Characterization of titanium oxide nanotubes growth through anodization in organic solvents

K A Lopez-Jaime¹, D Y Peña-Ballesteros¹,², and A Sandoval-Amador³,⁴
¹ Grupo de Investigaciones en Corrosión, Universidad Industrial de Santander, Bucaramanga, Colombia
² Centro de Materiales y Nanociencias, Universidad Industrial de Santander, Bucaramanga, Colombia
³ Foundation of Researchers in Science and Technology of Materials, Bucaramanga, Colombia
⁴ Instituto de Física Arroyo Seco, Universidad Nacional del Centro de la Provincia de Buenos Aires, Tandil, Argentina

E-mail: anderson84f@gmail.com

Abstract. The titanium oxide nanotubes have generated great interest in recent years because of the wide variety of applications in which they are used. The reason for this is the excellent surface properties that this material gets after of grow in the anodizing process. These properties can easily modify the electrochemical anodizing process. For this reason, we have analyzed the effect of electrolyte on the morphology and corrosion resistance of titanium oxide nanotubes grown at glycerol with 0.3% w/w ammonium fluoride and 2% v/v distilled water at 30 volts for 1 hour and ethylene glycol with 0.3% w/w ammonium fluoride and 2% v/v distilled water at 40 volts for 30 minutes. The morphology of the surfaces is observed by scanning electron microscopy. The resistance to corrosion of the samples is evaluated by potentiodynamic polarization curves in Hanks solution at 37 °C. The results of the nanotubes grew in glycerol have a length of 0.7 μm with a morphology of the bamboo type, while the nanotubes grown in ethylene glycol have a length of 3.3 μm and their morphology is smooth wall. Regarding the corrosion rate, it was determined that the nanotubes grown in glycerol have a higher corrosion rate. Because to these low corrosion rates it is considered that the two surfaces can be used as alternatives to modify orthopedic implant materials.

1. Introduction
Titanium (Ti) and Ti alloys have been used extensively in dental and orthopaedic implants [1]. Recently, increasing research efforts in metallic biomaterials have been invested for applications in non-conventional reconstructive surgery of hard tissues/organs, such as the application of shape memory alloys as vascular stents [2]. Despite their outstanding properties, the application of titanium-based implants is still limited as they are unable to meet all the clinical requirements. Therefore, various surface modification techniques have been used to improve their performance [3-6].

The naturally formed titanium oxide layer provides the desired inertness and biocompatibility [7]. However, this layer is easily damaged and produces the release of undesirable ions in the biological media [8-9]. One of the ways to achieve this has been through the accelerated growth of a nanostructured titanium oxide layer on the surface of metal implants to improve their biomedical effects [10-11].

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This surface modification for orthopaedic implants is usually performed by electrochemical anodization, where self-organized nanotubular oxide configurations can easily be created and controlled by changing the anodization conditions [12-13]. This nanoscale modification has been demonstrated to enhance protein adsorption and cell-implant interaction, and to improve osteoblast proliferation compared with the commercial surface treatments currently employed in implants [14].

Like so the biocompatibility of titanium alloys results from a thin titanium oxide layer that is present on the metal surface. The corrosion resistance of the surface oxide layer’s is influenced by the material’s composition and by the parameters employed during the anodization process [15-17].

For this reason, in this work, the aim is analysing the effect of electrolyte on the morphology and corrosion resistance of TiO2 nanotubes grown on Ti6Al4V alloy surfaces.

2. Methodology

In this investigation, Ti6Al4V ELI alloy discs with 13 mm diameter and 3 mm of thickness were used. The sample was polished by standard silicon carbide papers of different number from 120 to 1200 (3M). Then, the samples were rinsed by distilled water and dried in the air.

Before the anodization all samples were pre-etched in an acidic mixture HF: HNO3: H2O (1:3:10) for 30s and rinsed with distilled water and cleaned by sonication in ethanol for 15 minutes.

The electrochemical anodization process was performed in a custom-built electrochemical cell having two electrode configurations. For all experiments the distance anode-cathode was 20 mm. Two anodized conditions were used, in the first case an electrolyte solution of glycerol with 0.3% w/w NH4F and 2% v/v H2O was used. For this process the apply voltage was 30V for 1 hour and the cathode employing was a platinum mesh with magnetic stirring at 300 rpm [18]. In the second case the electrolyte solution was ethylene glycol with 0.3% w/w NH4F and 2% v/v H2O. The apply voltage was 40V for 30 minutes and using a copper mesh without agitation [19]. Electrolyte was prepared from reagent grade chemicals (Merck) and deionized water. Experiments were carried out at room temperature. All the anodized specimens are rinsed in an ultrasonic bath of 15 minutes in distilled water and then 15 minutes in ethanol, finally they are placed in an oven at 100 °C for 20 minutes for the drying process.

The surface and cross-sectional morphology of the anodized TiO2 nanotube layers were investigated by field emission scanning electron microscopy (FE-SEM, JEOL Quanta FEG 650).

