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ScienceDirect
Journal of the European Ceramic Society 28 (2008) 2325–2329
www.elsevier.com/locate/jeurceramsoc

Crystallography and thermal stability of textured Co-YSZ cermets from eutectic precursors

M.A. Laguna-Bercero, A. Larrea*, R.I. Merino, J.I. Peña, V.M. Orera

Instituto de Ciencia de Materiales de Aragón, C/María de Luna 3, C.S.I.C.-Universidad de Zaragoza, E-50.018 Zaragoza, Spain

Available online 4 March 2008

Abstract

Textured cubic yttria stabilized zirconia (Co-YSZ) cermets produced by reduction of laser-assisted directionally solidified CoO-YSZ lamellar eutectics presents a microstructure of alternating lamellae of YSZ and porous metal. This microstructure is expected to improve the gas flow, electronic transport and oxygen ions diffusion of the isotropic cermet. Moreover, the cermet presents long-term stability at fuel cell operating temperatures. The stability of the cermet is related to the lamellar microstructure and to the good metal–ceramic bonding developed after reduction of the CoO-YSZ eutectic. These materials are proposed as cermet anodes for Solid Oxide Fuel Cells.

Keywords: Directionally solidified eutectics; Microstructure-final; Thermal properties; ZrO_2; Fuel cells

1. Introduction

Nickel-zirconia cermets have been the dominant solid oxide fuel cells (SOFC) anodes. Nickel is most commonly used because of its low cost in comparison with other metals such as cobalt, platinum and palladium.[1] The functions of the yttria-stabilized zirconia (YSZ) matrix in the anode are to support the nickel-metal particles, to inhibit coarsening of the metallic particles at the fuel cell temperature, and provide oxygen ion conduction to the three-phase boundaries (TPBs) required for cell operation. In addition, the thermal expansion coefficient (TEC) of the anode is close to YSZ electrolyte.

One of the major concerns of SOFC anodes is the long-term stability during operation at high temperatures. The problem is the agglomeration of Ni particles in the cermet during operation, in part due to the non-wettability between the metallic phase and the ceramic YSZ.[2] This metal agglomeration by grain growth at high temperatures finally obstructs the porosity of the anode and eliminates the TPBs. To improve the metal/YSZ adhesion, several studies have been carried out by modifying the ceramic phase, but the problem is still essentially unresolved.[3,4]

Another disadvantage of the nickel-cermet anode arises from the promotion of the competitive catalytic cracking of hydrocarbon. Nickel catalyzes carbon fiber formation in the presence of CH_4, preventing the direct oxidation of methane in nickel-containing SOFCs.[5] For natural gas to be used as fuel, it needs to be externally or internally reformed with steam. Impurities in the fuel stream, particularly sulphur, also inhibit anode functionality.[6] The use of cobalt in SOFC anodes can also be an interesting alternative. Cobalt is more costly than nickel but offers potential advantages, including better catalytic properties and high sulphur tolerance.

We have prepared Co-YSZ cermets by reduction of CoO-YSZ eutectics produced by laser melting and directional solidification. The directional solidification processing of eutectic oxides (DSEO) produces composite materials with fine and very stable homogeneous microstructures whose morphology, including the phase size, can be controlled by the processing parameters.[7] It is a useful method for optimizing the microstructure of the functional layer in SOFC anodes.[8] The directional solidification of the eutectic oxide produces a precursor material consisting of alternate lamellae of CoO and YSZ, with typical lamellar width of about 0.5 μm. Complete reduction of CoO under H_2 atmosphere is favored by the fast oxygen ion transport by the YSZ phase and transforms the CoO lamellae into porous Co lamellae. The textured microstructure of the Co-YSZ cermet provides easy gas flow, good electrical conductivity and an appropriate thermal expansion coefficient ($\alpha = 10.7 \times 10^{-6}\,\mathrm{K}^{-1}$), which allows good thermochemical integration with the YSZ electrolyte.[9] Moreover, YSZ lamellae act as a mechanical barrier to prevent metal coarsening provided that metal–ceramic adhesion is strong

* Corresponding author. Tel.: +34 976 761958; fax: +34976 761957.
E-mail address: alarrea@unizar.es (A. Larrea).

