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TiO₂ nanotubes with tunable morphologies

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Titanium anodic oxide layers with a bottle shaped nanotubular structure have been grown in an electrolyte containing NH₄F, applying voltage steps. The grown layers were analyzed using scanning and transmission electron microscopy (SEM and TEM), and Rutherford backscattering spectroscopy (RBS). The results show that a concentration of 0.15 M of NH₄F in the anodizing bath, and a step of 10 to 20 V produces an oxide with a double morphology comprised of nanotubes at the oxide/metal interface and nanopores at the oxide/electrolyte interface of the anodic layer. Higher concentration of F[−] in the bath, 0.3 and 0.45 M NH₄F, enhanced the chemical dissolution of the anodic layer resulting in nanotubular structures along the oxide layer. Therefore, the bottle shaped nanotubular structures that show a well defined morphology are obtained in a bath containing a concentration of 0.3 M NH₄F and applying a voltage step of 10–20 V.

1. Introduction

In recent years, the growth and/or deposition of titanium thin films and titanium oxide layers have received considerable attention in a variety of fields of endeavour such as: tissue engineering, drug delivery systems, orthopaedic implants, gas sensors, lithium ion batteries, solar cells, photovoltaic devices and have therefore encouraged its study and development.^{1–7} Different techniques such as laser, sputtering, sol–gel, thermal oxidation, electrophoresis and electroplating have been used to obtain TiO₂ layers. Nevertheless, these techniques are limited when it comes to controlling the thickness of TiO₂ and/or when dealing with the lack of uniformity in the grown layer.^{8,9}

By contrast, the anodizing process allows the fabrication of uniform TiO₂ layers with a controlled thickness and a variety of nanostructures that differs from barrier to porous layers, depending on the composition of the electrolyte used and the growth conditions (temperature, stirring, voltage and/or current applied).^{10,11} Zwilling *et al.* in 1999 obtained self-organized TiO₂ nanoporous structures using diluted hydrofluoric acid solutions.¹² Subsequent works showed that in these HF containing solutions, the thickness of TiO₂ anodic layer was limited to 500–600 nm. The chemical dissolution resulting from the high acidity of the bath and the presence of fluorides,¹³ is responsible for this limitation in thickness. This drawback is overcome by the use of buffer solutions containing NaF or NH₄F (where the chemical dissolution is decreased), along with pH control of the anodizing bath, leading to TiO₂ layers up to 2 μm thick.^{14,15} It was precisely this increase in the thickness of the nanostructured TiO₂ layers which made it possible to expand the niche of applications of

TiO₂ layers in those uses in which the nanostructure and thickness are critical, such as TiO₂ fuel cells, which have improved their efficiency and service life by increasing the surface area.^{16,17}

However, in addition to thickness, it is also possible to modify the diameter of the nanotubes by varying the applied voltage. Mor *et al.*,⁵ fabricated porous TiO₂ layers with conical structures on titanium applying voltage ramps in an HF solution. The conical nanotubular layers had variable inner diameters throughout but the thickness of the oxide layer was limited to 200 nm. Similar nanostructures were obtained in organic electrolytes by applying ramps with ascending and descending voltages, leading to thicker anodic oxide layers and, therefore, greater surface areas of interest in the photocatalytic applications.^{18–22} Liu *et al.*²³ fabricated TiO₂ nanotubes with periodically changing morphology by using periodic pulses consisting of high and low voltages. However, the main drawbacks are either the instability of the organic baths, or the longer times required to achieve the desired thicknesses. In addition, most of the works are focused on pure titanium or titanium binary alloys and few papers are devoted to fabricate tailored nanotubes in the micrometer range on technologically relevant substrates such as Ti6Al4V alloy.

The objective of the present work is the growth of thick anodic layers in the micrometer range, with bottle shaped nanotubular structures in Ti6Al4V alloy in short times, less than two hours, and in aqueous anodizing baths that could be of interest for drug delivery control systems in orthopaedic prostheses. The work correlates the influence of the anodizing process parameters: the concentration of fluoride in the bath and the application of increasing voltage steps on the fabricated nanostructures.

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2. Experimental procedure

Ti6Al4V alloy specimens of ELI grade according to the standard ASTM F136-02 supplied by SURGIVAL were ground using successive grades of SiC paper to 1200 grade, degreased with a detergent and rinsed in tap water followed by deionised water.

