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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. TiO_2 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 ºC 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.

Keywords: Anodic oxidation; Titanium dioxide; Sulfuric acid.

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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 (TiO_2) 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 TiO_2 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, TiO_2 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 TiO_2 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 1. Titanium Grade 2 composition

Element	**C**	**Fe**	**H**	**N**	**O**	**Ti**
Composition (%)	<0.1	<0.3	<0.015	<0.03	<0.25	99.2