0955-2219/$ – see front matter
doi:10.1016/j.jeurceramsoc.2008.01.019

enough to avoid fast particle agglomeration in the porous metal lamellae.

Here we report on the long-term stability of the Co-YSZ cermet. For these studies we have prepared the cermets in the form of rods using the laser floating zone technique, but they can also be produced in the form of plates using the technique of laser melting and resolidification.[10]

2. Experimental procedure

We prepared precursor ceramic cylinders of 2 mm in diameter and 10 cm in length from a mixture of CoO (Aldrich, 99.99%), 8YSZ (8% mol Y_2O_3 stabilized ZrO_2 from Tosoh, 99.9%) by pressureless sintering at 1300 °C (12 h) and 1500 °C (30 min). Directionally solidified CoO-YSZ eutectic rods were produced from the precursor cylinders by the laser floating-zone method under Ar atmosphere to avoid CoO oxidation to Co_3O_4, as described in reference.[9]

SEM observations were carried out in a Jeol 6400 microscope on fractured samples by secondary electrons and on polished samples using backscattered electrons. We also performed Transmission Electron Microscope (TEM) experiments in CoO-YSZ and Co-YSZ transverse cross-sections to study the bonding between the phases. For the TEM experiments, transverse slices (~300 μm thick) were cut from the DSE and cermet using a diamond saw. These slices were plane-parallel grinded down to 40 μm thick, glued to a copper support and ion milled at liquid nitrogen temperatures using 5 kV Ar^+. X-ray pole figure experiments were performed in a Bruker D8 goniometer equipped with a 2D detector (General Area Diffraction Detector System from Bruker). The experiments were carried out on the polished surface of slices cut perpendicular to the rod growth direction. Multex Area software (Bruker) was used for preparing the diffraction experiments and building the pole figures.

Electrical conductivity experiments were carried out at room temperature using the 4 points DC method with a Keithley programmable current source and a Hewlett Packard 34401 microvoltmeter. The electrical current was applied parallel to the rod axis, and thus parallel to the porous metal channels. Hg porosimetry experiments were performed using a Poremaster-33 porosimeter (Quantachrome Instruments).

3. Experimental results

The samples used in this study were obtained after reduction at 850 °C of CoO-YSZ eutectics solidified at 100 mm/h. Channelled cermets with the lamellae perpendicular to the solidification front were obtained. The microstructure of the cermet is shown in Fig. 1. Lamellae width is about 400 nm for the YSZ and about 500 nm for the porous cobalt and, as previous results have shown, the overall cermet composition is (in vol%) 39.0 YSZ–34.8 Co–26.2 pores.[9]

We have performed X-ray and TEM experiments in order to study the CoO-YSZ and Co-YSZ orientation relationships and interfaces. Orientation relationships of the eutectic component phases have been determined by X-ray experiments. The analysis of the pole figures (Fig. 2) indicates that the crystallographic axes of both YSZ and CoO phases are parallel, $\{h\,k\,l\}_{CoO}//\{h\,k\,l\}_{YSZ}$, and the growth directions are $[1\,1\,1]_{CoO}//[1\,1\,1]_{YSZ}$. These growth directions are different to the previously reported $[1\,0\,0]_{c\text{-}ZrO_2}//[1\,1\,0]_{CoO}$ for the same eutectic but grown at lower rates.[11,12] As commented by Echigoya and Hayashi it seems that the preferred orientation changes as a function of the growth rate.[12] The interfacial planes have been studied by TEM, but the situation is not simple because in the transverse cross-sections that we analyzed the interfacial plane was not generally parallel to the eutectic growth direction.