The specimens were then chemically polished in a mixture of HF(40 wt%): HNO₃(70 wt%): H₂O with a volume ratio of 1:4:5 for 5 min, at room temperature under continuous agitation at 400 rpm, rinsed in distilled water and dried in cold air. The working area was 2.54 cm². Electrolytes containing 1 M NH₄H₂PO₄ and 0.15, 0.3 and 0.45 M NH₄F were prepared. Bottle shaped nanotubes were formed in a two-electrode cell. The specimens were anodized at stepped voltage with the first voltage (V_1) applied for 30 min followed by a second voltage step (V_2) applied for 60 min, as seen in Fig. 1. The temperature was controlled at 20 °C. Platinum mesh was used as a cathode. The voltages were applied using LAB/SM 1300 DC power supply (ET Power Systems Ltd). Current-time responses of anodizing were acquired at 0.1 Hz sampling rate using a zero-ohm ammeter connected in series with the electrochemical cell.

The plan-view morphology of the nanotubular oxide films was examined by field emission gun scanning electron microscopy (FEG-SEM) utilizing JSM6500F Philips instrument equipped with EDX facilities and a ZEISS Ultra 55 scanning electron microscope. Electron-transparent sections were prepared by scratching the surface of the anodized specimens with a scalpel and collecting the pieces of the oxide on a TEM grid. TEM grids were observed using a JEOL JEM 2010 instrument operated at 200 keV.

The stoichiometric composition of the oxide films was further determined by Rutherford backscattering spectroscopy (RBS), using the following non-Rutherford elastic backscattering cross sections: He⁺ ions with the energy of 3.045 MeV (resonant energy for ¹⁶O(α , α_0)¹⁶O reaction), 3.777 MeV (resonant energy for ¹⁹F(α , α_0)¹⁹F reaction) and 5.725 MeV (resonant energy for ²⁷Al(α , α_0)²⁷Al reaction) were produced by the van de Graff accelerator located at the Centro de Micro-Análisis de Materiales (CMAM), Madrid. The incident ion beam was normal to the surface of the specimen with 10 μ C dose scattered ions detected by a mobile detector at 165°. Data were interpreted using the SIMNRA program.

3. Results and discussion

3.1. Current density *versus* time response

In the following sections, the current transients recorded during anodizing process were evaluated to determine the influence of the composition of the anodizing bath and voltage steps applied, *i.e.* electric field, on the anodic layers grown.

3.1.1. Influence of the composition of the anodizing bath.

The current density *versus* time curves collected during the anodizing of Ti and its alloys, show significant growth aspects of the anodic oxide layer and its morphology.^{8,18,21,24} Fig. 2 shows the evolution of the current density *versus* time during the anodizing of the Ti6Al4V alloy in a 1 M NH₄H₂PO₄ bath with different concentrations of NH₄F applying voltage steps. In this figure, it is observed that the current-time transient, recorded for the different concentrations of NH₄F used, is similar to that described by other authors for the anodizing of Ti and its alloys in aqueous media.^{5,8} Three different stages are distinguished:

Electrolyte	time (min)		Voltage (V)		Nomenclature
	t_1	t_2	V_1	V_2	
1M NH ₄ H ₂ PO ₄	30	60	10	20	10-20V
			10	20	10-20V
			20	30	20-30V
			20	40	20-40V
			10	20	10-20V

Fig. 1 Fabrication conditions of nanotubes grown on Ti6Al4V.

Fig. 2 Current density–time responses of anodizing of Ti6Al4V at 10 V for 30 minutes followed by second voltage step at 20 V for 60 minutes (a), i vs. t response related to $V_1 = 10$ V for 30 minutes (b) and $V_2 = 20$ V for 60 minutes (c).

the growth of the high resistance oxide barrier layer – stage I; pores nucleation – stage II; and the steady state (growth of nanotubes)-stage III.

In this electrolyte, the pore initiation stage can be attributed to both the field-assisted ejection of Ti⁴⁺ ions into the electrolyte and the chemical dissolution of the oxide due to the presence of fluoride ions readily forming cavities within the oxide.

The three stages plotted in the current density *versus* time response are observed for each applied step voltage, $V_1 = 10$ V for 30 minutes and $V_2 = 20$ V for 60 minutes, Fig. 2b and c. The steady state current density recorded on stage III corresponding to the first applied voltage, $V_1 = 10$ V, is 0.2 mA cm^{−2} for the bath containing 0.15 M NH₄F and increases to 1.5 mA cm^{−2} for 0.45 M NH₄F, Fig. 2b. The steady current density recorded for the second voltage step, $V_2 = 20$ V, increases approximately 0.2 mA cm^{−2} compared to the values showed for the first voltage step for all the NH₄F concentrations studied, Fig. 2c.

