Structural analysis of ytria partially stabilized zirconia

M.E. Contreras, H. Orozco, and A. Medina-Flores*  
Instituto de Investigaciones Metalúrgicas, UMSNH, Edificio “U”, Ciudad Universitaria,  

I. Espitia  
Facultad de Ingeniería Química, UMSNH, Edificio “M”, Ciudad Universitaria,  

Recibido el 10 de septiembre de 2008; aceptado el 8 de diciembre de 2008

In this work, electrophoretic deposition of ZrO$_2$–8Y$_2$O$_3$ (YSZ) film was carried out on AISI 304 Stainless steel substrates. The obtained films were isothermally-treated at 700°C for 2h and cooled. The samples were analyzed in a FEG-TEM PHILIPS TECNAI F20, which has an information limit of 0.2 nm working at 200 Kv. The results obtained showed small precipitates of YSZ of 5 and 8 nm of size. On the deposited film the formation of the tetragonal and cubic phases of YSZ only were obtained and the monoclinic phase was not observed.

Keywords: HRTEM; YSZ; nanoparticles; clusters.

En este trabajo se llevó a cabo la deposición de (YSZ) ZrO$_2$–8Y$_2$O$_3$ como una película delgada de circona parcialmente estabilizada con itria sobre un substrato de acero inoxidable AISI 304. Las películas obtenidas se trataron térmicamente a 700°C durante 2 horas y, posteriormente, se enfriaron lentamente. La caracterización se llevó a cabo en un FEG-TEM PHILIPS TECNAI F20, el cual tiene un límite de información de 0.2 nm y trabaja con un voltaje de aceleración de 200 Kv. Los resultados mostraron la formación de precipitados de YSZ de entre 5 y 8 nm de tamaño. En la película de YSZ solamente se observaron estructuras tetragonales y cúbicas, pero no se observó ninguna estructura monoclinica.

Descriptores: HRTEM; YSZ; nanopartículas; agregados.

PACS: 61.46.+W; 68.37.Lp; 68.55.Jk

1. Introduction

Ceramic coatings of materials such as ZrO$_2$ are needed for a variety of applications like thermal or electrical insulation, reduced friction loss, increase wear and/or erosion resistance from oxidation, sulfidation and corrosion. Zirconia (ZrO$_2$) is an attractive material for thermal barrier coatings [1] because, compared with other ceramics, it has superior mechanical properties, such as high strength and fracture toughness combined with good wear resistance, and over all, a thermal expansion coefficient close to that of metallic substrates, it also has ion conductivity so it has application as solid electrolyte. However, ZrO$_2$ exists in three crystallographic phases [2] the monoclinic phase, which transforms to the tetragonal phase at 1000°C, the phase transformation of tetragonal to monoclinic phase is accompanied by significant volume expansion (approximately 3–5 vol.%). The addition of several oxides (Y$_2$O$_3$, CeO, MgO) can stabilize the cubic phase in zirconia, so the occurrence of monoclinic zirconia can be repressed. In the case of yttria partially stabilized zirconia (YSZ), rapid solidification during the thermal treatment allows the formation of tetragonal phase. For YSZ, the different phase’s transformation behavior is due to the stabilizing concentration of high-temperature phases and grain growth as the high oxygen vacancy, formed during high-temperature holding. The extra oxygen vacancy at room temperature displaces an oxygen ion from the equilibrium position in the tetragonal phase so the tetragonal–monoclinic transformation is suppressed. YSZ has been most actually successfully employed as oxygen ion conductor. The yttrium oxide dopant serves dual roles: it stabilizes the high temperature cubic phase in zirconia and also generates oxygen vacancies through the following defect reaction written in the Kroger–Vink notation:

$$Y_2O_3 \rightarrow 2Y^{2+}_{Zr} + 3O_o + \frac{1}{2}V_o \quad (1)$$

An oxygen vacancy (V$_o$) is created for every mole of the dopant Y$_2$O$_3$. The high oxide ion conductivity in YSZ is attributed to these oxygen vacancies showed in figure 1. The ductility of YSZ at 1000°C is maximum (about 0.1 s/cm) at about 10 mol.% yttria as it is showed by Strickler and Carlson; the activation energy is also near this composition. Figure 1 shows the mechanism of transport from an occupied anion lattice site to a vacant anion site in a fluorite oxide and the concentration of defects in yttria-stabilized zirconia

![Flourite type structure of YSZ.](image-url)
Table I. 304 Stainless steel composition.

