FORMATION OF TITANIUM OXIDE NANOTUBE ARRAYS BY CONTROLLING H₂O AND TIME THROUGH ANODIC OXIDATION

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ABSTRACT

Maintaining a constant voltage the growth of titanium oxide (TiO₂) with a tubular geometry was studied. Therefore, the optimal parameters for the growth of TiO₂ were established using an organic electrolytic solution with a total volume of 150ml, composed of water/hydrofluoric acid/ammonium fluoride/ethylene glycol. The anodization conditions were varied, such as: time (60 -215 min), electric potential (5 -20 V), water content (0.0 - 2.0 ml), and pH (4.8 - 5.1). In this procedure, the conformation of long, open nanotubes with smooth walls was achieved, obtaining a maximum length of 1.90 μm for the nanotubes. However, in some samples before and after annealing a remnant layer can be seen that extends over some regions of the surface of the nanotubes. By means of the current density curves-time (J vs.t), we were able to specify the distinct growth zones of the nanotubes. The samples also were studied structurally by means of X-ray with thermal treatment (ambient–450°C). In addition, it was determined, via ultraviolet-visible (UV-Vis) spectroscopy, that the band gap energy varies (3.45 eV–3.03eV).

Keywords: Nanotubes, Kinetics, TiO₂, Current, Anodization

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INTRODUCTION

Titanium-containing materials have been highlighted in recent decades due to their special applications in high-tech industries, especially in scenarios such as aerospace, energy, surgical, among other applications. During the last 20 years of study of TiO₂, it has been shown to have a very extensive range of applications. Among these are functional properties in photovoltaic devices^{1,2}, since it exhibits semiconductor characteristics with a gap of 3 eV, photocatalytic devices, gas sensors, and electrochromic devices, among others³⁻⁶. TiO₂ crystallizes in three different structures: rutile, anatase, and brookite^{7,8}. The differences in its crystal lattice give place to distinct densities and electronic band structures. Being a photosensitive material, it has applications in solar cells, especially anatase, this phase presents an absorption up to 387.5 nm in the UV region⁹. The crystallization of the material is determined by the optimum migration and ionic transport rate in the system, which favors the growth of the crystal¹⁰⁻¹². This effect also can be induced by organic electrolytes by varying the anodization parameters, or with an increase in the water content and the anodization time.¹³⁻¹⁵

The post-growth sintering process of TiO₂ is also a direct way to modify and improve the electronic and optical properties of the nanotubes. According to the literature, the brookite and anatase phases are meta stable polymorphs, and are transformed into rutile within a range of temperatures (400- 1200°C).^{16,17} This transformation is irreversible and takes place because of factors such as the presence of impurities and the size of the particles. The limitations imposed on the sintering process do not allow a transformation of the anatase phase to other phases such as rutile.¹⁸⁻²² In this work, we present a detailed study of the TiO₂

nanotubes that are classified as the third generation. As can be seen in the results, the composition of the electrolyte has a significant influence on the formation of the nanotubes.

According to the difference of electrolytes we use, the anodization conditions and dimensions of the resulting TiO_2 nanotube arrays they are classified in three generations. The first generation: aqueous electrolytes whose main base is hydrofluoric acid (HF). The second generation: buffered electrolytes (KF, NaF). In the third generation, we have polar organic electrolytes. Electrolytes such as glycerol, dimethyl sulfoxide, formamide or diethylene glycol, ethylene glycol, containing fluoride species such as NH_4F , NaF, and KF gradually appear.²³ This last-generation is very important because it offers a group of very useful characteristics, wide ranges of lengths, different tubular geometries, self-organized nanostructures with homogeneous growth, and small diameter nanotubes. It also allows the construction of hexagonal, smooth-walled nanotubes, depending on the water content of the solution²¹⁻²⁴.

In this work, three series of measurements were made in the following way: In the first series of samples, the pH, H_2O , was varied, maintaining a constant voltage of 20V and a time of 60 minutes and studying their results. Obtaining a better result for the sample with a pH of 4.9, an amount of water of 0.5 ml. In the second series of samples the pH (4.5), water (2.0 ml) and time (60 min) were kept constant, the voltage was changed from 5 - 15V. In this series, nanostructures were not obtained. Finally, several tests were carried out, maintaining constant pH (4.5), water (2.0 ml), voltage (20V) and changing the time until obtaining the longest structure without collapsing. The time recorded for this test was 215 minutes. As a test, the samples of series one were annealed in an oven at 450°C for two hours. In the results of the X-rays diffraction, we realized that the temperature was adequate for the appearance of the anatase phase with the peak (101), although, with very low intensity.