The increase in steady current density depending on the fluoride concentration in the bath indicates a greater chemical dissolution of the anodic layers with the fluoride content in the electrolyte.

The value of the final voltage (V_2) determines the features of the anodic oxide layer grown on the oxide/metal interface.^{18–21,25} Therefore, the charge density related to the thickness of the barrier layer is calculated by integrating the stage I from the current density *vs.* time response corresponding to the second voltage step. These values vary between 33–83 mC cm^{−2} depending on the fluoride concentration in the bath, Table 1. Assuming that all the charge are only employed to form a dense layer of amorphous TiO₂,²¹ the thickness of barrier layer varies from 18 to 45 nm, Table 1.

Similarly, by calculating the total charge density used in the anodizing process, it can be seen that the total charge density increases with the fluoride content in the bath, from 1.393 to 9.322 mC cm^{−2} (Table 1). Assuming an efficiency of 100% for the titanium anodizing process, the thickness of the anodic layer would be 758 nm for a concentration of 0.15 M NH₄F, 2615 nm for 0.3 M NH₄F, and 5071 nm for 0.45 M NH₄F, Table 1. However, as expected, the thickness values of the TiO₂ layers measured by SEM differ significantly from the theoretical values calculated, Table 1, as it will be discussed later. This difference is increased with the fluoride content in the bath due to the higher chemical dissolution of the anodic layer which occurs in

Table 1 Parameters of nanotubes formed in 1 M $\text{NH}_4\text{H}_2\text{PO}_4$ /[X] M NH_4F

[X] M NH_4F	Step (30–60 min)	Barrier film charge mC cm^{-2}	Expected barrier oxide thickness, nm^a	Charge C cm^{-2}	Expected oxide thickness, nm^a	NT inner diameter mouth ^b /bottom ^c , nm	Barrier layer thickness ^c , nm	Total thickness ^b , nm
0.15	10–20 V	33	18	1.393	758	~15/53	41	~661
0.3		69	38	4.807	2615	~47/69	39	~1355
0.45		83	45	9.322	5071	~63/65	40	~1585

^a Calculate for compact amorphous film assuming 100% current efficiency. ^b Measured by SEM. ^c Measured by TEM.

presence of fluorides since the dissolution rate of the oxide layer increases considerably with the F^- content.²⁶

3.1.2. Influence of the electric field. To study the influence of the electric field on the nanostructure of the anodic layers, the magnitude of the voltage steps was varied for a specific concentration of fluorides, 0.3 M NH_4F .

Fig. 3 shows the anodizing curves obtained for 0.3 M NH_4F solution using different voltage steps. The evolution of the i vs. t curves is similar to those described in Fig. 2. Thus, after applying a voltage step of 10 V, an abrupt decrease in the current density related to the formation of the oxide barrier layer is observed, followed by the nucleation of the pores which does not exceed 300 seconds. Finally, the current density is

maintained constant indicating that the steady state, in which the growth of the nanotubes takes place, has been reached (Fig. 3).

Upon applying the second voltage step, either 20 or 30 V, the current density at the steady state depicts higher oscillations than during the first voltage step of 10 V. This is due to the increase of the field-assisted dissolution of the anodic layer at voltages higher than 10 V, unbalancing the formation and dissolution of the anodic oxide layer.

The current density evolution at the steady state for a given $\Delta V = V_2 - V_1$, indicates that the current density depends primarily on the applied ΔV rather than on the absolute values of each step, V_1 and V_2 , see Fig. 3b and c.

Fig. 3 Current density–time responses of anodizing of Ti6Al4V in 1 M $\text{NH}_4\text{H}_2\text{PO}_4$ /0.3 M NH_4F at different voltage steps (a), with $V_1 = 10$ V (b), with $V_1 = 20$ V (c).

Nevertheless, in the last 30 minutes of the 20–40 V treatment, the current density increases continuously, without actually reaching any steady state, thus revealing a greater field-assisted dissolution of the anodic layer at high voltages.

The results suggest that the main process occurring at stage III (constant nanotubular layer thickness over time) is field-assisted dissolution instead of “flow assisted” due to the significant level of dissolution of the oxide layer in this aqueous media.

