of a nanotubular TiO$_2$ layer by anodic oxidation of Ti substrates using HF 1.5 wt%, with a potential of 20 V and 18 °C. However, in our experiments, after anodization under similar conditions (HF concentration, electric potential, duration time and temperature), a nanostructured oxide layer was not obtained (figure 1(a)), while anodizing performed at 12 °C, for 10 to 60 min produced a nanotubular layer with low degree of organization (figure 1(b)). In contrast, regardless of anodization time (8 to 60 min) and temperature (18 and 24 °C), the anodic oxidation of Ti using 1.5 wt% HF and 20 V has resulted in a surface covered with a compact oxide film, with uneven height and no indication of nanotubular oxide layer.

A reason for no formation of a nanotubular TiO$_2$ surface layer by anodizing in 1.5 wt% HF electrolyte, 20 V, at 18 and 24 °C, may be related to the concentration of fluoride ions in the electrolyte. A high concentration of F$^-$ (greater than 1 wt%) retard the titanium oxide formation, as the available Ti$^{4+}$ immediately reacts with the fluoride ions, forming [TiF$_6$]$^{2-}$. The final result would be similar to an electrolytic polishing process [12, 32].

Figure 1. SEM micrographs of Ti sample after anodizing in 1.5 wt% HF electrolyte, 20 V, for different temperature and time, respectively: (a) 18 °C and 8 min; (b) 12 °C and 10 min.
3.2. 0.5 wt% HF electrolyte

SEM images of Ti samples anodized by 30 min at different temperatures show different results: a compact oxide layer was produced at 24 °C, while a self-ordered nanotubular layer was produced at lower temperatures (18 °C and 12 °C, as shown on figures 2(a) and (b), respectively). No significant morphological differences were observed between these temperatures. This result is not in agreement with authors that bring the information that an ideal temperature range to TiO2 nanotube formation is around room temperature (20 °C–24 °C) [10, 12]. According to Ocampo and Echeverría [12], higher temperatures (~60 °C) reduce electrolyte viscosity promoting disorderly oxide dissolution; conversely, very low solution temperature (~5 °C) increases viscosity harming oxide dissolution, resulting in a TiO2 layer with low degree of organization.

By comparing anodized samples, prepared at the same temperature (12 °C), it was observed that longer anodizing time improves the uniformity of nanotubes. For anodizing time of 10 min, a nanotubular layer with low uniformity was formed. The organization of the nanotubular layer turns even better when anodizing time increases to 30 min and, then, to 60 min (figures 2(b) and (c), respectively). After 60 min, the organization degree of the nanotubular coating layer was already quite satisfactory. Following the formation of TiO2 nanotubes, the surface morphology increases with anodizing time, which reaches a stabilization after a time limit. Beyond this limit, in which self-organization degree of nanotubes is already high, the anodizing time no longer influences [10].

Regarding the nanotubular titanium oxide thickness, no significant changes were observed for samples anodized for 30 min and 60 min. The average thickness of the nanotubular TiO2 layer was determined as 262 ± 30 nm and 275 ± 10 nm, for anodizing time of 30 and 60 min, respectively (figure 3). This observation is consistent with previous results that, for a determined anodizing condition, the growth of the nanotubular titanium oxide layer reaches a saturation regime and, therefore, the layer thickness does not depend significantly on anodizing time, but self-ordering can be enhanced, until a certain limit, obtaining a nanotubular layer more homogeneous [10, 33].

EDS results indicate the presence of titanium, oxygen and fluorine in both samples, what suggests the fixation of elements that constitute the anodizing solution in the nanotubular layer formed on the titanium surface.

For these samples, prepared with same anodizing time and temperature, but at different anodizing potential, SEM analyzes revealed that the morphology of the nanotubular TiO2 layer was not uniform for the whole range of values (figure 4). For anodizing conducted at 10 V, a compact TiO2 layer was observed (figure 4(a)), for 15 V and 20 V (figures 4(b) and (c), respectively), a nanotubular layer of TiO2 was formed, but only for 20 V, a uniform layer with a high degree of self-organization was observed. For 25 V (figure 4(d)), a layer of disorganized oxide was formed. This behavior was not expected since some authors have reported to obtain TiO2 nanotubes in this same voltage range using fluoride-containing electrolytes [17, 27, 34].