In this work, we tried to find good parameters to obtain nanotubes of appreciable length, in particular, control the amount of water in the electrolyte. According to Raja et al.²⁵ a minimum amount of 0.18 wt% of water addition was required to form a well ordered TiO_2 nanotubular arrays. Nevertheless, the author Wieetal²⁶ state that the best conditions are: 0.5 vol.% H_2O after 4h anodization at 20 V. According to our results, we suggest that the best condition sare those of the sample of series three (pH=4.5, H_2O =2.0ml, 20V and 215 minutes).

EXPERIMENTAL

Material and Methods

For this study, a commercial sheet of titanium 0.03 mm in thickness was used, with 99.6% (grade 2) purity, previously sterilized. The anodic solution, of immersion, was composed of Sigma brand ethylene glycol (EG) organic solvent with molecular formula $\text{C}_2\text{H}_6\text{O}_2$, Panreac brand ammonium fluoride (NH_4F), Panreac brand hydrofluoric acid (HF) at 40%, and distilled water.

In the process of anodization, sheets of Ti with an area of exposition of 2.5 cm^2 were used as the anode and the cathode. This last-named variable was modified for a particular test, submerged in an electrolytic solution composed of ($\text{H}_2\text{O}/\text{HF}/\text{NH}_4\text{F}/\text{EG}$) and maintaining constant the concentration of $\text{HF}/\text{NH}_4\text{F}$ with 3 ml and 0.30g respectively were lied on previous work, in which NH_4F and HF were varied in the electrolyte and the nanotubes collapsed for 30V and 60 min.²⁷ For this reason, we decided to use less voltage in this work (20) and vary the water and time. It creates 8 tests, which allows evaluating the best results in terms of growth kinetics. The anodization voltage and the water concentration in the final composition of the chemical immersion solution (150ml) are varied over a period of 60 min. The growth of nanotubes at an extended anodization time of 215 min is also evaluated.

The process of sintering or annealing of the samples was carried out in a Vulcan 3-1750 flask at a heating speed of $2^\circ\text{C}/\text{min}$ until a temperature of 450°C was reached, and this was maintained constant for 2 hours. Afterward, they were allowed to cool down to room temperature. For the morphological characterization of the nanotubes, a VEGA3 SB scanning electron microscope was used. In the study of the size of the nanotubes, an image processing software was used, ImageJ.²⁸ With this program, it was possible to find the diameter of them. The different nanotube growth stages of TiO_2 were determined, recording anodization time and current.

The structural characterization of the samples was carried out using a Panalytical Empyrean diffractometer in the Bragg-Brentano configuration, at room temperature, with a step of 0.02° (2 θ) in continuous mode between 10° and 90° (2 θ). The diffractions are compared with a sintering process and

without it. The optical characterization of the samples of nanotubes was carried out by means of a spectrophotometer (Cary 5000 UV-vis) in the diffuse reflectance mode.

RESULTS AND DISCUSSION

In Figures-1, 2, and 3, the morphological study of the anodized samples of series 1, 2, and 3 (Table-1) is presented. In order to facilitate the visualization of the nanotubes, a mechanical force is applied to the titanium sheet, allowing fragmentation during the analysis of the nanostructures. In Fig.-1, the micrographs of the samples of series 1 can be seen, which correspond to the films where the concentration of H_2O varies between 1.5-0.0 ml in the chemical solution at an anodization time of 60 min and a potential of 20 V.

Fig.-1: SEM for the Samples of Series 1, Varying the Amount of Water for a Total Volume of 150 ml of Chemical Solution, the Potential of 20 V and time of 60 min

With respect to Fig.-1(a), nanotubes grown with a length of 0.10 μm are seen, as a result of the use of a volume of H_2O of 1.5ml. In some areas of the anodized film, some nanotubes are obstructed by a remnant layer, which does not allow to differentiate the upper part with the bar scale value 1 μm . For the test with 1.0 ml of H_2O , Figure 1(b), nanotubes with a length of 0.20 μm were obtained with the presence of a remnant layer. It can be seen in Fig.-1c that the maximum length of nanotubes was obtained with a minimum content of 0.5 ml of H_2O , with a value of 0.85 μm and a length of 0.22 μm without the addition of water.