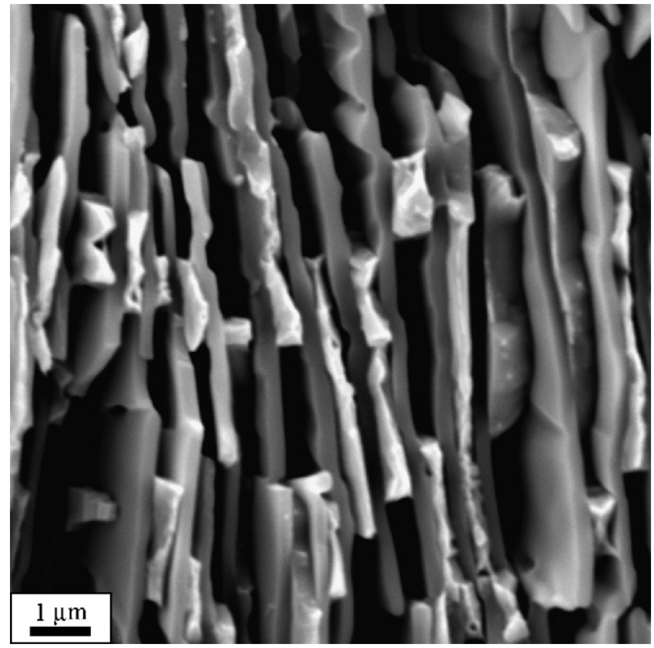

Fig. 1. SEM image of a Co-YSZ cermet.

Reduction has been studied by TEM in partially reduced samples where metallic Co and CoO coexist inside the same lamella, as shown in Fig. 3. Co-YSZ interfaces are formed by electrochemical reduction of the CoO-YSZ eutectic. CoO loses the oxygen that diffused rapidly through the YSZ, an excellent ionic conductor at the reduction temperature (850 °C). We performed electron diffraction experiments in those regions and concluded that the CoO crystallographic orientation is maintained during the reduction process, $\{h\,k\,l\}_{CoO}//\{h\,k\,l\}_{Co}$, in the same way as in the cermets studied by Echigoya et al.[13] We observed no crystallographic reorientation processes, as opposed to the previously reported Ni-YSZ cermets prepared by the same method.[14] Moreover, X-ray pole figures obtained in reduced Co-YSZ cermets (Fig. 4) showed that Co maintains the same crystallographic orientation as in the CoO phase. These experiments were performed on polished slices to avoid surface effects that could affect the CoO reduction behavior.

In order to test the microstructural stability of the Co-YSZ cermet we performed ageing experiments under a continuous flow of dry H_2/N_2 for 300 h at 900 °C and analyzed the samples by SEM before and after the ageing experiments. The micrographs showed that there is no microstructural evolution with time. Moreover, in order to determine the connectivity of cobalt

