# MICROSTRUCTURAL ANALYSIS BY SCANNING ELECTRON MICROSCOPY OF MESOPOROUS ALUMINA FILMS OBTAINED BY ANODIZATION

Vázquez, A. L.[1,2]*, Carrera, R.[1,2], Castillo, S.[1,2], Arce, E.[1], Castillo, N.[3], Morán-Pineda, M.[2]

[1] Departamento de Ingeniería Metalúrgica, ESIQIE-IPN, México D.F., México.
[2] Programa de Investigación y Posgrado, Instituto Mexicano del Petróleo, México D.F., México.
[3]CINVESTAV, Departamento de Física, México D. F., México.

*Corresponding author: avazquezd@ipn.mx

*Received: December 28th, 2007. Accepted: March 24th, 2008*
*Published on-line: May 30, 2008*

**ABSTRACT**
Mesoporous materials are both scientifically and technologically important because of the presence of voids of controllable dimensions at atomic, molecular, and nanometric scales. Over the last decade, there has been both an increasing interest and research effort in the synthesis and characterization of these types of materials. Well ordered mesoporous alumina materials with high surface area and a narrow pore size distribution were synthesized using anodization process. The purposes of this work are to study the physical and chemical changes in the properties of mesoporous alumina films produced by anodization in sulphuric acid by different pretreatments on the aluminium surface such as Mechanical Polishing [MP] and Electropolishing [EP]. The morphologic and physical characterizations of the alumina film samples were carried out by Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD). The average mesoporous diameter was 17 nm, and the morphological shape was equiaxial; thus, that pore distribution was the smallest of all with a homogeneous distribution.

**Key words:** electropolishing; anodization; mesoporous alumina.

## INTRODUCTION

Alumina ($Al_2O_3$) is the most frequently used support material not only because of its cost and structural stability, because it can be prepared with a wide variety of pore sizes and pore size distributions, but also because of its high activity as a catalyst support [1]. The anodization process is a good alternative to obtain adherent high surface supports; especially $Al_2O_3$ on aluminum which is suitable for catalytic processes for it yields a mesoporous $Al_2O_3$ layer; both present mechanical adherence and thermal resistance [2-4]. By controlling the different variables of the anodization process such as temperature, operational voltage and electrolyte, the diameter of the pores and the porosities can be varied [5-10]. Generally, among other electrolytes, $H_2SO_4$ yields films with the highest pore concentrations [2, 11]. The pretreatment of the aluminum surface before the anodization process is very important for properties such as morphology and structure than can be changed significantly. As long as the aim of this work is to study the alumina morphologic modifications obtained by the pretreatments, the aluminum anodization, in order to obtain improved physical properties of mesoporous $Al_2O_3$ as catalytic support.

## EXPERIMENTAL

Before anodizing, commercial aluminum foils with a thickness of 100 μm (3×1 cm) suffered two pretreatments: Mechanical polishing (MP) and Electropolishing (EP). In the MP, the aluminum foils were polished with emery papers grade 600, water rinsed and dried with acetone. In the EP, the aluminum foils were electropolished in a stirred $C_2H_5OH/HClO_4$ (5:1) mixture for 16 min at 100 $mAcm^{-2}$ and 9 °C. The power supply was an Agilent E3631A, which works in the 0-25 V range and 0-1 A.

The anodic oxidation process was conducted in a 1.6 M $H_2SO_4$ solution for 100 min at 30 °C by using a current density of 30 $mA \cdot cm^{-2}$ with steady stirring. The aluminum foil to be anodized was connected to the anode in the power supply, and was placed between two aluminum foils connected to the cathode in order to

anodization to take place on both sides of the anode. The power source was the one stated above. The obtained foils were dried at 120 °C for 30 min and calcined at 450 °C.

The study of the crystalline phase, morphology and thickness of the generated anodic alumina layer ($Al_2O_3$/Al) was carried out by applying the following techniques: 1) Scanning Electron Microscopy (SEM) by using a FEI NOVA 200 equipment with a High-resolution Field Emission-SEM column, Resolution @ optimum WD (High-vacuum): 1.0 nm at 15 kV (TLD-SE); and 2) X-ray diffraction, by using a DISCOVER-BRUKER D8 equipment; the measurements were performed at room temperature by using the Kα radiation of Cu and covering the 2θ ranging from 4 to 70°.

## RESULTS AND DISCUSSION

The effect of the mechanical polishing and electropolishing treatments on the aluminum surface on the thickness of the alumina layer generated by the anodization process is shown in Figure 1. The thickness measurements were performed by SEM at various points along the vertical dimension of the specimen to obtain the oxide thickness distribution and to calculate the mean thickness of the film. According to the results, a larger thickness (98μm) than that in the $Al_2O_3$/Al [MP] is obtained when applying electropolishing; the aforementioned could only depend on the aluminum pretreatment; and therefore, it could depend on the residual defects on the aluminum surface.