In Table-1, the micrographic values of the longitudinal size of the nanotubes and the synthesis parameters are summarized. As the water content is increased, the pH of the solution also increases. In table 1, it was not kept in common: 2 ml of H_2O , 20V and 60 minutes for the three series, because these tests had already been done in another work.²⁷ Where it was observed that from the 30V in these conditions the nanostructures collapsed. That is why it was decided to leave 20 V constant in this work, varying pH, time and water.

Table-1: Experimental Anodization Parameters for series 1, 2, and 3. Longitudinal Size of the Nanotubes

Set	pH	H ₂ O (ml)	V _{anod} (V)	t _{anod} (min)	L _{anod} (μ m)
1	5.1	1.5	20	60	0.10
	5.0	1.0			0.20
	4.9	0.5			0.85
	4.8	0.0			0.22
2	4.5	2.0	5	60	
			10		
			15		
3	4.5	2.0	20	215	1.90

Figure-2 shows the micrographs of the samples for which the applied voltage was varied between 5 V and 15 V, which corresponds to series 2. Using the experimental parameters of Table-1, the growth of the nanotubes was not obtained at a time of 60 minutes. In Fig.-2a, the micrograph that is a result of the application of 15V can be seen at the bar scale value 2 μ m. The formation of an anodic layer of barrier type TiO₂ can be observed.

Fig.-2: Micrographs of the Morphology of the Anodization Process of Series 2, Varying the Potential, Time of 60 min and 2 ml of Water in the Chemical Solution.

Here, no regions of tubular growth can be detected, and crackled zones are seen, where the anodic layer exhibits cracks. In the micrograph of Fig.-2b, a surface anodized with a voltage of 10 V is shown, and the topography of the film exhibits homogeneous wear. In addition, some pores and cracks can be seen, but the formation of an anodic layer is not seen. With respect to micrograph 2c, a zone that has undergone localized chemical attack on the surface of the substrate when an anodization voltage of 5 V was applied can be observed, and the presence of nanostructures is not apparent. From series 2, it can be inferred that at a voltage less than 20V and using 60 minutes of anodization, growth of nanotubes is not generated. This is due to the fact that there isn't a driving force sufficient to establish ionic transport across the barrier layer in the bottom part of the pore, causing a slower movement between Ti/TiO₂.

In Fig.-3a, the micrograph of the test corresponding to series 3 can be seen, with an anodization time of 215 min and at 20 V, where the growth of nanotubes with a length of 1.90 μ m can be observed. Figures-3b and 3c are amplified zones of the micrograph, which allow observing the open nanotubes formed, with smooth walls and without a remnant layer. This micrograph shows that the anodization time increases the length of the nanotubes in this chemical solution. Furthermore, there is no collapse of the nanostructures.

On the basis of the open circuit potential and under conditions of oxide formation, the different stages of growth of TiO₂ are evident, electrochemical reactions are presented between a substrate and an electrolyte that allow evaluating the growth rates. Often it is convenient to use polarization curves such as current density-time (J vs. t), where the growth of the oxide is monitored²⁹⁻³². In general, these curves interpret a fluctuation zone where two inflection points, J_{crit} and J_{max}, are exhibited, which shows the growth of tubular nano structures.

A critical value of the current density, J_{crit} , is reached when it decreases by several orders of magnitude, while the oxide film acquires greater thickness, and the passivation of the metal takes place, creating a dense film of limited ionic conduction called the barrier layer, thus establishing the first stage of growth. Then a maximum current density J_{max} is reached, where the barrier layer is chemically attacked by the ions present in the electrolyte, creating a porous layer of oxide. In the final part, the trans-passive region, the current increases as the anodization time passes, with the transition of the pores to tubular structures³³. Using a logarithmic scale of the curves of J vs. t , we were able to observe the different stages of the process of formation of the nanostructures.

Fig.-3: (a) Micrograph of the Test using an Anodization Time of 215 min, 2 ml of H_2O in the solution, and 20 V (Series 3). (b) Amplified Region of the Nanotubes. (c) Amplified Surface of the Nanotubes.

