NANOSTRUCTURED TITANIA FILMS PREPARED BY PI-MOCVD

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ABSTRACT
In the present work, titania films deposited on stainless steel substrate were prepared by pulsed liquid injection MOCVD; titanium isopropoxide was used as precursor and Ar as carrier gas, the substrate temperature was fixed in 600 °C. On the other hand, titania nanoparticles deposited on the hot-wall of the reactor were characterized. The materials were characterized by X-ray diffraction (XRD), transmission electron microscope (TEM), scanning electron microscope (SEM) and energy dispersive X-ray analysis (EDAX). Results obtained revealed that the films are constituted by titania with highly oriented anathase phase in the (200) direction and on the other hand, the particles collected in the reactor wall presented a range from 50 to 100 nm in size with a low intensity X-ray diffraction peaks of anatase phase.
The average particle size.

Keywords: Ceramics-thin-films; MOCVD; Titanium-isopropoxide; Nanostructure; titania.

PELÍCULAS DE TITANIA NANOESTRUCTURADA PREPARADAS POR PI-MOCVD

RESUMEN
En el presente trabajo, películas de titania depositadas en sustratos de acero inoxidable fueron preparadas por inyección líquida pulsada MOCVD; isopropoxido de titanio se usó como precursor y Ar como el gas de arrastre, la temperatura del sustrato se fijó en 600 °C. Por otro lado, se caracterizaron nanopartículas de titania depositadas en la pared caliente del reactor. Los materiales se caracterizaron por difracción de rayos X (XRD), microscopía de electrónica de transmisión (TEM), microscopía del electrónica de barrido (SEM) y análisis de energía dispersiva de rayos X (EDAX). Los resultados obtenidos revelaron que las películas están constituidas por titania altamente orientada de fase anatasa en la dirección (200) y por otro lado, las partículas recolectadas en la pared del reactor presentaron un rango de 50 a 100 nm en el tamaño con picos de difracción de rayos X de baja intensidad de fase anatasa.

Palabras claves: Películas-delgadas-cerámicas; MOCVD; Isopropóxido de titanio; nanoestructura; Titania.

INTRODUCTION

Titania (TiO_2) has applications in many areas: as catalyst, as photocatalyst, as gas sensor, in electrical, optical and optoelectrical applications, etc. On the other hand, this oxide has been considered responsible for the good biocompatibility with bone and excellent resistance to corrosion processes. Particularly, the passive oxide layer, often defined as an inert ceramic biomaterial grows slowly on the surfaces of titanium implants and contributes to the formation of apatite and bone-like tissue, thus allowing the onset of favorable cellular reactions [1-3]. Thus, various deposition techniques have been developed for depositing TiO_2 thin films, including evaporation, sputtering, thermal oxidation of titanium and the chemical vapor deposition CVD method. Among them, the CVD technique using metal-organic compound as a precursor, metal-organic chemical vapor deposition; (MOCVD) has many advantages, such as good conformal coverage, the possibility of epitaxial growth and selective deposition and the application to large area deposition. Also, this method is low cost and it is easy to control the deposition growth parameters. Thus the

MOCVD method is well known as one of the most powerful techniques and is suitable for stoichiometric and microstructural thin film deposition [4-8]. In the CVD process of titania, many different precursors, e.g., $TiCl_4$ and titanium alkoxides, have been used. The alkoxides have been preferred as the vapor pressure is fairly high and the deposition process can be carried out at rather low temperatures. Also, there is no risk of chlorine contamination in the deposit [9-11]. In this work, deposition on steel 316 of titania films was carried out by innovative pulsed liquid injection MOCVD technique (PI-MOCVD) . This technique is based on repetitive injections of microdoses of solution of a volatile precursor, flash evaporation, vapour transport by a carrier gas and decomposition on a hot substrate, the reactant and carrier gas that flows through the reaction chamber are regulated by means of electronic mass flow controllers. One advantage of liquid injection CVD over classical CVD is that it places less demands on the precursor in terms of volatility and stability [12-13].