The XRD patterns for the anodic alumina generated by anodization with different pretreatments of the aluminum surface are shown in Figure 2. At 450ºC, amorphous alumina was obtained, as it can be seen in Fig. 2A, B in the 2θ angle ranging from 22 to 35 degrees; and by both methods there is a preferential aluminum orientation in the plane [200]; and by EP there is a better orientation in the plane [220]; which indicates that the phase transformation from Al to $Al_2O_3$ occurs more easily; nevertheless, thermal treatments should be necessary to obtain a crystalline phase.

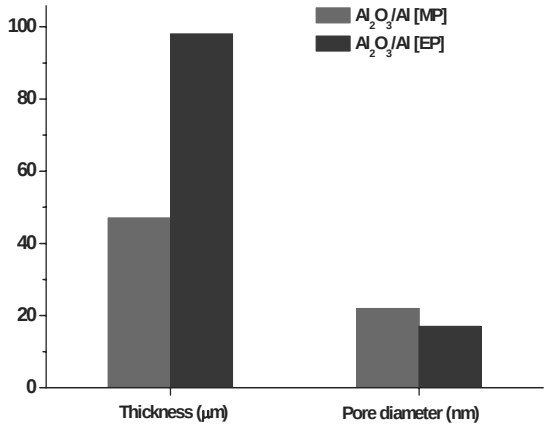


Fig. 1. Relationship between the pretreatments on the aluminum surface and the physical properties on the $Al_2O_3$/Al supports.

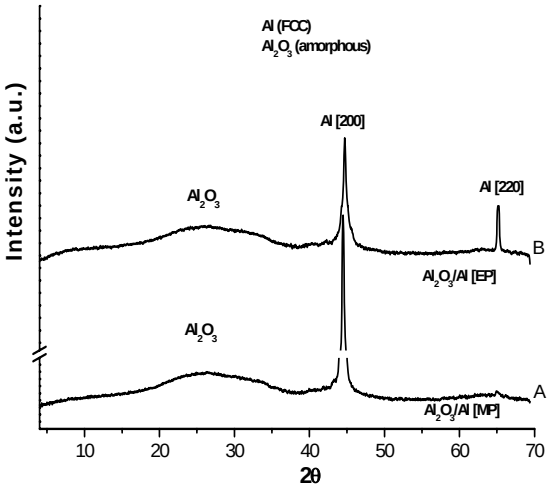


Fig. 2. XRD patterns of the catalytic supports: (A) $Al_2O_3$/Al [MP]; (B) $Al_2O_3$/Al [EP].

The pore diameter distribution of the alumina generated by anodization, either by the MP or EP pre treatments, was found (Figure 3). The pretreatment of the aluminum surface influences the morphology and the structure of the resulting $Al_2O_3$ layer. It can be seen that by using electropolishing (EP) a better distribution and a smaller average mesoporous pore size were obtained. This is in agreement with the study of Bocchetta et al. [12], they applied three different aluminum pretreatments: electropolishing, mechanical polishing and chemical

attack; and alumina membranes were fabricated by aluminum anodizing in aqueous solutions: 0.4 and 0.04M $H_3PO_4$; and 0.15 M oxalic acid solutions. According to their results, more ordered structures with cylindrical and parallel channels, were achieved starting from electropolished surfaces and 0.15 M oxalic acid, having an average pore size in the order of 90 nm.

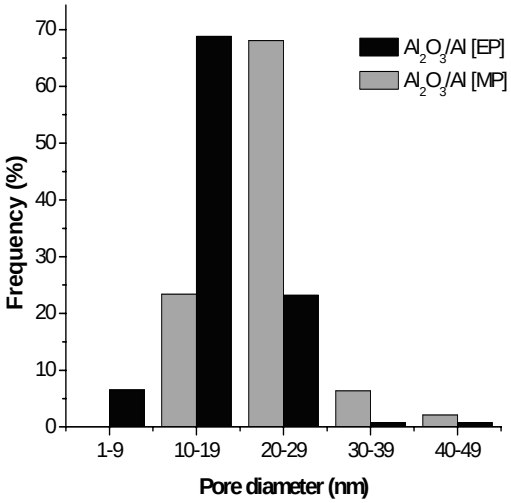


Fig. 3. Pore size distributions of the $Al_2O_3$/Al [MP] and $Al_2O_3$/Al [EP] supports.

By comparing the pore size and pore distribution, the SEM micrographs reveal that [EP] samples present a smaller pore size and a better pore distribution (Figure 4). The sample obtained by EP, presents a minor roughness in comparison with that in the MP sample which show uneven roughness.

