Porous titanium dioxide coatings obtained by anodic oxidation for photocatalytic applications

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Abstract

The aim of this work is to obtain porous titanium dioxide with good efficiency for photocatalytic environmental applications. TiO₂ coatings were obtained by anodic spark deposition, at constant applied potential (150 V), using a platinum cathode and 0.5 M sulfuric acid as electrolyte. Samples of titanium Grade 2 were used as substrate, metallographically prepared until 1 μm diamond surface finishing. The variables of the process were temperature (25 and 40 °C) and anodization time (5 and 10 min). Samples obtained at 40 °C showed a higher current density than those obtained at 25 °C and the potential reached by these samples was lower than those obtained at 25 °C. These results are attributed to an increased electrolyte conductivity. Optical microscopy images of the oxides obtained at 40 °C showed heterogeneity in color, indicating a non-uniform oxide thickness. This coincides with the images obtained by scanning electron microscopy that revealed “valleys” where the material did not present porosity. On the other hand, the oxides obtained at 25 °C showed a complete homogeneous porous structure. The average pore diameter was reduced with the increased oxidation time and temperature of the electrolyte. An increase of the crystalline anatase phase was observed with an increase of the anodization time; besides, rutile formation was observed, probably due to the final potential achieved by the samples.

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1. Introduction

Heterogeneous photocatalysis is an advanced process used in water treatment, useful to purify wastewaters or drinking water, and widely developed in the last 30 years (Fujishima and Zhang (2006), Malato et al. (2009), Litter and Quici (2010)).

In this process, a semiconductor in contact with a fluid (liquid or gaseous) is irradiated with light of energy equal to or higher than its band-gap and; as a result, electrons are promoted from the conduction band (CB) to the valence band (VB), creating electron-hole pairs that induce redox reactions in the fluid. Consequently, changes in the chemical structure of a pollutant, usually mineralization, are possible (De Lasa et al. (2005), Litter (2005)). Because most of the reactions take place on the semiconductor-fluid interface, the use of materials with high surface area has particular interest.

Titanium dioxide (TiO₂) is the most used photocatalyst due its low cost, chemical and thermal stability, low toxicity and relative high catalytic activity, especially of its crystalline anatase phase. Several papers report reactions mechanisms, chemical kinetics and details on the photocatalytic efficiency of this oxide for removal of pollutants (Legrini et al. (1993), Hoffmann et al. (1995), EPA (1998), Munter (2001), Blesa and Cabrero (2004), Litter (2009), Chong et al. (2010), Litter and Quici (2010), Levy et al. (2012), López Loveira et al. (2012)). If the semiconductor is coated on a suitable surface, the expensive separation step of the semiconductor from a liquid phase can be avoided; on the other hand, the coating is indispensable for the use of the material on gas phase reactions.

The preparation of TiO₂ coatings can be made by different techniques, such as anodic plasma-chemical treatment, sol-gel process, anodic oxidation under potentiostatic or galvanostatic mode, thermal oxidation, etc. (Kuromoto et al. (2007)). In the present work, TiO₂ was prepared by a potentiostatic anodic oxidation, which is one of the most simple and economic methods. In this process, redox reactions are induced by direct current flow between an anode and a cathode immersed in an electrolyte. The variables that affect the characteristics of the synthesized oxide (morphology, chemical composition, thickness and crystal structure) are concentration, pH and temperature of the electrolyte, cell potential, anodization time and current density (Sul et al. (2001), Diamanti and Pedeferri (2007), Song et al. (2009), Vera et al. (2009), Vera et al. (2010), Vera et al. (2014)).

Previous research shows that the use of cell potentials higher than 100 V during the anodic oxidation process results in porous oxides due to the formation of sparks or electric arcs. The process begins where the preexisting oxide is mechanically weak, and the dielectric breakdown allows the establishment of an arc between different points of the coating, resulting in the local increase of current densities and temperature (close to 8000 °C) and leaving pores where the arc was formed. This is an alternative to the anodic oxidation technique, called anodic spark deposition, whereby porous coatings are obtained; using this technique the oxides can reach a thickness of several microns and allows to synthesize crystalline oxides (Diamanti and Pedeferri (2007), Song et al. (2009)).

The aim of this study was to obtain porous TiO₂ coatings by anodic spark deposition, with the purpose of their application in photocatalytic processes.

2. Material and methods

2.1. Substrate preparation

Commercial pure titanium, Grade 2 according to ASTM B367 classification (3 cm × 2 cm × 0.2 cm), was used as the substrate; composition is shown in Table 1. The substrate was mechanically polished with SiC abrasive papers from # 120 to # 1500, followed by the use of diamond paste of 1 micron (Praxis) lubricated with ethylene glycol (Cicarelli) for 30 minutes in a polishing machine (250 rpm). After that, the substrates were cleaned with detergent and water, sprayed with alcohol and finally dried with hot air.

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Fe</th>
<th>H</th>
<th>N</th>
<th>O</th>
<th>Ti</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition (%)</td>
<td>&lt;0.1</td>
<td>&lt;0.3</td>
<td>&lt;0.015</td>
<td>&lt;0.03</td>
<td>&lt;0.25</td>
<td>99.2</td>
</tr>
</tbody>
</table>
2.2. Anodic spark deposition

Anodic oxidation of the substrate was performed on spark conditions, at a constant applied potential of 150 V, using a platinum cathode located at 5 cm from the titanium anode and 0.5 M sulfuric acid (Cicarelli) as the electrolyte. The variables of the process were temperature (25 and 40 ºC) and time (5 and 10 min), which allowed to obtain oxides under four different conditions (see Table 2). After oxidation, the samples were cleaned with water, sprayed with alcohol and finally dried with hot air.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Temperature (ºC)</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T25t5</td>
<td>25</td>
<td>5</td>
</tr>
<tr>
<td>T25t10</td>
<td>25</td>
<td>10</td>
</tr>
<tr>
<td>T40t5</td>
<td>40</td>
<td>5</td>
</tr>
<tr>
<td>T40t10</td>
<td>40</td>
<td>10</td>
</tr>
</tbody>
</table>

During the process, the cell potential and the current density were recorded to follow the evolution of these parameters.

