Effect of the oxygen diffusion in the anatase-rutile transformation in a TiO$_2$ nanotubes array obtained by electrochemical anodization.

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Abstract. Titanium dioxide is a key material in the development of alternative energy sources like water splitting and dye-sensitized solar cells. Its photochemical and photoelectrochemical properties are affected by the specific crystal structure. Titanium dioxide nanotubes array obtained by electrochemical anodization shows an amorphous structure and a thermal treatment is needed before its application in solar energy systems. In this work, we evaluated the influence of the oxygen diffusion on the grain boundaries of the substrate on the anatase-rutile transformation of a TiO$_2$ nanotubes array supported in a titanium foil. The nanotubes array was obtained by electrochemical anodization applying 25 V for 5 hours using an electrolyte of 0.5 % wt NH$_4$F, 10 % Vol deionized water in glycol. The anodized samples were treated at 450 °C for 12 hours to obtain a uniform anatase structure. After that, a second heat treatment was performed at 650 °C different times between 2 to 8 hours to analyze the anatase-rutile transformation. The treated nanotubes array was analyzed by SEM and the results were compared with the theoretical models of transformation in the wall of the tube and the oxygen diffusion in the grain boundaries of the substrate obtaining an agreement between the theoretical model and experimental results.

1. Introduction.

Greenhouse gases generated using fossil fuels are the principal cause of global warming with a direct impact on human health and the environment [1]. To improve the efficiency of the alternative energy sources several types of research have been focused on the development and upgrade of material properties [2]. Titanium dioxide has been used as a key material in two relevant process relatives to the energy generation: water splitting and solar cells. Dye-Sensitized solar cells developed by professor Grätzel use TiO$_2$ nanoparticles or nanotubes as photocatalysts material for energy conversion. TiO$_2$ is an n-type semiconductor that can be found in nature as brookite, anatase or rutile [3]. The TiO$_2$ phases define its final photochemical properties. Degussa P-25 is the most used catalysts in the photochemical and photoelectrochemical application, it has a two-phase mixture, these are anatase and rutile. Both phases show a tetragonal crystal structure but with different network parameters, creating a reconstructive transformation. In the nanometric scale, this reconstruction of the crystal cell could modify the morphology of the titanium dioxide nanoparticles, because the particles are shaped just by few cells [4,5]. In the specific case of the TiO$_2$ nanotubes synthesized by electrochemical anodization, the obtained structure is amorphous, and an appropriated heat treatment process is needed to transform it into anatase or anatase-rutile, where the transformation depends on the temperature, time and
atmosphere of the furnace. Yu et al. [6] proposed that the anatase-rutile transformation begins at the bottom of the nanotubes generating the progressive destruction of the nanotubes array. In our previous work [7] we identified by scanning electron microscopy that the transformation is affected by the grain boundaries of the titanium base material. The aim of this study is to evaluate the oxygen diffusion in the grain boundaries and its influence in the anatase-rutile transformation on the TiO2 nanotubes array comparing theoretical models with the experimental results of heat treatments at 650 °C for different times.

2. Experimental Section.

2.1. Synthesis of TiO2 nanotubes array by electrochemical anodization.
TiO2 nanotubes array were synthesized by an electrochemical method using a titanium foil (99.7 % purity) as a substrate. The samples were cleaned with ethanol and pickling with hydrofluoric acid, nitric acid, and H2O solution. The electrolyte used for the anodization was a mixture of 0.5 % wt of NH4F distributed by PanReac Applichem ITW reagents and 10 % Vol deionized water in glycol solution (Laboratorios León S.A). The anodization was performed using a two electrodes cell, with a titanium foil as working electrode and a platinum wire as the counter electrode, the experiments were made at ambient temperature applying a constant DC voltage of 25V for 5 hours using a power source BHK-MG 200W KEPCO.