The structure of the porous alumina generated by aluminum anodization has been described as a close-packed array of approximately hexagonal columnar cells, each of which contains an elongated, roughly cylindrical pore extending between the external surface of the film and the $Al_2O_3$–Al interface, as shown in Fig. 4b; and the morphological shape was equiaxial.

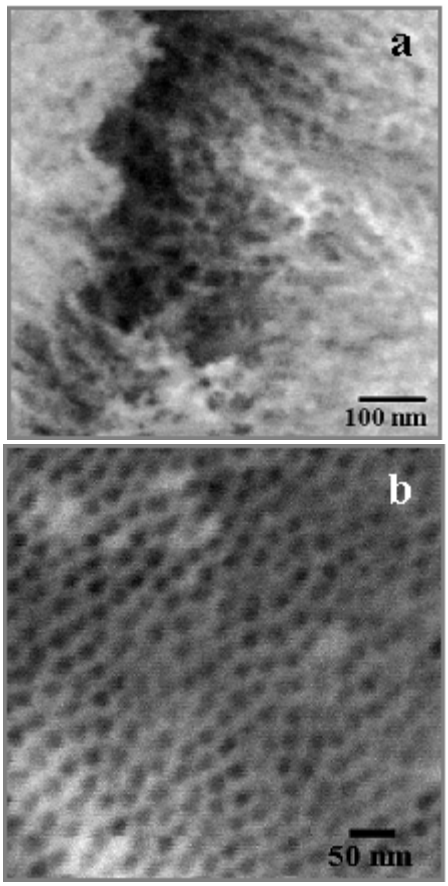


Fig. 4. SEM micrographs of the pore distributions in (a) $Al_2O_3$/Al [MP]; (b) $Al_2O_3$/Al [EP].

## CONCLUSIONS

Ordered mesoporous alumina by anodizing was synthesized with high reproducibility and different pretreatments of the aluminum surface before the anodization process produce different morphologies and different mesoporous sizes. In particular, the electropolishing treatment was the best option to obtain alumina layers with a remarkable small average mesoporous size (17 nm), equiaxial pore shape and a homogeneous distribution; and high film thickness. According to the obtained results, the surface treatments used in this work (EP principally) could be applied to develop coated monoliths with loaded PGM active metals, to be used in the treatment of VOC emissions in stationary sources.

**ACKNOWLEDGMENTS**

The authors want to thank the support offered by IMP, CONACyT and CIDIM-IPN; and for the technical support to Rufino Velázquez Lara.

**REFERENCES**

[1] Ertl G., Knözinger H., Weitkamp J. (1999). "Environmental Catalysis", Wiley-Vch Eds. Weinheim, pp. 192.

[2] Burgos N., Paulis M., Montes M. (2003) "Preparation of $Al_2O_3$/Al monoliths by anodisation of aluminium as structured catalytic supports" *J. Mater. Chem.* 13 :1458-1467.

[3] Hönicke D. (1983). "Formation of an $Al_2O_3$-coated catalyst with a metallic core by anodic oxidation of aluminium" *Appl. Catal* 5:179-199.

[4] Nourbakshs N., Smith B.J., Webster I.A., Wei J., Tsotsis T.T. (1991). "Metal deposition in porous anodic alumina films under hydrotreating conditions" *J. Catal.* 127:178-189.

[5] Fedotiev N.P., Grilijes S.P. (1972) "Electropulido y Anodización de Metales", Gustavo Gili, eds. Barcelona, pp. 188.

[6] Lizarde Ruíz L. (1984) "Teoría y Práctica de la Lucha contra la Corrosión", González Fernández J.A., Ed., Grafimad S. A., Madrid, pp. 461.

[7] Patermarakis G., Nicolopoulos N. (1999) "Catálisis over Porous Anodic Alumina Film Catalysts with Different Pore Surface Concentrations" *J. Catal*. 187:311-320.

[8] Shawaqfeh A.T., Baltus R.E. (1998) "Oxygen pumping characteristics of yttria-stabilized-zirconia" *J. Electrochim. Acta* 43:2699-2708.

[9] Patermarakis G., Papandreadis N. (1992) "Study on the mechanism of oxide hydration and oxide pore closure during hydrothermal treatment of porous anodic $Al_2O_3$ films" *Electrochim. Acta* 37:125-131.

[10] Patermarakis G., Papandreadis N. (1993) "Effect of the structure of porous anodic $Al_2O_3$ films on the mechanism of their hydration and pore closure during hydrothermal treatment" *Electrochim. Acta* 38:1413-1420.

[11] Thomson G.E., Furneaux R.C., Wood G.C. (1978) "Electron microscopy of ion beam thinned porous anodic films formed on aluminium" *Corros. Sci* 18:481-498.

[12] Bocchetta P., Sunseri C., Chiavarotti G., Di Quarto F. (2003) "Microporous alumina membranes electrochemically grown" *Electrochim. Acta* 48:3175-3183.