3.2. Film morphology

In this section, the film morphology of the anodic layers fabricated using different anodizing conditions were characterized using scanning electron microscopy and transmission electron microscopy.

The morphology of the nanotubular layers fabricated in Ti6Al4V alloy by applying 10–20 V voltage steps in baths containing different NH_4F concentrations is shown in Fig. 4. In all cases the formation of nanotubes preferentially grown in the α -phase, enriched in aluminium, along with the dissolution of the oxides in β -phase is observed. Such morphology has been widely described for F^- containing aqueous electrolytes. The absence of porous structures in the β -phase relates to the high solubility of vanadium oxides formed on this phase.^{5,8,12,15,27,28}

The micrographs gathered in Fig. 4 show the influence of the NH_4F concentration in the nanotube inner diameter in the mouth, which varies from 15–63 nm for 0.15 M and 0.45 M NH_4F , respectively, Table 1. This increase in the inner diameter of the nanotube is a result of the chemical dissolution of the nanotube walls due to the presence of fluorides in the electrolyte,^{27,29} according to the following reaction:

Fig. 4 Scanning electron micrographs. Morphology of the anodic layers grown at $V_1 = 10$ V for 30 minutes and $V_2 = 20$ V for 60 minutes on Ti6Al4V using (a) 0.15 M, (b) 0.3 M and (c) 0.45 M NH_4F .

This reaction may be further enhanced by the weakness of the bond between adjacent Ti and O due to the electric field (field-assisted dissolution).

Additionally in Fig. 4b and c it can be observed that in some areas the mouths of nanotubes appear to be plugged by a white oxide. This oxide is the result of the solubilization of the titanium and precipitation in form of hydrated species ($\text{TiO}(\text{OH})_2$ or $\text{Ti}(\text{OH})_4$).^{24,28,30,31}

The thickness of the grown layers measured by SEM varies from 661 nm for the anodic layer fabricated in the bath with the lowest concentration of fluoride, up to 1585 nm approximately, for the layer obtained in a bath with the highest concentration, 0.45 M NH_4F , Table 1.

Fig. 5a–f show the cross section of the anodic layers. Nanotubular structure can be distinguished in α -phase, while cavities caused by the preferential dissolution of the oxide formed in β -phase are observed.

It is important to highlight that the lowest concentration of fluoride, 0.15 M NH_4F , promotes a layer with double nanoporous-nanotubular structure, Fig. 5a–b. This complex morphology comprises an outer nanoporous part (~ 180 nm thick) and inner nanotubular part. In the literature this bi-layered structure has been reported on pure titanium³² but also on Ti6Al4V.²⁷ The explanation about the mechanism for the

Fig. 5 Cross sections of anodic layers fabricated at 10–20 V in 1 M $\text{NH}_4\text{H}_2\text{PO}_4$ with (a and b) 0.15 M, (c and d) 0.3 M and (e and f) 0.45 M of NH_4F .

transition from nanoporous to nanotubular structure is unclear. According to Crawford *et al.*,³² the nanotubes grow deeper into the alloy due to the competition of oxide growth and chemical dissolution at the bottom of the nanotube. As nanotubes continue to grow, the nanoporous layer is subjected to chemical dissolution, resulting in thinning and eventual disappearance.

Conversely, the layers grown in baths with 0.3 M and 0.45 M NH_4F have just a nanotubular structure throughout the thickness, Fig. 5c–f. The nanoporous layer disappears at higher concentration of fluorides in the bath, 0.3 and 0.45 M, since the nanoporous layer is subjected to a most intense chemical dissolution due to the higher fluorides presence in the bath.

The thickness of the barrier layer at the bottom of the nanotubes is about 40 nm, Table 1, suggesting an oxide growth rate of 2 nm V^{-1} within 60 min of anodizing.