2.3. Characterization of the samples

The surface of obtained oxides was observed by optical metallographic microscopy (Arcano 616®) and by a scanning electron microscopy (SEM, FEI, Quanta 200®). Topography and morphology of the oxides were analyzed. Using the Image J software, the mean diameter of the pores was determined as the average of 50 measurements made at pores in horizontal and vertical direction. The crystalline structure of oxides obtained at 40 ºC was identified by the glancing incidence X-ray diffraction (GI-XRD) technique with a glancing angle of 1° (Panalytical, Empyrean).

3. Results and discussion

3.1. Cell potential and current evolution

The cell potential evolution for the T25t10 and T40t10 samples is shown in Fig. 1. In the case of oxides obtained at 25 ºC, the cell potential increases faster than in the case of those prepared at 40 ºC. This result is consistent with those obtained by Sharma (1992), who attributed this behavior to an increase of the electrolyte conductivity due to the increase of temperature. In Fig. 2, the current density curves obtained during the anodic oxidation process are presented.

Figures 1 and 2 show a behavior characteristic of a constant potential growth of an anodic oxide. Formation and thickening of the oxide layer as a result of a balance between dissolution reactions described by the point defect model (Macdonald (2011), Vera (2013)) and the anodic film growth produce a gradual increase in the resistance to current flow, which generates a progressive decrease in the current density and a gradual increase in the cell potential value. Similar results were reported by Zwilling et al. (1999), indicating that the thickness of the porous oxide layer is increased with the anodization time up to an equilibrium value.
Fluctuations of cell potential and current density values observed in Figs. 1 and 2 would be the result of a substrate-oxidation-breaking cycle that occurs during anodic spark deposition (Vera (2013)).

An increase in the electrolyte temperature produces an increase in the current density (Fig. 2), consistent with the cell potential curves (Fig. 1), which can be attributed to an increase in the electrolyte conductivity with temperature (Sharma (1992)).

The experiments showed a good repeatability; the cell potential and current density curves of the substrates oxidized for 5 min were overlapped to those oxidized for 10 min, and are not presented in the preceding figures.

3.2. Optical microscopy

Micrographs of the obtained oxides taken with a metallographic optical microscope are shown in Fig. 3. The optical microscopy images of the oxides obtained at 40 °C present heterogeneity in color, indicating a non-uniform oxide (Capek et al. (2008)), while those oxidized at 25 °C have a more uniform color.
3.3. Scanning electron microscopy

The SEM images of the oxides (Fig. 4) show pores observed in darker gray, distributed over the entire surface. The shape of the pores with the highest edges, crater-type morphology, could be an evidence of gas evolution. A related experimental observation is that, in all the experiments, bubbles appeared over the platinum cathode, and, increasing the voltage, a constant bubbling of oxygen began to appear on the anode surface during the formation of the oxide. In this regard, Teh et al. (2003) suggest that the evolution of oxygen bubbles is responsible for the generation of defects sites, among which the arc is then established.

Consistent with the results of the optical micrographs, the samples oxidized at 40 °C show "valleys", where the material did not show porosity and the thickness of the oxides was lower (Capek et al. (2008)). Furthermore, the oxides obtained at 25 °C show a complete homogeneous porous structure.

The average pore diameter obtained from the SEM images for each sample is presented in Table 3.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Average diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T25t5</td>
<td>114</td>
</tr>
<tr>
<td>T25t10</td>
<td>100</td>
</tr>
<tr>
<td>T40t5</td>
<td>81</td>
</tr>
<tr>
<td>T40t10</td>
<td>72</td>
</tr>
</tbody>
</table>

Values observed in Table 3 indicate that the average pore diameter is reduced by increasing the electrolyte temperature and the anodization time. This behavior is consistent with that found by Yetim (2010), who noted that the decrease in temperature results in oxides with larger pore diameter. This is complemented by Gabe (2002), who pointed out that the increase in the temperature at which the oxide is obtained produces materials with lower density and hardness.
3.4. X-ray diffraction

For photocatalytic processes, TiO$_2$ materials with a crystalline structure are desirable, especially with a high anatase:rutile ratio because of the higher photocatalytic activity of the anatase phase. Diffractograms of samples obtained at 40 °C are shown in Fig. 5.

![Fig. 5. Diffractograms of T40t5 and T40t10 samples.](image-url)
An increase of the crystalline anatase phase was observed with an increase of the anodization time, besides the formation of rutile, probably not as a direct effect of the anodization time but to the final potential achieved by the samples, as shown by Yang et al. (2004) and Diamanti and Pedeferri (2007).

4. Conclusions

It can be anticipated that the synthesized porous TiO$_2$ coatings have favorable characteristics as materials with potential application in photocatalytic processes due to their high porosity and the presence of a crystalline anatase phase in the samples. This research will be supplemented by testing the microhardness and the photocatalytic activity to determine the optimal synthesis parameters.

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