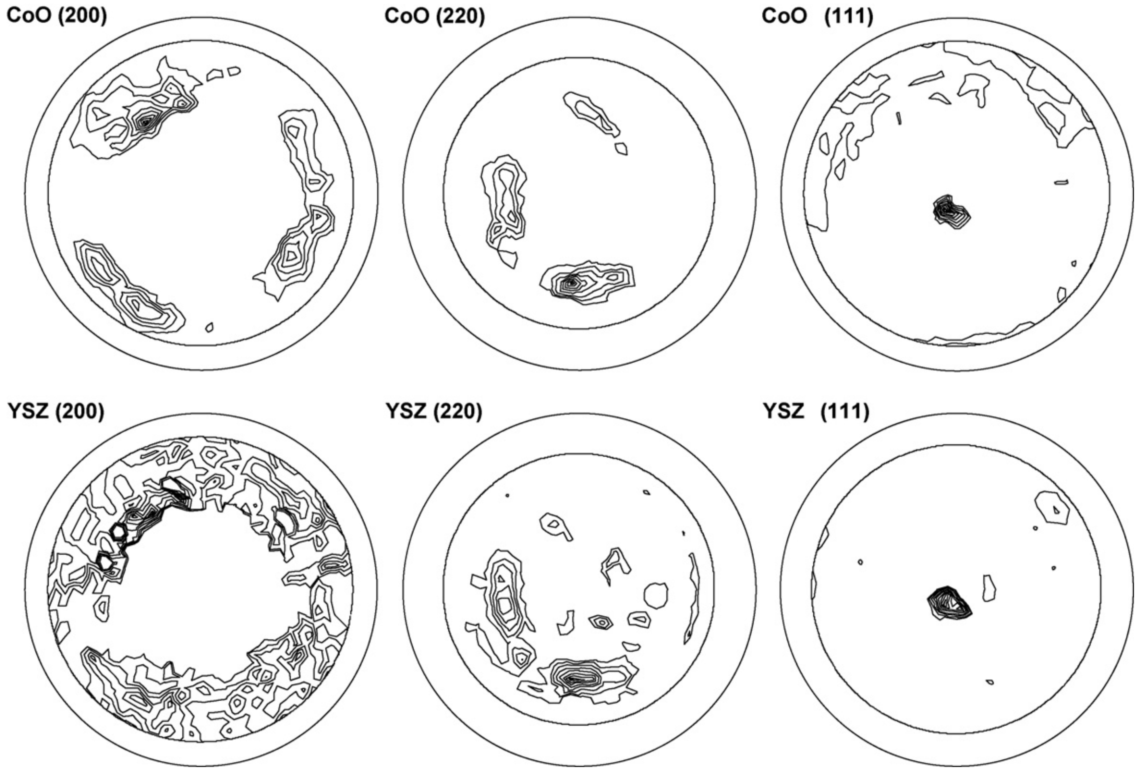

Fig. 2. X-ray pole figures of the transverse cross-section of a CoO-YSZ eutectic (equal area projection).

particles, we measured the electrical conductivity of the same sample at RT before and after the ageing. These results (Table 1) showed no signs of degradation with ageing. We also measured the pore size distribution before and after the treatment by Hg porosimetry. In Fig. 5 we represent the pore size distribution of the Co-YSZ cermet before and after 300 h under reducing atmosphere. This distribution is narrow and centred on about 200 nm, and there is no significant evolution of pores with the ageing treatment.

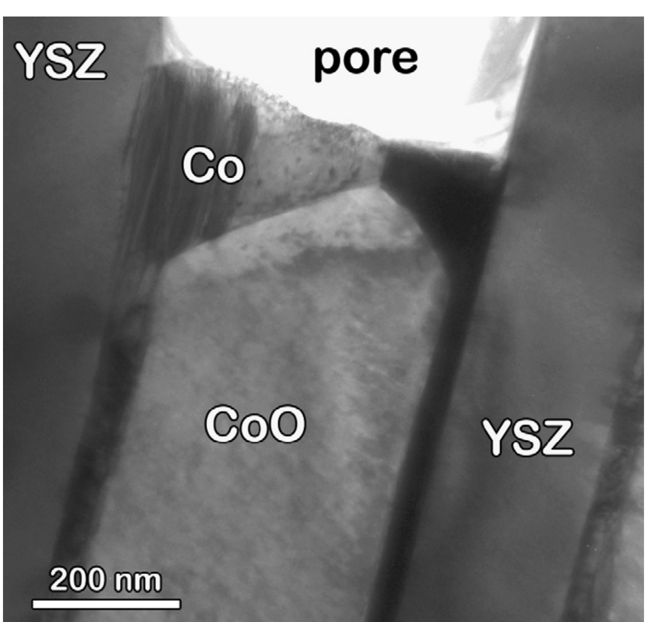

Fig. 3. TEM image of the initial reduction stage of a CoO lamella. Image obtained in a transverse cross-section.