Figure 5(a) shows XPS survey spectrum of a sample anodized in 0.5 wt% HF electrolyte, for 60 min, at 12 °C and anodizing voltage of 20 V. Despite the sputtering process, XPS spectrum (figure 5(a)) presents a C 1 s peak, although in much smaller intensity, compared to the spectrum of as-prepared sample. After sputtering procedure, the observed ratio of O 1 s and Ti 2p peak areas, corrected by their relative sensitivity factors [35], is about 2.32. Ar and F peaks were also observed in the XPS survey spectrum. The observed Ar is probably due to ion implantation on the sample’s surface during the sputtering process, while F species come from anodizing process with a fluoride-based electrolyte. Figures 5(b)–(d) present high-resolution XPS spectra of nanotubular TiO2 surface. The O 1 s peak, presented in figure 5(b), was fitted with three components, centered at the energies of 531.0 eV, 532.1 eV and 533.2 eV. The peak component at 531.0 eV is assigned to oxygen species bonded to

Figure 2. SEM micrographs of Ti sample after anodizing in 0.5 wt% HF electrolyte, 20 V, and for different temperature and time, respectively: (a) 18 °C and 30 min; (b) 12 °C and 30 min; (c) 12 °C and 60 min.
titanium ions (Ti$^{4+}$) in TiO$_2$ [36], while the smaller components at 531.3 eV and 533.2 eV, are attributed to oxygen deficient phases of TiO$_2$, known as Magnéli phases (Ti$_{n+1}O_{2n}$) [37] and hydroxide groups (OH), respectively. Ti 2p peak shows a typical doublet structure composed with different oxide components, as shown in figure 5(c). The high resolution spectra was deconvoluted into three components (doublets): a main component, centered at 458.8 eV and 464.3 eV, assigned to Ti$^{4+}$ species in TiO$_2$, a second doublet centered at 457.1 eV and 462.6 eV, corresponding to Ti$^{3+}$ species in Ti$_2$O$_3$, and a smaller shoulder at energies 455.0 eV and 461.2 eV, corresponding to Ti$^{2+}$ [38]. This result suggests that the nanotubular layer is mostly formed by titanium oxide TiO$_2$. However, small amounts of both TiO and Ti$_2$O$_3$ are formed in the titanium oxide layer by anodizing process. The F 1 s spectrum (figure 5(d)) was fitted with one component centered at 685.4 eV. It was assigned to metal fluoride [39], presumably hexafluorotitanium [TiF$_6$]$^{2-}$.

3.3. 0.5 wt% HF + 1 mol l$^{-1}$ H$_3$PO$_4$ electrolyte

For samples anodized at the temperature of 20 °C, different results were obtained for different anodizing times. For the shorter anodizing times (10 min and 30 min), no nanotubular layer was observed, as shown in figures 6(a) and (b). On the other hand, for longer anodizing time (60 min and 90 min), the formation of a fairly uniform nanotubular TiO$_2$ layer, with average nanotube diameter of about 80 nm, as presented in figures 6(c) and (d), was observed.

The average thickness of the obtained nanotubular oxide layer was in the range of 500 to 580 nm (figures 7(a) and (b), respectively), a higher value if compared to the nanotubular layer obtained by anodizing in 0.5 wt% HF electrolyte. The reason may be due to the presence of H$_3$PO$_4$ in the electrolyte, which acts as buffering specie [17]. It has been previously established that the final nanotubular layer thickness is essentially the result of an equilibrium between electrochemical formation of TiO$_2$, at the pore bottom, and the chemical dissolution of
Figure 4. SEM micrographs of Ti substrates after anodizing in 0.5 wt% HF electrolyte, 12 °C, 60 min, and different anodizing potential: (a) 10 V, (b) 15 V, (c) 20 V, (d) 25 V.

Figure 5. XPS spectra of Ti samples anodized in 0.5 wt% HF electrolyte, 20 V, 60 min, and 12 °C.
this TiO$_2$ in a solution containing F$^-$ ions [33]. Thus, a higher dissolution rate of oxide will result in a thin oxide layer. According to Macák, Tsuchiya and Patrick [40], the dissolution rate of TiO$_2$ depends on the pH values of the solution. The more acidic the solution, the greater oxide dissolution. Using a buffer solution, the acidification caused by oxidation of Ti inside the nanotube can be controlled and a thicker layer of TiO$_2$ can be obtained.

EDS analysis of Ti samples anodized using HF $+$ H$_3$PO$_4$ electrolyte indicates the presence of titanium and oxygen at the samples, even for Ti samples where a compact layer (without nanotube) was noticeable (figure 8). In addition, a small amount of fluorine and phosphor, elemental species from the electrolyte, was observed for the Ti samples that presented a nanotubular coating layer. In the case of phosphorous, a component of the major calcium phosphate compound found in bone and dental tissues, hydroxyapatite [Ca$_{10}$(PO$_4$)$_6$(OH)$_2$ or HA], it is suggested that the presence of this element may help to accelerate the osseointegration process, according to previous literature results [41–43]. It is also observed that Ti peak intensity decreases with increasing anodization time. This is mainly due to the increasing of titanium oxide layer with anodizing time, which progressively buries the metallic titanium substrate.

