CHANNELED Ni-YSZ CERMETS PRODUCED FROM NiO-YSZ EUTECTICS BY LASER MELTING

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ABSTRACT

NiO-YSZ was produced by directional solidification of eutectics (DSE) using laser melting. This technique produces highly structured material consisting of NiO and YSZ lamellae with variable interlamellar spacing depending on growth conditions. The microstructure is homogeneous and the material mechanically stable during thermochemical reduction. Complete reduction of the NiO produces a porous cermet alternating lamellae of Ni and YSZ. The coefficient of thermal expansion of the cermet is that of the YSZ skeleton. Reaction kinetics at different temperatures during the reduction process was studied by gravimetric methods and SEM experiments, showing that the reduction process seems to be controlled by the O²⁻ diffusion through the YSZ phase. TEM experiments reveal that the low-energy interfaces formed during the eutectic growth are maintained after reduction. These interfaces are expected to prevent particle coarsening and give a long-term stability to the anode during operation at high temperatures. Resistivity values and pore distribution present no degradation after 300 hr at 900°C under H₂/N₂ atmosphere. This stability is an improvement for its use as a functional layer in solid-oxide fuel cell (SOFC) anodes.

INTRODUCTION

Applications for porous cerments are found in many advanced areas of technology, including gas reactions and fuel cells. Solid oxide fuel cells (SOFCs) typically include a porous Ni-YSZ (yttria-stabilized zirconia) cermet anode and a tight YSZ thin layer as electrolyte. The cermet presents gas permeation and both electronic and ionic conduction through metallic Ni and YSZ, respectively, thus increasing the density of triple phase boundary (TPB) points where the anode electrochemical reaction takes place. The microstructure of the anode and anode-electrolyte interface is a crucial issue to reduce the polarization loss of the cell (1). Conventionally, Ni-YSZ cerments are produced by reduction of a NiO-YSZ ceramic to yield about 30 to 40% porosity as well as good electronic and ionic conduction. The ceramic is prepared with fine and homogeneous powders to get as many TPB points as possible. However, grain coalescence at working temperatures (600° to 1000°C) is a severe concern for using these ceramic electrodes. Lamellar electrodes produced by reduction of oxide-oxide melt grown eutectics have been proposed as an alternative to these dispersed electrodes (2,3) based on its textured fine microstructure. In this case, the porous metallic phase should be constrained between the narrow spaces left by the ionic conductive YSZ phase lamellae. This
lamellar microstructures and the presence of low energy interfaces between phases are expected to give to the anode long-term stability during operation.

Several years ago, Revcolevschi et al. produced crystallographically aligned metal-oxide cermets by reduction of directionally solidified oxide eutectics (4,5). In particular, they studied the kinetics of the reduction of NiO to metallic Ni in NiO-CaSZ (calcia-stabilized zirconia) oxide-oxide eutectics at 1075°C under CO/CO₂ atmosphere (6). The authors also suggested the existence of an electrochemical local cell process where the oxygen ion diffusion to the surface proceeds via the cubic zirconia electrolyte lamellae and the electrons through the conducting metallic Ni phase. The final product was a composite of dense Ni and CaSZ alternating lamellae. The large volume reduction of about 40% resulting from the NiO to Ni transformation was accommodated by large cracks in well-oriented and massive samples, which degrade the mechanical properties of the cermet. Dickey et al. (7) also reported for this material that Ni and ZrO₂ remain crystallographically aligned, presenting a strong bonding between phases.

Recently, we reported the production of lamellar Ni-CaSZ porous cermet plates by surface laser melting and directional solidification of NiO-CaSZ structured eutectic ceramics (8). Chemical reduction treatments in H₂ atmosphere transformed the NiO into porous metallic Ni. In this paper we report on the fabrication of NiO-YSZ eutectic oxides by the laser floating zone technique. We have studied the influence of the composition and solidification parameters in the eutectic microstructure. The transformation of the oxide-oxide eutectics into porous cermets has been done at different temperatures between 600° and 900°C to ascertain which reduction mechanism controls this process. For this study, we chose monolithic and homogeneous directionally solidified eutectic rod samples. The best processing conditions to obtain fine, thermally and mechanically stable, homogeneous porous cermets with controlled microstructures, as well as their electrical conductivity, have been determined.