The equipment used for electrochemical measurement consisted of a three electrodes cell, a computer controlled potentiostat/galvanostato Gamry PCI 4-750. A graphite high purity rod was used as a counter electrode and Ag/AgCl (3M KCl) as reference electrode. Hanks solution was used as electrolyte. The potentiodynamic polarization behavior of the samples was performed applying a scan from -500 mV to +2500 mV (versus open circuit potential) at a scanning rate of 1 mV/s. All the electrochemical experiments were carried out at 37°C to simulated body conditions.

3. Results

Figure 1 shows the behavior of the current versus time transients obtained after the anodizing process of the Ti6Al4V samples in organic electrolytes of ethylene glycol and glycerol respectively. As can be seen, the curves show the typical behavior of the growth process of titanium oxide nanotubes reported in the literature [20]. It is also possible to observe that the ethylene glycol anodizing process causes the highest current peak 163 mA, so it is expected that it will achieve a denser barrier layer than that obtained in the anodizing process with glycerol, which achieved a maximum of 10.3 mA current in the first two seconds. [21-22].

The morphological characterization of the TiO2 nanotubes was carried out by scanning electron microscopy and can be seen in Figure 2. There it can be seen that the layer of nanotubes grown in Ethylene glycol (Figure 2(a)) has a non-homogeneous surface morphology with highly nanotubes. Disordered, however the cross section of this layer reveals a morphology of smooth wall nanotubes. On the other hand, the layer grown in glycerol (Figure 2(b)) has a well-defined surface morphology, with spaced and partially organized nanotubes. However, its cross section reveals a bamboo-like morphology.
which is associated with the formation of oxygen bubbles during the nanotube formation process. The morphological parameters of greater interest in this type of nanostructures are summarized in Table 1.

Figure 1. Current transient recorded during anodization of Ti6Al4V alloy in organic electrolytes.

Figure 2. FESEM images of TiO$_2$ nanotubes anodized in (a) Ethylene glycol with 3% w/w N$_4$HF and 2% v/v H$_2$O for 1 hour at 30 V and (b) Glycerol with 3% w/w N$_4$HF and 2% v/v H$_2$O for 30 minutes at 40 V.

Table 1. Morphological parameters of TiO$_2$ nanotubes grown in organic electrolytes

| Sample       | Pore Diameter (nm)  | Wall Thickness (nm) | Tube Length (µm) |
|--------------|---------------------|---------------------|-------------------|
| ethylenglycol| 64.0 ± 11.06        | 33.0 ± 10.23        | 3.21 ± 0.11       |
| glicerol     | 85.16 ± 13.99       | 27.37 ± 5.55        | 0.59 ± 0.02       |

Figure 3 shows the polarization curves for the Ti6Al4V alloy with nanotubes grown in ethylene glycol and glycerol. It can be observed how the anodic branches show an active -passive transition in all cases. The sample of nanotubes grown in glycerol electrolyte has the most noble corrosion potential with respect to the pure alloy and the sample with nanotubes grown in ethylenglycol. On the other hand, the nanotubes grown in ethylenglycol have lower current density than the nanotubes grown in glycerol, which represents a lower corrosion rate for these first ones, which indicates a protective nature, thus giving a better performance in corrosion processes [23-24]. The resultant corrosion potential
(E$_{\text{corr}}$), corrosion current density (I$_{\text{corr}}$), and corrosion rate are summarized in Table 2, where E$_{\text{corr}}$ represents the substrate’s tendency to corrode and I$_{\text{corr}}$ represents the protection efficiency [25].

![Figure 3. Potentiodynamic polarization curves obtained for the TiO$_2$ nanotubes grown in organic electrolytes.](image)

| Sample          | E$_{\text{corr}}$ (V) | I$_{\text{corr}}$ (A cm$^{-2}$) | Corrosion Rate (mpy) |
|-----------------|------------------------|---------------------------------|----------------------|
| Ti6Al4V         | -0.053                 | 2.09E-08                        | 6.89E-09             |
| Ethylene glycol | -0.197                 | 4.68E-08                        | 1.54E-08             |
| Glycerol        | -0.012                 | 2.27E-07                        | 7.50E-08             |

This difference in corrosion speed can be attributed to the fact that, as shown in the SEM images, the length of the nanotubes grown in ethylene glycol is less than that of the nanotubes grown in glycerol and the diameter of the latter is greater, thus allowing for a greater direct attack to the metallic substrate.

4. Conclusions
The mechanism of the growth of TiO$_2$ nanotubes becomes an ethylene glycol work represents the most effective process to develop a TiO$_2$ nanotube film with good corrosion resistance at low cost. These properties can be attributed to the low energy consumption observed in the current versus time curve. It is also due to the good corrosion resistance of the nanotubes layer, so this surface is the most recommended for orthopaedic materials applications.

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