Next, the current density is shown as a function of time for series 1 and 2. For practical reasons of visualization, it is only shown in the graphs of the region of interest in the first minutes of anodization, since in this region the different stages of growth are exhibited.

Figure-4 represents the behavior of the current density (J) as a function of time when the concentration of the chemical solution is altered (Series 1). The volume of water is varied from 0.0 ml in increments of 0.5 ml up to 1.5 ml. It can be seen in Fig.- 4 that the current density (J) decreases in all the samples and remains constant between 5.3 and 5.1 mA/cm^2 starting at 550 s for curves (b)-(d) with a volume of 0.5 ml and 1.0 ml, respectively. Nevertheless, curves (a), with the content of H_2O of 1.5ml maintain a constant current density of 6.9 mA/cm^2 for (c) without water content in 7.4 mA/cm^2 at the same time interval.

In this figure (Fig.- 4) the fluctuation of the curves can be seen in the first 100 seconds of anodization. Two inflection points are exhibited for all of the curves except curves(a), where no point of inflection can be seen. This behavior can possibly be attributed to the conductivity and ionic mobility in the chemical solution. When the electrolyte does not have a source of oxygen added to the chemical solution, the organic solvent (EG) has hygroscopic property, that is to say, it absorbs oxygen from the humidity of the environment. This explains the growth of the nanotubes without any water content. In Fig.-4 the inset shows, the different curves (b),(c), and (d) are shown on a logarithmic scale, which allows clearly identifying the stages of growth. It can be seen that the current decreases, exhibiting three slopes, and each one of them is associated with the stages of growth of TiO_2 .

In Fig.-5, the behavior of the current density for series 2 is recorded, where different anodization voltages are used (Table-1). In this figure, curve (a) corresponds to a voltage of 15 V, curve (b) to 10 V, and

curve(c) to 5V of anodization. After 600s, the record of the current density stabilizes at a constant value of 4.2mA/cm^2 for the curve (a), and 3.2 and 2.4mA/cm^2 , respectively, for curves (b) and (c). Curves (a), (b), and (c) of Fig.-5 exhibit a strong decrease in the current density in the first seconds of anodization, without exhibiting inflection points J_{crit} and J_{max} , which is congruent with the micrographs of Fig.-2, where there is no evidence of the growth of nanotubes.

Fig.-4: J-t (Current Density - Time) Curves of the Anodization of Ti under a Voltage of 20 V for Series 1, (a) 1.5, (b) 0.5, (c) 0.0 and (d) 1.0 ml of Water. The inset shows the Log J vs. log t with Stages I, II and III of the Growth of the TiO_2 Nanotubes for (b), (c) and (d).

Fig.-5: Behavior of the Current Density as a Function of the Anodization Time for Series 2.

Fig.-6: Comparison of the Diffractions for Series 1 (a) without (b) with the Thermal Process at 450°C.

In Fig.-6, the different diffractions of the tests of series 1 are compared with and without thermal treatment. The results of the X-ray diffraction establish a crystalline phase in the samples of nanotubes to which a process of sintering was not applied (Fig.- 6). This result is directly related to the parameters of anodization and chemical solution used.

In series1, only the anatase (A) phase was seen, characterized by exhibiting a tetragonal crystal system for all of the tests. By means of the comparison of the various diffraction patterns, it was found that the nanostructures are stable at temperatures of 450°C. Nevertheless, it can be seen that the intensities of the peaks characteristic of anatase increase with the temperature.

Comparing the results of x-ray diffraction of Fig.-6. One can observe the Fig.- 6(a) the measurements for the samples of series 1 anodized without calcination. In Fig.-6(b) we present the x-rays diffraction of the series one with the calcined samples. In this graph, we observe a low-intensity peak at $2\theta = 25^\circ$, which corresponds to (101) of the anatase of TiO_2 . There is no evidence of changes in the morphology of the nanotubes with the process of sintering; therefore they do not appear in this article. We measure the x-rays diffraction of Fig.-6(a) and (b) under the same conditions. To observe the peak (101) more intensities necessary to make an XRD with more time.