MATERIALS AND METHODS

Deposition of titania films was carried out by pulsed liquid injection MOCVD (PI-MOCVD). Prior to the deposition, the surfaces of the substrates were cleaned by acetone. Thus, pieces (1x1 cm) of a steel 316 were used as substrates, fixed to the holder by a DUPONT 4929 conductor paste. Titanium (IV) isopropoxide liquid ($Ti(OC_3H_7)_4$; 99.9 %, Aldrich Chemical) was used as precursor, the solution container was kept at room temperature during the injection process. The pressure in the system was kept at 10 Torr with the Ar gas as the carrier. The substrate temperature was set at Ts=600 °C (central part of the reactor). Temperatures in the evaporation zone and along the vapor transport line were Te=Tv=280 °C. The injection frequency was computer-controlled at tI=0.5 s. The initial volume of the solution was 30 ml, it was finished once the solution container was completely empty, with a micro-dose of 6.25 x 10^{-3} ml per pulse.

The titania oxide film deposited on steel was smooth and shiny, with a light brown hue, free of pin-holes, strongly adherent and showed no apparent peeling on substrate. On the other hand, white TiO_2 powders were deposited on the wall of the reactor (quartz tube), which were characterized separately.

A Low Vacuum Scanning Electron Microscopy (SEM-LV) and Energy dispersive X-ray Analysis (EDAX) were performed using a JEOL JSM 5900LV equipped with an Oxford X-ray microprobe to analyze the surface composition and morphology of the samples. X-ray diffraction studies were performed using a Siemens D5000 diffractometer with CuKα radiation. Characterization by Transmission Electron Microscopy was conducted on a JEOL-1010 TEM, at a voltage of 200 kV.

RESULTS AND DISCUSSION

A complete exploratory study achieved by SEM to the titania films shown no serious morphological differences among the different films. The SEM micrograph in Figure 1 shows the morphology of the film, the films have a uniform surface morphology, with faceted grains present throughout.

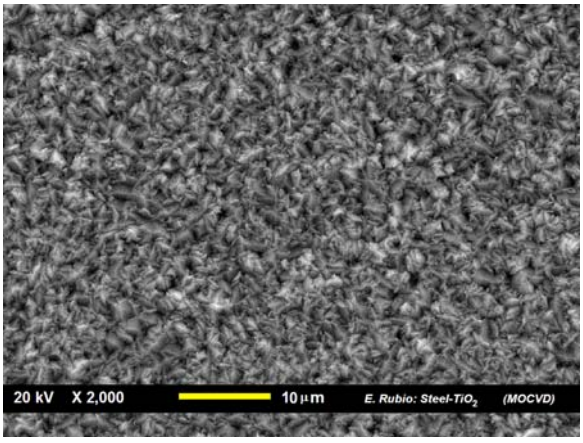

Fig. 1. Scanning electron micrograph of the surface of the film produced on steel 316 substrates at 600 °C.

The faceting observed is characteristic of preference to the orientation in the materials. With a mayor magnification in the same zone (fig. 2), it is possible to appreciate a rough surface composed by nanoparticles joined each other and aligned forming a film highly oriented and crack- free.

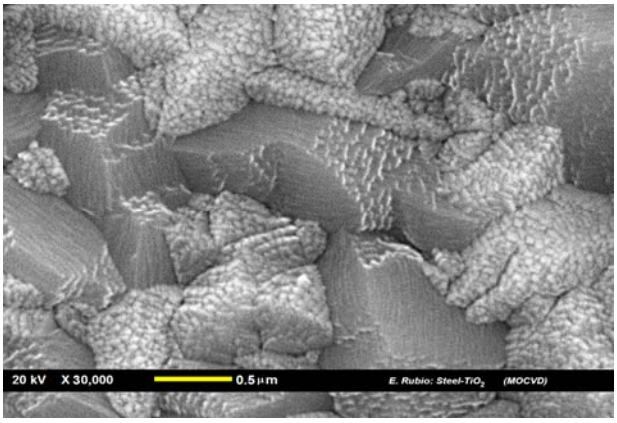

Fig. 2. Scanning electron micrograph of the surface of the film produced on steel 316 substrates at 600 ^{o}C.