2.2. Heat treatment.
The anodized TiO2 nanotubes array has an amorphous structure. To evaluate the phase transformation on the arrays, the samples were treated by two consecutive heat rounds. The first one maintaining the samples at 450 °C and the second treatment maintaining the temperature at 650 °C. For both treatment the heating rate was 20 °C.min⁻¹. The holding time for the first treatment was 12 hours. To evaluate the kinetics of the anatase-rutile transformation the holding time of the second treatment was varied between 2 and 8 hours. The treatment was performed using a Carbolite CWF-BAL furnace.

2.3. Characterization of the samples.
The TiO2 nanotubes array were analyzed by SEM (Scanning Electron Microscope) Microscopy Quanta 650 FEG (Field Emission Gun) equipped with Energy-dispersive X-ray spectroscopy (EDS) and operated at 25 kV.

3. Result and discussion.

3.1. Synthesis of TiO2 nanotubes array by electrochemical anodization.
Figure 1(a) shows the chronocamperometric response of two independent tests obtained during the potentiostatic anodization of the foils. In the first part of the curve, between the initial time and hundred seconds, the current shows a progressive reduction related to the formation of a compact oxide layer. The concave zone, between hundred and five hundred seconds, is known as the transition region, where the homogeneous layer is becoming in a barrier layer until reaching a maximum local where the formation of barrier layer finished. The excess time is related to the formation of the TiO2 nanotubes array [8] Figure 1(b) shows that the obtained TiO2 nanotubes array has a homogeneous distribution in the surface, a regular size with an average diameter of 53.26 ± 14.54 nm and a smooth wall with a thickness of 13.64 ± 1.32 nm. The spectrum showed in figure 1(c) was obtained by EDS analysis of the surface of the sample. The two main constituents are titanium and oxygen, confirming the expected formation of TiO2 in the surface, the rest of the elements detected could be related to residues of the preparation and anodization solution. Due to the penetration of the high-energy beam used during the analysis, it can be said that the measure includes the nanotubes array and the first layer of the substrate, therefore the relation O/Ti give us a qualitative information of the surface oxidation of the samples. In this case, the O/Ti relation calculated in function of the atomic percent was 1.01.
To modify the crystal structure of the TiO$_2$ nanotubes from amorphous to anatase phase, a heat treatment was performed at 450 °C, during 12 hours in an air atmosphere. Figure 2(a) shows a top view of the heat treated nanotubes array, the average diameter of the tubes was 65.64 ± 8.26 nm and the wall thickness 13.64 ± 1.52 nm. The difference in the diameter of the tubes in comparison with the previously obtained value (without heat treatment) could be related to the difference in the density of the amorphous and anatase phases [9]. The side view of the nanotubes arrays denotes that the nanotubes array present an average length of 1.65 ± 0.04 μm and do not suffer physical damage during the treatment (figure 2(b)). In this case, the obtained O/Ti relation was 1.19 (figure 2(c)), indicating an incorporation of oxygen by atomic diffusion.

Figure 2. TiO$_2$ nanotubes array after heat treatment at 450 °C. (a) top view watching by SEM (b) side view watching by SEM (c) Elemental composition by EDS.

3.2. Anatase-rutile transformation model.
Our previous works [4,7] suggest that during the heat treatments at elevated temperatures, between 600 °C and 800 °C, the anatase-rutile transformation occurs simultaneously in the nanotubes wall and around the grain boundaries of the substrate. These processes could be explained by the following reactions:

$$\text{TiO}_2 \text{ (anatase)} \rightarrow \text{TiO}_2 \text{ (rutile) nanotubes walls}$$  \hspace{1cm} (1)

$$\text{Ti} + \text{O}_2 \rightarrow \text{TiO}_2 \text{ (rutile) grain boundary}$$  \hspace{1cm} (2)