The images of the cross-section of the anodic layers obtained by TEM clearly show the change in the nanotube inner diameter from the bottom to the mouth with the applied voltage step, Fig. 5d and f. Table 1, shows the inner diameters of the mouth and of the bottom of the nanotubes grown applying the stepped voltage, 10–20 V for the three anodizing baths. It can be seen that the best defined bottle shaped nanotubular structures are obtained for the bath containing 0.3 M NH_4F . The design of bottle-shaped nanotubes with thicknesses greater than micrometer, is specially interesting for controlled drug delivery systems in orthopaedic prostheses.³³

In addition, by applying different voltage steps, in a bath containing 0.3 M NH_4F promotes changes in the nanotubular structures with regard to those previously described, Fig. 6a–h. The anodizing process performed at 10–30 V, Fig. 6c–d, shows poorly defined pores throughout the surface area, while the layers grown at 20–30 V Fig. 6e, show better defined nanotubular structures, similar to those obtained at 10–20 V, Fig. 6a. In the 20–40 V treatment, Fig. 6g, the formation of the nanotubes is not homogeneous over the entire surface, showing that the film loses integrity and collapses.

Values of the inner diameter in the mouth and in the bottom of the nanotubes are included in Table 2.

Nanotubes inner diameter depends primarily on the applied voltage since the voltage determines the electric field strength across the oxide, thus affecting the migration of ions and ultimately the nanotube inner diameter. The upper diameter (mouth diameter) is related to the value of the first applied voltage during the growth of the anodic layers. Layers which are grown with an initial voltage of 20 V (20–30 V and 20–40 V) have a larger pore diameter, in the range of 63–67 nm, compared to layers grown with an initial voltage of 10 V (10–20 V and 10–30 V) with diameters comprises between 39–47 nm, Table 2. Nanotubes bottom diameter depends on the second applied voltage. Values vary from 69 nm for 20 V to 90 nm for 40 V.

Assuming an efficiency of 100% for the titanium anodizing process, the thickness of the anodic layer fabricated using the different voltage steps applied ranges between 2600 and 2800 nm, Table 2. The thickness of the anodic layers measured by SEM are about 1400 nm for all anodic layers except for the layer grown at 20–40 V, which showed a smaller thickness, 1187 nm,

Fig. 6 Scanning electron micrographs. Morphology of the anodic layers grown in 1 M $\text{NH}_4\text{H}_2\text{PO}_4$ + 0.3 M NH_4F at (a and b) 10–20 V, (c and d) 10–30 V, (e and f) 20–30 V, (g and h) 20–40 V.

Table 2. This difference can be attributed to the stronger electric field at 40 V compared to that obtained at lower applied voltages. This implies that there is a higher dissolution rate for the oxide being formed. This is clearly revealed in the anodizing curves, by the increasing current density recorded at stage III pointing out that a steady state is not reached, Fig. 3.

For the oxide layers fabricated, either in the solutions containing different fluoride concentrations, or varying the voltage steps, Fig. 5 and 6, the formation of ribs on the wall of the nanotubes is observed. Ribs have been widely described in the literature in aqueous electrolytes and organic electrolytes with a water content higher than 5%.^{18,34–36} Its formation occurs in a non-continuous way and is due to several factors such as the aggressiveness of the anodizing bath; mechanical stress generated during the growth of nanotubular oxide; the expansion factor; and the electric field generated by applying high voltage.

Table 2 Parameters of nanotubes formed at different voltage steps

Electrolyte	Step		Charge (C cm ⁻²)	Expected oxide thickness ^a , nm	NT inner diameter mouth/bottom, nm	Total thickness ^b , nm	Name
	V ₁ 30 min	V ₂ 60 min					
1 M NH ₄ H ₂ PO ₄ + 0.3 M NH ₄ F	10 V	20 V	4.807	2615	~47/69	~1355	10–20 V
	10 V	30 V	4.946	2690	~39/57 ^c	~1383	10–30 V
	20 V	30 V	4.999	2720	~67/90	~1450	20–30 V
	20 V	40 V	5.207	2839	~63/90 ^c	~1187	20–40 V

^a Calculate for compact amorphous film assuming 100% current efficiency. ^b Measured by SEM. ^c Measured at half of the oxide.

The inward migration of O²⁻ ions during anodization fills the volume of metal consumed, but the outward migrating Ti⁴⁺ ions do not contribute to growth at the metal/oxide interface but pass directly into the solution. Fluoride ions migrate inward at twice the rate of oxygen ions across the layer and form a fluoride-rich layer at the metal/oxide interface. This fluoride-rich layer is more soluble in the anodizing electrolyte than the relatively pure TiO₂ forming the majority of the layer thickness. The dissolution of the fluoride rich layer placed between the nanotubes walls (TiF₄), according to reactions (2) and (3), increases the inter-space distance between the nanotubes. Therefore, the electrolyte accesses throughout the inter-space, and promotes the growth of a new barrier layer between the walls of adjacent nanotubes to form the ribs, in accordance with reaction (4):^{27,35,37}

Fig. 6h shows that the greater amplitude of the voltage step, *i.e.* 20–40 V, favours the formation of ribs along the nanotube to a greater extent than the other conditions studied. Moreover, in this case it appears that the inter-space distance is greater than at lower voltages thus indicating greater field-assisted dissolution of the nanotube walls at the highest applied voltages.

