DUPLEX Y₂O₃-ZrO₂/Al₂O₃ NANOCOMPOSITES AS SOLID ELECTROLYTES

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ABSTRACT

Dual phase 50/50 Y₂O₃-ZrO₂/Al₂O₃ nanocomposites with extremely fine microstructure were prepared using high purity commercial powders. High density sintered bodies were achieved at temperatures as low as 1450°C. Mechanical properties of these type of materials are adequate for self-supporting SOFC devices. Electrical conductivities are lower than those without alumina, following classical theory, however the zirconia grains are not fully percolated. New microstructures with intragranular dispersed alumina particles should be designed for still improved properties.

INTRODUCTION

One challenge for the Material Scientists is to design composites which possess high performance in two or more technological areas. Particularly, the formulation of materials that can be used simultaneously in both electrical and structural applications is an objective in modern material technology. Zirconia and alumina are widely considered as leading materials in these areas, respectively.

There exist a number of works devoted to improving the mechanical performance of stabilized zirconia, and in some cases adding alumina as second phase (1-3). Nevertheless, there are few studies on the electrical and mechanical response of duplex composite materials Al₂O₃-ZrO₂, i.e. composites with 50/50 volume ratio between each phase (4,5), where none phase acts as matrix. These materials are very interesting because they have relevant and specific microstructural effects, as for example a remarkable grain growth inhibition and a perfect interpenetration of both phases. Duplex fine microstructures can exhibit superplasticity at high...
temperatures (6) which is an unusual behaviour for a ceramic material. Further, compact bodies with small grain size generally possess high strength.

If microstructures achieved are extremely fine, in the nano-scale range, the compact bodies have been called "Nanocomposites". Such materials show remarkable mechanical strength as described by Niihara (7). The microstructures attained in some duplex compacts can be classified within the term of nanocomposite. From the electrical point of view, the introduction of isolant particles such as Al₃O₂, into the zirconia matrix would reduce the total electrical conductivity; however, if zirconia particles are strongly percolated it may cause no significant decrease in conductivity.

The objective of this work is to prepare and electrically characterize by Impedance Spectroscopy Method two types of duplex materials, namely t-zirconia-alumina and c-zirconia-alumina.

**EXPERIMENTAL**

High purity and commercially available powders of Al₂O₃, c-ZrO₂, and t-ZrO₂, both stabilized with yttria, have been employed. The main characteristics of these powders are summarized in Table I. Two compositions have been prepared using the same ratio of 50/50 by volume: i) Al₂O₃ + c-ZrO₂, and ii) Al₂O₃ + t-ZrO₂, hence forth referred to as AZC and AZT respectively. Alumina and zirconia powders were mixed in a teflon lined attritor using Y₂O₃-ZrO₂ balls as milling media.

After milling, powders were dried, screened and isostatically pressed. In order to select an appropriate sintering schedule, the shrinkage curves for samples AZC and AZT were obtained with an LVDT dilatometer. Finally, pressed bars of both samples were sliced and sintered for electrical measurements.

Microstructural observation was performed at the SEM on polished and thermal etched samples at 1450°C during 15 min.

Impedance spectra were obtained by using a HP impedance analyzer in the frequency range of 10 Hz - 10⁷ Hz, and at temperatures from 300°C to 1000°C, in platinum paste electroded disk surfaces, using the two-point method.
RESULTS AND DISCUSSION

a) Densification and microstructure.

Figure 1 shows the shrinkage curve for AZT and AZC samples as a function of temperature. According to these plots, maximum densification rates are attained around 1250°C and end point densification is reached in the samples at 1500°C. Accordingly, specimens were sintered at 1450°C for 1 hour reaching densities of 5.0 and 4.8 g/cm³ for AZT and AZC composites, respectively.

SEM microstructures of the samples are depicted in Figures 2a, 2b and 2c. Two main features can be observed: first, the totally interpenetrating phase network at high volume fraction, and second, the average grain sizes of both phases, alumina and zirconia, are certainly nanoscale < 500 nm size. Alumina particles were of similar sizes in the two materials investigated, but zirconia grains in the duplex Al₂O₃/c-ZrO₂ material seem larger than duplex Al₂O₃/t-ZrO₂ composite. The interpenetrating character can avoid the total zirconia grain percolation, which is the main factor to keep the electrical conductivity similar to those of alumina-free zirconia compacts.