4. Discussion

Co-YSZ cermets produced by reduction of DSEO samples are expected over time to have a long-term stability at high temperatures. First, the lamellar microstructure of the cermet prevents the coarsening of cobalt particles in the perpendicular direction to the lamellae, because the YSZ skeleton sustains cobalt particles and pores acting as a barrier to the growth of metallic particles. In addition, the good metal–ceramic adhesion limits the coarsening in the direction parallel to the lamellae. This is a very relevant aspect in channelled cermets because the porous metal lamellae, besides expediting gas transport and electronic conduction, also facilitate the coarsening of the metallic particles assuming they are not well-bonded to the YSZ lamellae.

In channelled Ni-YSZ cermets prepared by the same route we have recently reported the formation of four different kinds of low-energy interfaces.[14] Two of these interfaces were formed after a crystallographic reorientation of Ni that leads to the development of an epitaxial Ni-YSZ interface. However, in the present case we have not observed such crystallographic reorientation

Table 1
Electronic conductivity before and after the ageing treatment

	Electronic conductivity (S/cm)
Before ageing	$(2.7 \pm 0.3) \times 10^4$
After ageing	$(2.6 \pm 0.3) \times 10^4$

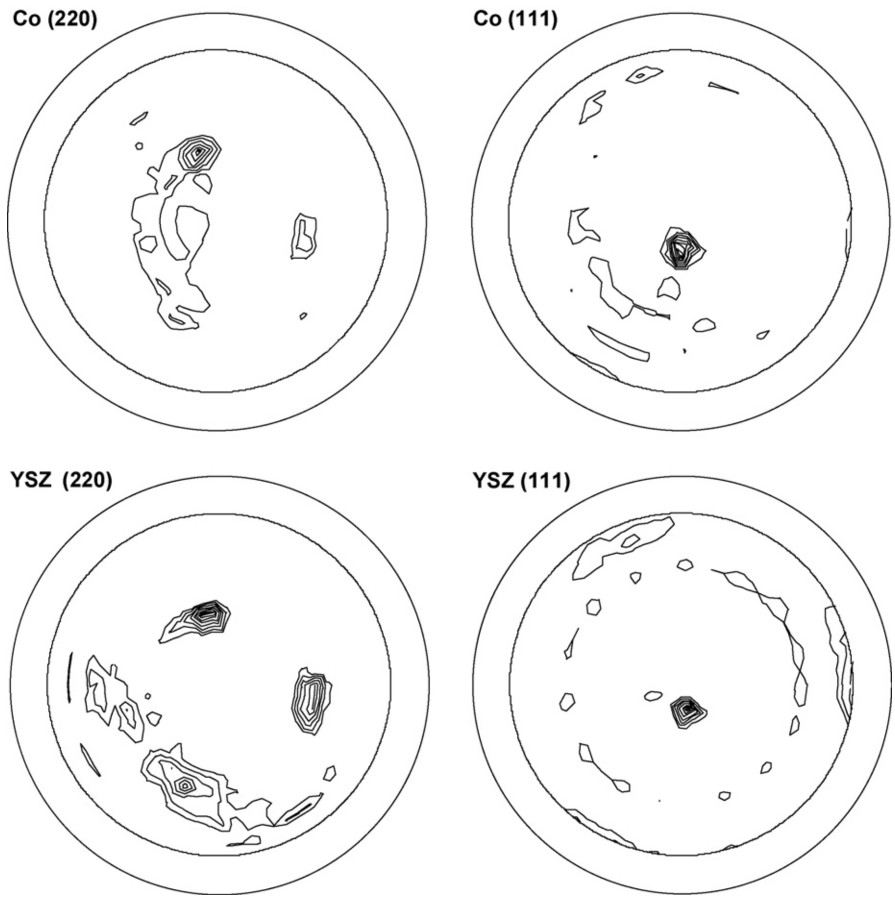

Fig. 4. X-ray pole figures of the transverse cross-section of a Co-YSZ cermet (equal area projection).

processes, indicating that the Co-YSZ interfaces formed directly by topotactic reduction, $\{h\,k\,l\}_{CoO}//\{h\,k\,l\}_{Co}$, are presumably stable enough that the evolution to a lower-energy interface is not necessary.