3.3. Efficiency of film formation and composition

In order to determine the composition of the anodic layers and estimate the efficiency of the anodizing process, the oxide layers were analysed by means of Rutherford Backscattering Spectroscopy (RBS).

Fig. 7a presents the RBS spectra corresponding to the anodic layers grown at voltage steps 10–20 V in electrolytes with different NH₄F concentrations. All the spectra show a well-defined peak in channel 475 associated with oxygen, with the same number of counts, but with different width. The most significant difference among the spectra collected in Fig. 7a, is depicted in the slope plotted between channels 850 and 950 and is related to the presence of titanium in the anodic layer. As the concentration of fluoride in the electrolyte increases, the formation of a more pronounced step is observed. This step is

Fig. 7 Rutherford backscattering analysis spectra for anodic oxide films formed on Ti-6Al-4V in 1 M NH₄FH₂PO₄ + [x] M NH₄F electrolyte at 10 V for 30 min and 20 V for 60 min, acquired at 3.777 MeV (a) and fitting of the spectra for the film formed in 0.15 M NH₄F (b) circles-original data, solid line-simulation.

related to the different thickness of the anodic layers, while the slope can be attributed to: differences in the roughness of the metal/oxide and oxide/surface interfaces; porosity of the grown layer; and heterogeneity of the oxide formed.

RBS spectra show a similar trend in the thickness of the anodic layers in relation to that measured by SEM. The layer fabricated in 0.15 M NH₄F has the lowest thickness, while those grown in 0.3 M and 0.45 M NH₄F are thicker and similar between them.

In order to determine the composition and thickness of the oxides grown, the simulation of RBS spectra was conducted

using the SIMRA software, Fig. 7b and 8b. In order to simulate these complex oxide layers, the fitting of the spectra was performed assuming various layers of varying composition and thicknesses. The results show good agreement between the fitted and experimental data, for all cases.

The composition of the anodic layers in 10^{15} atoms per cm^2 and at.% is gathered in Table 3. It can be observed that the chemical composition for the layers fabricated in solutions containing different NH_4F concentrations are similar among them, showing 33 to 34 at.% for oxygen, 47 to 51 at.% for titanium, 4 to 7 at.% for aluminium, 3 at.% for vanadium and fluorine contents about 9–10 at.%, Table 3.

The composition of the layers was determined assuming the stoichiometric formation of V_2O_5 , Al_2O_3 and TiF_4 . The average molecular composition of the nanotubes formed on Ti6Al4V alloys can be expressed as $\text{TiO}_{1.24} \cdot 0.080\text{TiF}_4 \cdot 0.067\text{Al}_2\text{O}_3 \cdot 0.044\text{V}_2\text{O}_5$ for the layer grown in 0.15 M NH_4F while for the layers grown at 0.3 and 0.45 M NH_4F , the titanium oxide is composed of $\text{TiO}_{0.92}$ and $\text{TiO}_{0.98}$, respectively, Table 3. Similar contents of TiF_4 , Al_2O_3 and V_2O_5 are found for layers fabricated with 0.3 M and 0.45 M NH_4F .

RBS spectra for layers grown in an electrolyte with 0.3 M of NH_4F and different voltage steps, Fig. 8a, are similar to those obtained for the anodic layers grown with different

concentrations of NH_4F . A well-defined oxygen peak of similar width is observed in all growth conditions. There are no great differences in thickness between the layers. The anodic oxide layer fabricated at 20–30 V is slightly thicker, while the layer grown at 20–40 V, has the lowest thickness. These results are in agreement with those measured in the SEM images as is summarised in Table 2.