<table>
<thead>
<tr>
<th>Element</th>
<th>Composition (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.08% Max</td>
</tr>
<tr>
<td>Mn</td>
<td>2.00% Max</td>
</tr>
<tr>
<td>Si</td>
<td>1.00% Max</td>
</tr>
<tr>
<td>Cr</td>
<td>18.00 – 20.00% Max</td>
</tr>
<tr>
<td>Ni</td>
<td>8.00 – 10.50 Max</td>
</tr>
</tbody>
</table>

2. Experimental procedure

Using as precursors salts ZrOCl₂ 8H₂O and YCl₃ (Aldrich 99%), which were prepared as aqueous solution. Substrates of stainless steel 304 were used for the deposition of zirconia yttria hydroxil gel. The electrodeposition was performed in glass cell with a volume of 300 ml. After electrodeposition process, the samples were exposed to thermal treatment at 700°C for 2 hours. Table I shows a 304 stainless steel composition; we used this material because it serves as electric contact (interconnection) and ceramic support. The requirements of the interconnection are good electronic conductivity, stability in oxidizing and reducing atmospheres and a thermal expansion close to the ceramic material.

3. Results and discussions

The electrophoretic deposition of ZrO₂ –8Y₂O₃ (YSZ) film method produced a film composed of a solid solution of YSZ spherical shaped clusters of nanoparticles with size range less that 15 nm, as can be seen in the TEM micrographs, Figs. 2a and 2b, of a piece of film scratched from the 304 stainless steel substrate. The bright field image in Fig. 2a shows that the film is formed by interconnected nanoparticles aggregates. In the dark field image (Fig. 2b), it is possible to observe the presence of bright spherical shaped clusters which are crystalline according with the Brag’s law. The energy dispersive spectroscopy in Fig. 3 exhibits peaks that correspond to Y and Zr from YSZ phase, Fe, C, Ni, Mn, Cr, and Mo signals correspond to the 304 stainless steel substrate and the Cu signal corresponds to the support grid. This indicates that no contamination occurred during the process.
last OH− linked to the Zr and Y cations reacts to form an oxo bridge between two metals, Zr-O-Zr, Y-O-Y and Zr-O-Y. After those condensation reactions, the condensed products have high density and positive surface charge so they are attracted and deposited on the cathode surface. The deposited particles are nanometric as a result of the oligomeric condensation products due to the controlled conditions in the electrodeposition bath. The insert in Fig. 4, shows that the clusters are formed by nanocrystalline particles, some of them are flake-like another are disk-like. The particles are superimposed and are physically linked. Figure 5 presents the HRTEM images of the cluster’s thinner area. Figure 5a shows the image obtained of the one tetragonal YSZ particle along the [110] axis, and a cubic YSZ particle in the [001] axis can be seen in the Fig. 5b. This result probes that the consolidation temperature used was enough to obtain the YSZ crystallization in both phases. The solid solution formation by this deposition method is also an important result.

4. Conclusions

The electrophoretic deposition of ZrO2-8Y2O3 produced a film composed of a mixture of YSZ, in the tetragonal and cubic phases were obtained at 700°C. TEM analysis showed that the film was formed by spherical shaped clusters of nanoparticles with sizes ranging from 5 to 12 nm with a cubic and tetragonal structure.

* Corresponding author; e-mail: ariosto@jupiter.umich.mx
Phone: +52 (443) 3223500 Ext. 4018, fax: +52 (443) 3223500 Ext. 4010.