Scanning electron microscopy of heat treated TiO$_2$ nanotubes arrays obtained by anodic oxidation

D I Naranjo$^1$, S J García-Vergara$^1$ and S Blanco$^1$

$^1$ Universidad Industrial de Santander, Bucaramanga, Colombia

E-mail: siblanco@uis.edu.co

Abstract. Scanning electron microscopy was used to investigate the anatase-rutile transformation of self-organized TiO$_2$ nanotubes obtained on titanium foil by anodizing and subsequent heat treatment. The anodizing was carried out at 20V in an 1% v/v HF acid and ethylene glycol:water (50:50) electrolyte at room temperature. The anodized samples were initially pre-heat treated at 450°C for 4 hours to modify the amorphous structure of TiO$_2$ nanotubes into anatase structure. Then, the samples were heated between 600°C to 800°C for different times, in order to promote the transformation to rutile structure. The formation of TiO$_2$ nanotubes is evident by SEM images. Notably, when the samples are treated at high temperature, the formation of rutile crystals starts to become evident at the nanotubes located on the originally grain boundaries of the titanium. Thus, the anatase - rutile transformation has a close relationship with the microstructure of the titanium, more exactly with grain boundaries.

1. Introduction

TiO$_2$ nanotubes are a material whose architecture offers great internal surface area and their ordered nature makes them an excellent medium for the transference of electrons between the different interfaces on which it is desired to work [1]. In addition, TiO$_2$ is an oxide with unique properties including good photocatalytic behaviour, ability to detect some substances in the medium, biocompatibility and could be used for photocurrent generation [1,2]. The synthesis of TiO$_2$ nanotubes can be performed by different routes such as electrochemical anodization, sol-gel synthesis, hydrothermal treatment and vapor deposition [3-6]. However, it is the electrochemical synthesis that has allowed better manipulation of the process parameters to improve the characteristics of the final product [1,8]. The application of TiO$_2$ nanotubes is closely related to their crystalline structure (anatase, rutile or brucita) for this reason the understanding of the polymorphic transformations by post-anodized heat treatments has been explored widely [9-12]. The TiO$_2$ nanotubes obtained by anodizing are amorphous. The first transformation that takes place in the arrangement of nanotubes is from the amorphous structure to anatase. The anatase-rutile transformation takes place at temperatures between 600 to 900°C [13-15]. Regarding the transformation mechanism, Yu et. al. proposed a process of progressive transformation as a function of temperature, where rutile is initially formed at the metal-oxide interface at 600°C [13]. With the incrementation of the temperature to 700°C, the transformation occurs at the top of the nanotubes and finally the total transformation and collapse of the tubular structure occurs when the temperature rises to 900°C. On the other hand, Fang et al. suggested that the transformation starts at the metal-oxide interface at 600°C and progressively evolves from the base of the TiO$_2$ nanotubes to the upper part at 750°C [14]. Clearly, the phase
transformation processes are affected by the temperature and duration of the heat treatment, since its parameters affect the thermodynamics and the kinetics of the transformation. The present work studies the effect of these parameters on the morphology of the TiO$_2$ nanotubes arrays formed by anodizing in a fluoride containing electrolyte.

2. Experimental

2.1. Sample preparation
TiO$_2$ nanotubes arrays were obtained by anodizing of commercially pure titanium foil with a surface area of 4cm$^2$. The titanium samples were polished with alumina paste to obtain a mirror-like surface finish. Subsequently, the specimens were washed with bi-distilled water and cleaned in ethanol using an ultrasonic bath for 15min. The anodizing was carried out at 20 V in an electrolyte comprising 1% v/v HF acid and ethylene glycol:water (50:50) for 90min at room temperature. The anodizing was performed in a cell with two (2) electrodes, where the titanium samples acting as the anode and a platinum wire as the cathode in a DC VOLT power supply GP5003.

2.2. Heat treatment
The anodized samples were initially pre-heat treated at 450°C for 4h in order to modify the amorphous anatase structure of TiO$_2$ nanotubes. The pre-heat treatment was done to ensure that subsequent heat treatments only promoted anatase - rutile transformation. Then, the anodized and pre-heat treated samples were heated to 600, 650, 700 and 800°C for 40, 60, 120, 180, 240, 300, 360, 420 and 480min, in order to study the anatase-rutile transformation. The heat treatments were performed in a STableTemp Coler Parme furnace using an oxidizing atmosphere.

2.3. Characterization of the coatings
The morphology of TiO$_2$ nanotubes arrays obtained by anodizing and modified with subsequent heat treatments was characterized using a QUANTA 650 FEG-ESEM scanning electron microscope, operated at 25kV.

3. Results and discussion

3.1. SEM evaluation of morphology changes promoted by heat treatment
Figure 1 shows a homogeneous distribution of the TiO$_2$ nanotubes arrays formed by anodizing along the surface. The nanotubes have an average diameter of 100nm and a length between 300 and 400nm.

![Figure 1](image)

**Figure 1.** Scanning electron micrographs of titanium anodized in 1% v/v HF+(50/50% v/v) water/ethylene glycol electrolyte at 20V for 90min. (a)-(b) Surface and (c) Cross-section.