The composition of the titanium oxide layers is similar in all cases, showing 33 to 36 at.% for oxygen, 45 to 47 at.% for titanium, 7 at.% for aluminium, 2 to 3 at.% for vanadium and fluorine contents about 9–12 at.%, Table 4. The layer grown at 20–30 V presents a slightly higher Ti/O ratio, showing an average molecular composition expressed as $\text{TiO}_{0.98} \cdot 0.094\text{TiF}_4 \cdot 0.111\text{Al}_2\text{O}_3 \cdot 0.045\text{V}_2\text{O}_5$, while the oxide grown at 20–40 V, revealing a lower ratio of Ti/O, is composed of $\text{TiO}_{0.87} \cdot 0.073\text{TiF}_4 \cdot 0.098\text{Al}_2\text{O}_3 \cdot 0.039\text{V}_2\text{O}_5$, Table 4.

The efficiency of the anodizing process has been estimated using the expression that relates the concentration of titanium obtained from RBS spectra (concentration of Titanium in 10^{15} atoms per cm^2 , second column in Tables 3 and 4) and the calculated from the charge recorded during the anodizing (Tables 1 and 2), assuming that all the charge is consumed to oxidize titanium (100% efficiency):

$$\text{Efficiency} = \frac{\text{Ti atoms per cm}^2(\text{RBS})}{\text{Ti atoms per cm}^2(\text{current} - \text{time curves})} \times 100 \quad (5)$$

where the Ti atoms per cm^2 are estimated as follows:

$$\text{Ti atoms per cm}^2(\text{current} - \text{time curves}) = \text{charge recorded} \times 1.5597 \times 10^{18} \text{ at C}^{-1} \quad (6)$$

$$1.5597 \times 10^{18} \text{ at C}^{-1} = 275 \text{ nm C}^{-1} \times \frac{\rho N_A}{W_M} \quad (7)$$

being $275 \text{ nm cm}^2 \text{ C}^{-1}$ the titanium consumed by charge unit, ρ the titanium density, N_A the Avogadro's number and W_M the titanium molecular weight.

The results reveal an efficiency about 34.2% for the bath containing 0.15 M NH_4F , and 12.4% for the bath with 0.45 M NH_4F , Table 3. The efficiency decreases with the fluoride concentration in the bath despite the influence of the F^- content on the charge, as can be seen in the increasing current density response described in the curves in Fig. 2. This means that not all the collected charge is used to grow the titanium oxide, but that part of it is due to either the dissolution of both the nanotubes formed in the α phase and the oxidation of the β -phase, or to the oxygen evolution at the anode. The higher the fluoride concentration in the anodizing electrolyte, the lower the process efficiency. This response has been also described for TiO_2 anodic layers fabricated in similar electrolytes at constant voltages.^{27,28}

The efficiency of the anodizing process performed in the present work, applying voltage steps, Table 4, is 22–25%. It appears that efficiency of the anodizing process is not influenced by the voltages or by the ΔV applied. The results suggest that the growth efficiency depends mainly on the chemical dissolution of the oxide due to the fluoride presence in the

Fig. 8 Rutherford backscattering analysis spectra for anodic oxide films formed on Ti-6Al-4V in 1 M $\text{NH}_4\text{FH}_2\text{PO}_4$ + 0.3 M NH_4F electrolyte at different voltage steps, acquired at 3.777 MeV (a), fitting of the spectra for the film formed at 10–30 V, (b) circles-original data, solid line-simulation.

Table 3 Composition of the nanotubular films ($\times 10^{15}$ atoms cm^{-2}), and at.% of each element, formed on Ti6Al4V in 1 M $\text{NH}_4\text{H}_2\text{PO}_4$ electrolyte containing different NH_4F concentrations, applying a voltage step of 10 V for 30 minutes and 20 V for 60 minutes

Film NH_4F	Ti ($\times 10^{15}$ at cm^{-2} /at.%)	O ($\times 10^{15}$ at cm^{-2} /at.%)	F ($\times 10^{15}$ at cm^{-2} /at.%)	Al ($\times 10^{15}$ at cm^{-2} /at.%)	V ($\times 10^{15}$ at cm^{-2} /at.%)	Average molecular composition	Efficiency (%)
0.15 M	743/33	1142/51	221/10	92/4	60/3	$\text{TiO}_{1.24} \cdot 0.080\text{TiF}_4 \cdot 0.067\text{Al}_2\text{O}_3 \cdot 0.044\text{V}_2\text{O}_5$	34.24
0.30 M	1760/34	2389/47	485/9	346/7	145/3	$\text{TiO}_{0.92} \cdot 0.074\text{TiF}_4 \cdot 0.106\text{Al}_2\text{O}_3 \cdot 0.044\text{V}_2\text{O}_5$	23.53
0.45 M	1802/33	2594/47	536/10	383/7	156/3	$\text{TiO}_{0.98} \cdot 0.080\text{TiF}_4 \cdot 0.115\text{Al}_2\text{O}_3 \cdot 0.047\text{V}_2\text{O}_5$	12.42