b) AC Impedance Study

The impedance spectra at 300°C of the AZT and AZC nanocomposites are depicted in Figure 3. Spectra for two zirconia materials, 3Y₂O₃-TZP and 8Y₂O₃-FSZ, characterized by tetragonal and cubic phases respectively, were also drawn for comparison. These zirconia compacts were prepared in the same way described in the previous section. It can be seen that, for nanocomposites a semicircle overlapping was noted. The values of the electrical conductivity are so high that it is not possible to associate them to any alumina contribution to the electrical conduction. Therefore, the appearance of semicircles at this temperature is due: first, the zirconia grains are percolated but not totally (see Figs. 2a and 2b) and secondly, alumina grains behave, of course, as isolators. However, comparing to the alumina-free zirconia impedance spectra, the duplex nanocomposite samples show a quite unusual interphase behaviour and alumina grains seem to govern partially the boundary conduction process, provoking an approximation of relaxation time values, or in other words, the capacitance values of the bulk and grain boundary of zirconia phases.
A typical deconvolution of semicircles allows to separate bulk and interphase electrical contributions. The grain boundary-interphase electrical conductivity curves are shown in Figures 4 and 5. In all the samples investigated a straight line was observed. The activation energy for conduction is recorded in Table II. The activation energy does not change significantly, which means that the alumina phase does not contribute to the oxygen vacancy conduction mechanism but acts both as typical potential barrier for vacancy movement, and also as a capacitance modifier phase.

The values of total conductivity of the nanocomposites as well as the zirconia materials introduced for comparative purpose are shown in Table II. As can be seen, the electrical conductivity of the composites is lower than of the zirconia materials. This behaviour is explained using the classical theory. Following this theory, the conductivity of a composite with spherical second phase isolator particles is described by the equation:

$$\sigma_d = \frac{(1-f)\sigma_0}{1+0.5f}$$

In our case, $\sigma_0$ is the zirconia conductivity, $\sigma_d$ the nanocomposite conductivity and $f$ is the alumina volume fraction. Substituting the appropriate values in this formula, conductivity values ($\sigma_{\text{class}}$ in Table II) show a good agreement with the experimental conductivity values ($\sigma_{\text{exp}}$).

According to the experimental conductivity results and the microstructural observations of the dual composites, it seems that the interpenetrating features do not allow zirconia grains to be fully percolated and it should be possible to design new nanocomposite microstructure(8), where alumina particles are not located mainly in intergranular position, but mostly in intragranular location.

In order to maintain the electrical conductivity, the next target is to produce nanocomposite duplex microstructure where zirconia grains are fully percolated, and the alumina nanoparticles are mostly intragranular located inside the zirconia grains. In that case, mechanically self-supporting solid electrolytes can be used in SOFC devices.
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Table I. Characteristics of the starting powders.

|                  | Particle Size (μm) | Y$_2$O$_3$ Content (mol %) | Impurity Content (wt %) | BET (m$^2$/g) |
|------------------|--------------------|-----------------------------|-------------------------|---------------|
| Al$_2$O$_3$      | 0.5                | --                          | <0.03                   | 10            |
| c-ZrO$_2$       | 0.3                | 8                           | <0.05                   | 16            |
| t-ZrO$_2$       | 0.3                | 3                           | <0.05                   | 16            |

* Condea HPA-0.5
+ Tosoh zirconia FZ-8Y
& Tosoh zirconia TZ-3Y

Table II. Total conductivity and activation energy of the nanocomposites and the plain zirconia materials.

| Material | $\sigma_{exp}$ (1000°C) x (s.cm$^{-1}$) | $\sigma_{class}$ (1000°C) x (s.cm$^{-1}$) | $\Delta E_{bulk}$ (eV) | $\Delta E_{boundary}$ (eV) |
|----------|----------------------------------------|------------------------------------------|------------------------|-----------------------------|
| AZT      | 1.53                                   | 1.75                                     | 1.07                   | 1.04                        |
| 3Y-TZP   | 5.64                                   | --                                       | 0.98                   | 1.11                        |
| AZC      | 4.40                                   | 3.06                                     | 1.14                   | 1.13                        |
| 8Y-FSZ   | 7.09                                   | --                                       | 1.13                   | 1.20                        |
Figure 1. Shrinkage vs temperature for AZC and AZT samples (heating rate 2°C/min)
Figure 2. Microstructure of the composites AZT (a and b) and AZC (c and d)
Figure 3. Impedance spectra at 300°C for AZT, AZC, 3Y-TZP and 8Y-FSZ samples.
Figure 4. Log conductivity as a function of temperature for AZT-3Y/TZP.

Figure 5. Log conductivity as a function of temperature for AZC-8Y/FSZ.