Figure-7 simulates the crystalline structure of the anatase phase and the positions of the atoms of Ti and O, having the data of the x-rays diffraction of Fig.-6(b). The parameters found in the simulation appear in Table-2. The result, to submitting the samples of Fig.-(a) at high temperature (greater 450°C leads to a rearrangement of the Ti,O, bonds by contracting the volume of the unit cell. The lattice parameters in the anatase phase of the samples of series one are observed in Table-2, these results are comparable with those of the literature³⁴. In the literature according to Kavei et al with the XRD standards for samples calcined up to 500°C, the authors observed only the anatase phase of TiO_2 ³⁵. For higher temperatures, there was the presence of Rutile. The parameters found by the authors for the anatase structure by Rietveld refinement they found: $a = b = 3.7834$ (6)(Å) and $c = 9.5043$ (7)(Å). In Table-2 our results are comparable since we obtained $a=b=3,730$ (Å) and $c= 9,370$ (Å).

Fig.-7: (a) Crystalline Structure. (b) Octahedron Chain of the Ti_4O_8 Phase.Table 2: Crystallographic Parameters for the Anatase Phase with Chemical Formula Ti_4O_8 Series 1.

	Crystallographic Parameters			Lattice parameters	
Crystalline System	Tetragonal	No	a(Å)	b (Å)	c(Å)
Space group	I41/amd	1	3.730	3.730	9.37
Space group number	141	2	3.804	3.804	9.64
		3	3.785	3.785	9.52
		4	3.785	3.785	9.54

Fig.-8: (a) Reflectance Spectrum for Series 1. (b) Calculation of Bandgap Energy (Gap) for Series 1.

Table-3: Results for the energy gap (E_g) for Series 1

Set	H ₂ O(ml)	E _g (eV)
1	1.5	3.45
	1.0	3.03
	0.5	3.42
	0.0	3.15

The calculation of the band gap energy (E_g) is carried out by means of the reflectance spectra in the diffuse UV-visible mode. In Fig.-8, the reflectance spectrum for series 1 can be seen, taking a wavelength of around 750 nm, of interest for determining the corresponding band gap energy.

In the spectra of Fig.-8, special attention should be paid to the band gap energy of the series, where there is evidence, by means of scanning electron microscopy, of the growth of nanotubes of TiO₂. In Table-3, it can be seen that the water content significantly modifies the values of the band gap energy (E_g). These values run from 3.15 eV in the absence of water, a condition that allows obtaining nanotubes of 0.22 μ m, up to 3.42 eV when 0.5 ml of water is added to the chemical solution, when nanotubes of 0.85 μ m in length are grown. Our band gap results for TiO₂ are comparable to those found in the literature, which are around 3.2 eV.³⁶⁻³⁸

The band gap energy could be influenced by the sectorized presence of a remnant layer. This layer is in contact with the nanotubes of TiO₂, creating a hetero- bonding of the semiconductor-semiconductor type, altering the energy values. According to the literature, physical and chemical processes eliminate the remaining layer, thus generating energy values that correspond only to the phases that constitute the test under study, since there is no electronic interchange between the remnant layer and the nanotubes³³. Also, the band gap energy is affected by the absence of water in the electrolyte, since ions of OH⁻ can be injected into the crystalline structure of TiO₂, generating electronic changes.

CONCLUSION

This study allowed establishing the optimal synthesis parameters for the growth of nanotubes of TiO₂, with a chemical solution made up of (0.5 ml H₂O/0.30 g NH₄F/3mlHF/EG), using an anodization voltage of 20V. The rapid growth of nanotubes with a length of 0.85 μ m was achieved in a time of 60 min and a pH of 4.9. It can be seen that the anodization time increases the length of the nanotubes. With a time of 215 min, nanotubes with a length of 1.90 μ m are obtained, without collapse of the nanostructures. Through the behavior of the graphics I Vs t was evidenced that for voltages between 5 V and 15 V, there is no formation of nanotubes using a chemical solution made up of (2.0 ml H₂O/0.30 g NH₄F/3ml HF/EG) in a time of 60min.

Observing the micrographs of all the series, a remnant layer can be seen that extends over some regions of the surface of the nanotubes. This layer negatively affects applications, since it obstructs the cavity of the nanotubes and also causes electronic changes. This remnant layer was not observed in all the regions, since other regions presented a confirmation of long and open nanotubes with smooth walls. It was seen that with a post-growth thermal treatment of the samples at 450⁰C, the sintering process did not affect the morphology of the nanotubes. Nevertheless, it can be seen that the intensities of the peaks characteristic of anatase increase with the temperature.

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[RJC-5265/2019]