Figure 6 shows SEM micrographs of Ti samples prepared in HF 0.5 wt% $+$ 1 mol l$^{-1}$ H$_3$PO$_4$ electrolyte, 25 V, 20 $^\circ$C, and anodizing time of (a) 10 min, (b) 30 min, (c) 60 min, (d) 90 min.

Figure 7 illustrates SEM micrographs of Ti samples anodized at 20 $^\circ$C for 90 min with different temperature (10 $^\circ$C to 24 $^\circ$C), confirming the production of a nanotubular titanium oxide layer. However, Ti samples anodized at 20 $^\circ$C and 24 $^\circ$C presented a surface morphology with better organization and homogeneity, with the best result obtained for 20 $^\circ$C. For samples anodized at 10 $^\circ$C and 15 $^\circ$C, the substrate surface was covered with a non-uniform nanotubular TiO$_2$ layer.

SEM micrographs of Ti substrates after anodizing at 20 $^\circ$C for 90 min (figure 10) confirmed the production of a self-ordered nanotubular TiO$_2$ layer for the entire anodizing potential range and revealed the effect of anodizing potential on the nanotube diameter. The average nanotube diameter and standard deviation values are presented in table 2.

Figure 11 shows a plot of the average nanotube diameter as a function of the anodizing potential with a linear fitting curve confirming an approximately linear dependence, in agreement with previous results [17].

The applied voltage directly affects the diameter of TiO$_2$ nanotube during the anodizing process. A possible explanation to this dependence is, since the formation of nanotubes is caused by the action of F$^-$ ions in the oxide layer, and the migration of these ions is under the influence of the applied voltage, the higher the applied voltage, the larger the electric field and hence, the greater the amount of ions acting on a same area in the oxide layer. As a consequence, the larger the applied voltage the larger the nanotube diameter [10, 27].
Figure 12(a) shows XPS survey spectrum of samples anodized in 0.5 wt% HF + 1 mol l⁻¹ H₃PO₄ electrolyte, for 90 min, at 20 °C, and applied voltage of 20 V. The intensity ratio of the O 1 s and Ti 2p peaks, corrected by relative sensitivity factors [35] is about 2.79. The survey spectrum of this sample indicates the presence of phosphorous species which is a clear result of the addition of H₃PO₄ in the HF electrolyte. The O 1 s high-resolution spectrum was fitted with three components centered at 531.0 eV, 532.5 eV and 533.2 eV, as

Figure 7. SEM micrographs of lateral cross section produced by FIB on the Ti sample surface after anodizing in 0.5 wt% HF + 1 mol l⁻¹ H₃PO₄ electrolyte, 25 V, 20 °C, and anodizing time of 60 min (a) and 90 min (b). 1—Nanotubular TiO₂ layer, 2—metallic Ti substrate.

Figure 8. EDS spectra of Ti samples after anodizing in 0.5 wt% HF + 1 mol l⁻¹ H₃PO₄ electrolyte, 25 V, 20 °C, and anodizing time of 10, 30, 60 and 90 min.
shown in figure 12(b). They are related to oxygen bonded to titanium ions (Ti^{4+}) in TiO_2 species, titanium oxide in Magnéli phases and OH groups on the surface, respectively. The energy shift of about 0.4 eV observed in the peak component associated to Magnéli phases, as compared to the spectrum of anodized sample in 0.5 wt% HF, is an indication of the change on the composition ratio of the different oxide species, i.e., TiO, TiO_2 and Ti_2O_3. This change is confirmed by the Ti 2p high-resolution spectrum (figure 12(c)), which was deconvoluted into two components: a doublet centered at 458.8 eV and 464.3 eV, assigned to Ti^{4+} in TiO_2 species, and a second doublet centered at 457.1 eV and 462.6 eV, related to Ti^{3+} in Ti_2O_3 species. Therefore, unlike the sample anodized with 0.5 wt% HF, TiO was not identified for the sample prepared in 0.5 wt% HF + 1 mol l^{-1} H_3PO_4 electrolyte. F 1 s high-resolution spectrum, presented in figure 12(d), was fitted by a component centered at 685.4 eV, identified as metal fluorine [39].