Reaction (1) is thermally activated at over 600 °C [10] and its kinetic was theoretically explained by Shakibania [11] considering spherical nanoparticles. Reaction (2) occurs around the grain boundaries and is limited by the oxygen diffusion from the surface [12]. Assuming that both reactions could occur simultaneously, and no interference occurs between them we can calculate its influence in the transformation at the certain temperature during the time. Assuming that the nanotubes walls are composed by spheroid crystals of anatase figure 3(a) we can use the equation proposed by Shakibania [10] to obtain the fraction that has become rutile ($\alpha$).
\[ \alpha = 1 - \frac{\left(1+kt \frac{1}{m}\right)^3}{\left(1+\frac{k_1N_0}{k_2}\right)(e^{k_2t-1}+1)} \]  

Where \( t \) is the time in hours, \( m \) the particle size, and \( k_1N_0, k_2, \) and \( k \) are specific constants obtained for certain temperature [13]. Calculating the value of the constant at 650 °C and assuming that the particle size is equal to the wall thickness we obtained the transformation curve shown in figure 3. This transformation implies a reduction in the volume of the tubes, that is graphically described in the sequence showed in figure 3(a). Before the heat treatments the nanotubes have an amorphous structure, going through the anatase and ending in rutile structure. During the transformation from anatase to rutile, the nanotubes array is destroyed by network parameter changes.

![Figure 3](image_url)

**Figure 3.** Transformation of amorphous-anatase-rutile. (a) transformation profile of TiO\(_2\) nanotubes array (b) behavior of transformation through the time.

\[ C_{(y,t)} = 1 - \text{erf} \left( -\frac{y}{2\sqrt{D_{gb}t}} \right) \]  

Where \( y \) is the oxygen penetration depth in meters, \( D_{gb} \) is the diffusion coefficient in the grain boundary in m\(^2\).s\(^{-1}\) and \( t \) is the stay time in hours.

\[ D = D_0 e^{-\frac{Q}{RT}} \]  

To obtain the diffusion coefficient was necessary to apply the Arrhenius equation (3) suggest by Perez et al [14], where \( R \) is the ideal gas constant in kJ.mol\(^{-1}\).K\(^{-1}\), \( T \) is the temperature in Kelvin, \( D_0 \) and \( Q \) are constants obtained experimentally for the oxygen diffusion in titanium [13,15] The graphs shown in figure 4 compare the experimental O/Ti profile variation obtained by EDS analysis (figure 4 (a)) with the theoretical oxygen diffusion profile (figure 4 (b)), can be appreciated that both profiles shows same tendency.
Figure 4. Relation of diffusion of oxygen through the time. (a) experimental diffusion data obtain by EDS (b) 3D theoretical graphic with oxygen concentration, time and penetration

As a result of previously mentioned, the final model suggested can be seen in Figure 3(a) where the transformation of rutile is generated in the walls of the nanotubes and in the grain boundaries, the proportion and the penetration of this transformation vary respect to time in different proportions.

Conclusions.

TiO$_2$ nanotubes array synthesized by electrochemical anodization shows a homogenous morphology with respect to diameter, wall thickness, and length. The thermal treatments of titanium dioxide nanotubes array suggest oxygen diffusion. The evidence is provided by EDS spectrum where titanium anodized without heat treatment present a lower O/Ti relation than the samples with heat treatment. The anodic nanotubular layer does not change the morphology after applying the heat treatment at 450 °C at this temperature happens the anatase transformation. Anatase-rutile transformation at 650 °C depends on the oxygen concentration and the time of the heat treatment. At this temperature, the TiO$_2$ nanotubes with anatase phase are partially reconstructed and the rutile crystals are formed. The rutile transformation deforms the nanotubes array and change the network parameter, this transformation began in the grain boundaries of the titanium foil. So, the oxygen is the limit reagent because this element is the principal contributor to the transformation of the rutile phase. The mathematic model knows how much is transform from anatase to rutile from the grain boundaries and walls of TiO$_2$ nanotubes as well as the kinetics of this transformation. Highlighting the two different transformations, the first one is from TiO$_2$ anatase to TiO$_2$ Rutile on the nanotubes arrays and the second is the oxidation in the region near the grain boundaries bulk.

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