In our previous work [16] we confirm by SEM analysis that after heat treatment of the anodized samples at 450°C the morphology of the TiO$_2$ nanotubes arrays does not change compare with the
samples without heat treatment. Further, the heat treatment time does not affect the original morphology. At this temperature the amorphous TiO$_2$ generated by anodizing is transformed into anatase. When the calcination temperature increases to 800ºC, the nanotube arrays are completely destroyed and only dense rutile crystallites with size largest 100nm are observed [13]. The collapse of the tubular structure occurs because the anatase-rutile transformation is reconstructive, originating the rupture and reform of the bonds. The network parameters of the tetragonal crystalline network of the rutile are larger than the network parameters of the tetragonal crystalline network of the anatase [17].

![Image](image1.png)

**Figure 2.** Scanning electron micrographs of titanium anodized in 1% v/v HF+(50/50% v/v) water/ethylene glycol electrolyte at 20V for 90min, with or without heat treatment (HT) at 650ºC. (a) No HT, (b) HT for 60min and (c) HT for 480min.

The evolution of the anatase-rutile transformation was studied from the morphological changes of the TiO$_2$ nanotubes arrays after heat treatment at 650ºC. Figure 2(a) shows a homogeneous nanotube array before annealing. Figure 2(b) reveals a localized variation of the nanotube array in the shape of interconnected lines after 60min of heat treatment, which contrasts with a structure of collapsed nanotubes (Figure 2(c)), due to the reconstruction of its crystalline structure from anatase to rutile after of 480min of heat treatment. When comparing the pattern generated by the union of these interconnected lines, with the microstructure of the substrate, it is observed that these patterns are related with grain boundaries. This may suggest that the anatase-rutile transformation is favoured at the grain boundaries of the substrate.

![Image](image2.png)

**Figure 3.** XRD patterns of titanium. Pure titanium without anodizing (a), titanium anodized in 1% v/v HF+(50/50% v/v) water/ethylene glycol electrolyte at 20V for 90min (b), titanium anodized as (b) and pre-heat treated at 450ºC for 4 hours (c), titanium anodized as (b) and heat treated at 600ºC for 4 hours and titanium anodized as (b) and heat treated at 700ºC for 4 hours.

In order to support the above statement, regarding the appearance of rutile crystals in the TiO$_2$ nanotube array when subjected to different heat treatment times at 650ºC, the X-ray diffractogram obtained for anodized and pre-heat treated samples at different conditions is presented in Figure 3. The
anatase - rutile transformation is confirmed above 450°C, as the signal corresponding to the anatase phase decreases as the signal of the rutile phase increases with increasing temperature.

3.2. Proposed evolution model

Based on the sequence of morphological changes that were evidenced at different times of heat treatment at 650°C on the TiO₂ nanotubes arrays obtained by anodizing, a mechanism for the anatase-rutile transformation is proposed from the analysis of the images obtained by SEM (Figure 4).

In the initial phase of heat treatment, a variation in morphology of the nanotubes array occurs preferentially in those located at the grain boundaries of the substrate (Figure 4(a)-(b)). This morphological variation is associated with the appearance of the first rutile crystals. As the heat treatment time increases, rutile crystals appear on the TiO₂ nanotubes located within the areas demarcated by the grain boundaries (Figure 4(c)-(d)), being clearly evident at 420 min of treatment (Figure 4(e)-(f)). After 480 min the anatase-rutile transformation reconstructs the morphology of the TiO₂ nanotubes arrays obtained by anodizing, shifting from amorphous TiO₂ nanotubes to rutile crystals [9,13,14].

Figure 4. Scanning electron micrographs of titanium anodized in 1% v/v HF+(50/50% v/v) water/ethylene glycol electrolyte at 20V for 90 min and then heat treated to 650°C for different times. (a)-(b) 60 min, (c)-(d) 360 min and (e)-(f) 420 min.

Previous observations can be schematically represented in a 3-stage model presented in Figure 5.

a. Start of the anatase-rutile transformation on the TiO₂ nanotubes located at the grain boundaries of the substrate.

b. Progress of the anatase-rutile transformation on the TiO₂ nanotubes located inside the grains of the substrate.

c. Collapse of nanotubular structure and formation of rutile microcrystals.
Figure 5. Schematic diagram of the proposed evolution model for anatase-rutile transformation in TiO$_2$ nanotubes at 650°C.

4. Conclusions
The thermal treatments of TiO$_2$ nanotubes arrays provided evidence that not only the crystal structure is modified with temperature, but also changes in the morphology of the anodic nanotubular layer. When the temperature does not exceed 450°C morphologically changes are not observed, but amorphous-anatase transformation is presented. At 650°C anatase and rutile phases are observed. This transformation is associated with a change in the network parameters, which generated degenerative morphological changes at the grain boundaries of the substrate. At higher temperatures, the TiO$_2$ undergoes a nearly complete transformation and the nanotubes are completely destroyed and well-defined rutile crystals are observed.

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