The energy for surface diffusion increases, as does the growth rate, resulting in more rapid lattice incorporation on low energy crystal planes.

The chemical composition of the coatings was determined by X-ray microanalysis, the point analysis of the film was carried out and the characteristic X-ray spectrum was obtained (Fig. 3).

Only Ti and O were detected in a ratio of Ti:O of 1:2. This result indicates that the film consisted of TiO_2.

A great quantity of material was not deposited on the substrate but spread out in the inlet and outlet of the hot chamber of the reactor wall. TEM analyses were made with this material. Thus, Figure 4 a–b shows TEM bright field images, samples show aggregated particles with semispherical shape. From the figure 4-a, we can see that the primary particle size is 20-50 nm in the case of particles collected in the inlet of the chamber reactor. The average particle size increased slightly from 50 to 100 nm in the particles collected in the outlet of the chamber reactor (fig. 4-b).

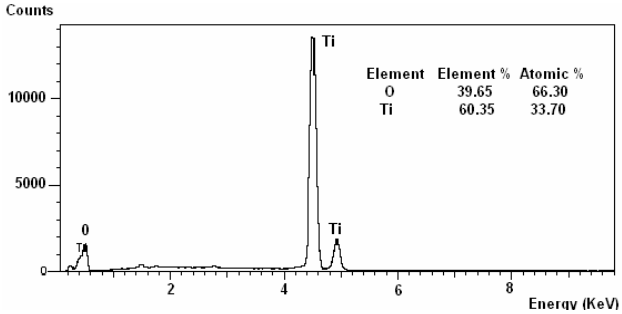

Fig. 3. Energy dispersive X-ray Analysis of the surface of the film produced on steel 316 substrates at 600 ^{o}C.