Metal–ceramic interfaces in cermets prepared by reduction of DSE present, in general, good adhesion properties. Coupled eutectic growth is characterized by the formation of low-energy interfaces in order to minimize the interfacial energy, and generally leads to the formation of low-index oxide–oxide interfaces. Besides the matching between oxygen sublattices, ionic charge balance at the interface is a requirement for low-energy interfaces in ionic compounds.[15] Moreover, recent theoretical calculations indicate that strong bonding is obtained when both interfacial planes are polar,[16] and detailed HREM studies of the c-ZrO_2-NiO interface showed that the interface is formed by a common oxygen plane, maintaining the cation–anion sequence across the interface.[17] In our CoO-YSZ DSEO the low-index planes parallel to the growth direction, $\{2\,2\,0\}$ planes, are not polar and the system is probably looking for other interfacial planes not parallel to the growth direction. As a consequence, after reduction of the transition metal oxide, the interface is formed between cobalt and YSZ polar planes. *Ab initio* Density Functional Theory (DFT) calculations of metal–ceramic interfaces show that adhesion between metal and polar ceramic surfaces is stronger than in the case of non polar ceramic surfaces.[18] The electric charge at a polar surface is not compensated, resulting in a high surface reactivity and consequently a good adhesion with the metal surface.

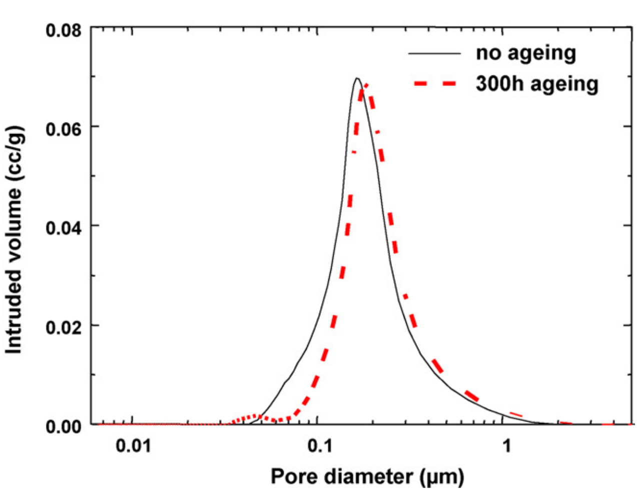

Fig. 5. Mercury porosimetry measurements obtained before and after the ageing treatment (300 h at 900 °C).

Ageing experiments confirm the long-term stability of the Co-YSZ cermets produced from reduction of a self-assembled DSEO, corroborating the good metal–ceramic adhesion of these cermets. The electrical conductivity values remain constant after the ageing treatment. It is important to note that the electrical conductivity of the Co-YSZ cermet is three times greater than the channelled Ni-YSZ cermet produced the same way,[9] and almost one order of magnitude greater than in an isotropic Ni-YSZ cermet of the same composition.[19] Moreover, the pore size distribution represented in Fig. 5 show that pores are about 200 nm in size in both aged and non aged samples. Only a small shift to bigger diameters can be appreciated in the aged samples.

5. Conclusions

We have produced textured porous cermets by reduction of CoO-YSZ directionally solidified eutectics. Before reduction the eutectic growth directions are $[1\,1\,1]_{CoO}$//$[1\,1\,1]_{YSZ}$. During reduction of CoO to Co, cobalt maintains the crystallographic orientation of cobalt oxide and no reorientation processes were observed. Apparently the Co-YSZ interfaces formed in this way ensure good stability of the material over time. The channelled microstructure of the cermet could improve the anode performance, assuring fluent gas flow and electronic conduction through the porous metallic lamellae.

Acknowledgements

Financial support from projects MAT2003-1182 and MAT2006-13005-C03-01, as well as from the European Social Fund, is acknowledged. We are indebted to P. Lozano (Instituto de Nanonociencia de Aragón, Spain) for her technical assistance in the pole figure experiments.

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