Table 4 Composition of the nanotubular films ($\times 10^{15}$ atoms cm^{-2}), and at.% of each element, formed on Ti6Al4V in 1 M $\text{NH}_4\text{H}_2\text{PO}_4$ + 0.3 M NH_4F , at different voltage steps

Film	Ti ($\times 10^{15}$ at cm^{-2} /at.%)	O ($\times 10^{15}$ at cm^{-2} /at.%)	F ($\times 10^{15}$ at cm^{-2} /at.%)	Al ($\times 10^{15}$ at cm^{-2} /at.%)	V ($\times 10^{15}$ at cm^{-2} /at.%)	Average molecular composition	Efficiency (%)
10–20 V	1760/34	2389/47	485/9	346/7	145/3	$\text{TiO}_{0.92} \cdot 0.074\text{TiF}_4 \cdot 0.106\text{Al}_2\text{O}_3 \cdot 0.044\text{V}_2\text{O}_5$	23.53
10–30 V	1842/34	2429/45	630/12	372/7	132/2	$\text{TiO}_{0.93} \cdot 0.093\text{TiF}_4 \cdot 0.109\text{Al}_2\text{O}_3 \cdot 0.037\text{V}_2\text{O}_5$	25.73
20–30 V	1938/33	2724/46	668/11	387/7	158/3	$\text{TiO}_{0.98} \cdot 0.094\text{TiF}_4 \cdot 0.111\text{Al}_2\text{O}_3 \cdot 0.045\text{V}_2\text{O}_5$	24.72
20–40 V	1674/36	2121/45	447/10	303/7	124/3	$\text{TiO}_{0.87} \cdot 0.073\text{TiF}_4 \cdot 0.098\text{Al}_2\text{O}_3 \cdot 0.039\text{V}_2\text{O}_5$	22.13

electrolyte more than the field-assisted dissolution of the oxide and field-assisted ejection of Ti ions into the electrolyte.

4. Conclusions

In this paper it has been demonstrated that it is possible to design TiO_2 oxide layers with bottle-shaped nanostructures by controlling the anodizing electrolyte and the applied voltage steps.

For the anodic layer fabricated applying voltage steps of 10–20 V, the F^- concentration mainly influenced the inner nanotubes diameter, which also depends on the value of the voltage applied. Electrolytes with low fluoride concentration, 0.15 M NH_4F , lead to anodic layers with double morphology, nanoporous on the oxide/solution interface and nanotubular on the metal/oxide interface. Conversely, at higher fluoride concentrations, 0.3 M and 0.45 M NH_4F , only a nanotubular oxide layer with variable inner diameter along the layer is fabricated. Therefore, the growth of bottle-shaped nanotubular oxide layers is achieved only when apply a voltage steps using the adequate fluoride concentration in the electrolyte. The best bottle-shaped morphology is obtained in the anodizing bath containing 0.3 M NH_4F with a inner diameter about 47 nm at the mouth and about 69 nm at the bottom. This anodic layer is homogeneous and thicker than one micrometer.

Other voltage steps, 10–30 V, 20–30 V or 20–40 V, applied in the same anodizing bath-0.3 M NH_4F – lead to oxide layers thicker than the micrometer but their nanostructures are not well defined.

Ribs on the wall of the nanotubes are observed for the oxide layers fabricated, either in the solutions containing different fluoride concentrations, or varying the voltage steps. Nevertheless, the formation of ribs are favoured for the greater

amplitude of the voltage step, *i.e.* 20–40 V, than the other conditions studied. Additionally, the inter-space distance is also greater at 40 V than at lower voltages thus indicating greater field-assisted dissolution of the nanotube walls at the highest applied voltages.

The efficiency of the anodizing process decreases with the fluorides concentration in the bath, from 34.2% for 0.15 M NH_4F , 22% for 0.3 M NH_4F to 12.4% for 0.45 M NH_4F , and is practically constant for the different voltages applied, about 22–25 %. It appears that efficiency of the anodizing process depends mainly on the chemical dissolution of the oxide due to the fluoride concentration in the electrolyte more than the field-assisted dissolution of the oxide and field-assisted ejection of Ti ions into the electrolyte.

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