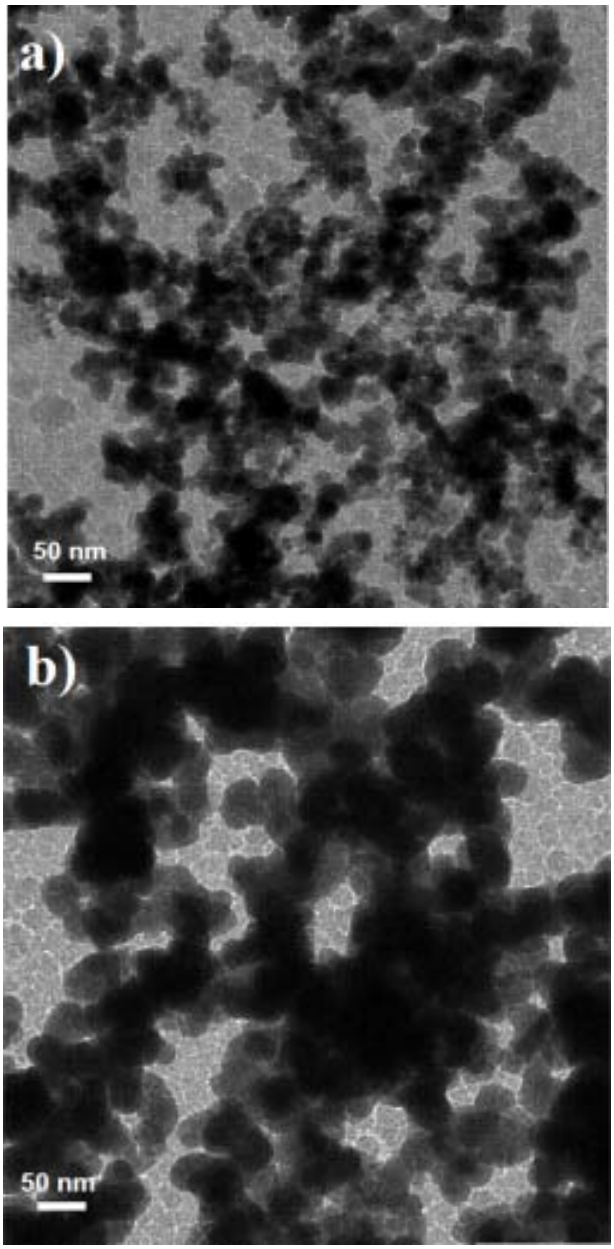

Fig. 4. TEM image of dendritic TiO_2 nanoparticles deposited in the a) inlet and b) outlet of the reactor chamber wall.

The XRD pattern of the titania film reveal only the anatase phase (Fig.5), with a strong reflection corresponding to the (200) planes, clearly stronger than the (101) reflection. Bragg reflection of (105) planes are also stronger than the (101).

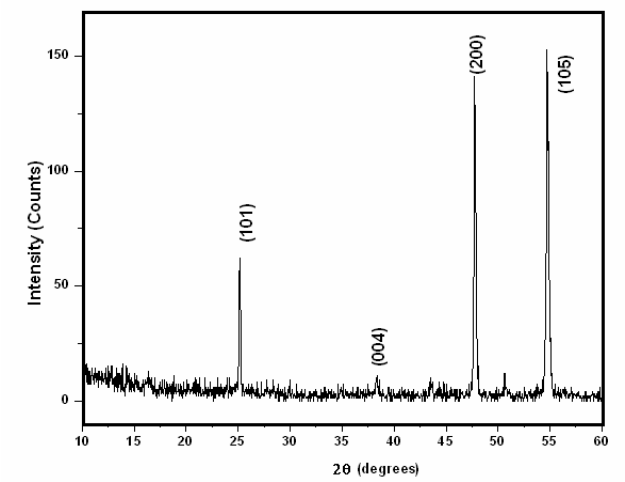

Fig. 5. XRD pattern of the titania film deposited on steel 316 at 600 °C.

Fig. 6 is a XRD pattern for TiO_2 nanoparticles collected on reactor wall. The low intensity diffraction peaks confirms that the particles are partially crystalline (mainly amorphous) with an anatase structure which has a tetragonal Bravais lattice.

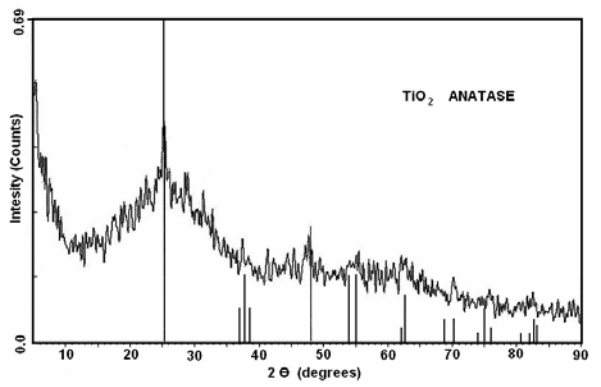

Fig. 6. XRD pattern of the TiO_2 nanoparticles deposited in the reactor chamber wall.

CONCLUSIONS

The pulsed-injection MOCVD has demonstrated the capability to produce high titania oxide films on steel 316 successfully, with acceptable homogeneity and adherent, using a simple and non-expensive equipment. The characterization results suggested the following conclusions. Highly oriented, stoichiometric TiO_2 thin film with anathase phase were successfully deposited on steel 316 substrate at 600 °C. On the other hand, the analysis by TEM of the particles deposited in the wall of the quartz reactor suggests the possibility to produce nanoparticles in appreciable quantities for this technique.

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