Summarizing, our results showed that by using either 0.5 wt% HF or 0.5 wt% HF + 1 mol l^{-1} H_3PO_4 electrolytes a uniform nanotubular TiO_2 layer can be produced by anodic oxidation of metallic titanium substrates. However, when using 0.5 wt% HF, a uniform self-organized nanotubular layer was achieved after 60 min, conversely, it take longer to get the same result (about 90 min) with the HF + H_3PO_4 electrolyte. On the other hand, the anodizing process in 0.5 wt% HF electrolyte produced a thinner layer as compared to a sample anodized in HF + H_3PO_4, that presented a final thickness 50% higher. It was shown that the anodizing temperature is another key issue to control the production of a nanotubular TiO_2 layer with uniform morphology. Our experimental results revealed that by using the HF + H_3PO_4 electrolyte, the temperature window to produce a uniform nanotubular TiO_2 layer is from 15 °C to 24 °C, a broader range as compared to the results obtained using 0.5 wt% HF electrolyte, which requires to control the anodizing temperature in the range of 12 °C to 18 °C. Finally, an accurate control of the average TiO_2 nanotube diameter was achieved only for the anodic oxidation of titanium by using the HF + H_3PO_4 electrolyte.

4. Conclusions

An optimized and reproducible route for obtaining a uniform layer of nanotubular titanium oxide on metallic Ti substrate by anodic oxidation using an aqueous electrolyte was established. It was observed a strong dependence on surface morphology of the preparation conditions applied in the anodizing process: electrolyte composition, anodizing potential and temperature. The results allowed to identify the individual contribution of each parameter on the nanotubular TiO_2 layer morphology. The HF concentration is a key point: high concentration
of F– ions increases the oxide dissolution rate, producing an excessively thin oxide layer or completely dissolving it, as with 1.5 wt% HF electrolyte. Evaluating the effect of anodization time, it was observed an equilibrium between oxide formation and dissolution is reached, and after this point, it does not significantly influence the morphology of the TiO2 nanotubular layer. It has also been observed that a different temperature range is

![Figure 10. SEM micrographs of Ti samples after anodizing in 0.5 wt% HF + 1 mol l⁻¹ H₃PO₄ electrolyte, 20 °C, 90 min, and different values of anodizing potential: (a) 1 V, (b) 5 V, (c) 10 V, (d) 15 V, (e) 20 V, (f) 25 V.](image)

| Potential (V) | Average nanotube diameter (nm) |
|--------------|-------------------------------|
| 1            | 12 ± 3                        |
| 5            | 21 ± 5                        |
| 10           | 36 ± 8                        |
| 15           | 58 ± 11                       |
| 20           | 78 ± 8                        |
| 25           | 103 ± 20                      |

Table 2. Average TiO2 nanotube diameter as a function of anodizing potential, for Ti samples anodized in 0.5 wt% HF + 1 mol l⁻¹ H₃PO₄ electrolyte, 20 °C, and 90 min.
required for each electrolyte solution, in order to form a nanotubular coating, rather than a compact titanium oxide layer. For 0.5 wt% HF electrolyte, it was observed that the ideal temperature for nanotubular layer formation is around 12 °C, while for 0.5 wt% HF + 1 mol l⁻¹ H₃PO₄ electrolyte, it forms in the range of 20 °C–24 °C. As previously observed, the average diameter of TiO₂ nanotubes varies linearly with the applied voltage, which allows a thorough control of the oxide layer morphology. This dependence was verified for 0.5 wt% HF + 1 mol l⁻¹ H₃PO₄ electrolyte but not for 0.5 wt% HF electrolyte. It was still observed that presence of H₃PO₄ increased the oxide layer thickness, behaving as a buffer in solution, decreasing the dissolution of the titanium oxide.
In conclusion, the best result was obtained for anodic oxidation of Ti substrates using 0.5 wt% HF + 1 mol L$^{-1}$ H$_3$PO$_4$ electrolyte, anodizing time of about 90 min and temperature of 20 °C. Using these parameters, a uniform self-organized nanotubular TiO$_2$ layer was produced with narrow distribution and accurate control of the nanotube diameters over a broad range (10 to 100 nm) and average layer thickness of 550 nm. The elemental analysis performed by EDS confirmed the production of a titanium oxide layer on the Ti substrate. In addition, the presence of phosphorus suggests the fixation of electrolyte species on the nanotubular oxide layer, which could be explored to tailor, in a controlled fashion, the chemical composition of the nanotubular oxide layer on Ti implant devices. XPS analysis showed that nanotubular titanium oxide coating is composed mostly by TiO$_2$. However, significant amounts of Magnéli phases TiO and Ti$_2$O$_3$ may also be present.

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