Moreover, it is known that some amount of Ni can be dissolved into the YSZ phase during processing. This may reduce the ionic conduction of the cermet significantly, and in fact the formation of tetragonal zirconia precipitates has been reported (9). The clean YSZ skeleton, which has been analyzed to determine the properties of the matrix, was isolated by chemically removing the metal phase.

**EXPERIMENTAL RESULTS AND DISCUSSION**

**Experimental Techniques**

NiO (Aldrich, 99.99%), ZrO₂ (Alfa, 99.9%) and Y₂O₃ (Aldrich, 99.99%) powders were milled, calcined, mixed, and pressed. Rods 1.4 mm in diameter and 50 to 100 mm in length were prepared from a mixture of the oxide powders by pressureless sintering during 12 hours at 1300°C and 0.5 hours at 1500°C. Directionally solidified eutectic rods were produced from the precursor ceramic cylinders with a CO₂ continuous wave laser using the floating zone-method, as described elsewhere (10,11). The thermal gradient at the growth front was about $G = 6 \times 10^5$ °C/m. Samples were isothermally and isochronally treated in a 4% H₂-N₂ gas mixture at temperatures from 600° to 900°C in a tubular furnace. The progress of the reduction process was followed by gravimetric
methods. The microstructure of the samples was studied by optical microscopy (OM), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). SEM micrographics and electron probe microanalysis (EPMA) were carried out with a JEOL 6400 microscope equipped with a Link Analytical eXL analyzer. TEM micrographs and diffraction experiments were obtained with a JEOL 2000 FXII microscope. Optical diffuse reflectance spectra were measured using a Praying Mantis accessory for a Cary 500 spectrophotometer (Varian) and BaSO₄ as a standard. The conductivity measurements were performed using the four-point configuration at RT using a 220 Keithley Programmable current source and a Hewlett Packard 34401A microvoltmeter. Mercury porosimetry was performed with a PoreMaster-33 (Quantachrome Instruments) porosimeter. Thermal expansion coefficients were measured within the 20° to 900°C range using a Mettler TMA 40 dilatometer. Chemical composition of the YSZ phase was obtained by energy dispersive spectroscopy (EDS) microanalysis using a Link Analytical analyzer fitted to a Jeol 2000 FXII TEM. For these experiments the Cliff-Lorimer method was used (12), where the Cliff-Lorimer sensitivity factors were experimentally measured from appropriate compound standards.

**Microstructure and Composition**

The microstructure and composition of the samples play a crucial role in determining their suitability from the point of view of applications. For example, in Figure 1 we illustrate frequently encountered limitations. On the left we show the microstructure of a well-ordered lamellae sample after reduction. As can be seen, dense instead of porous metallic lamellae are obtained. The enormous strains resulting from the volume change taking place during the NiO to Ni reduction are accommodated by large cracks, as previously observed by Bonvalot-Dubois et al. (6). Another matter of concern is the presence of primary phases if the composition of the eutectic is not well adjusted, as in the micrograph on the right.

![Figure 1. SEM micrograph (L) of a transverse cross section for a completely reduced Ni-YSZ cermet showing residual stress accommodation cracks produced during reduction (light phase - Ni, dark - YSZ, black - pore) and optical micrograph (R) of a transverse cross section showing a non-reduced sample with YSZ primary phase (light phase - NiO, dark - YSZ).](image-url)
We are seeking samples with a very fine eutectic microstructure (lamellae 1 µm thick or less), without cracks and able to support the large strains associated with the reduction processes. We observed that severe cracking due to reduction (Figure 1 left) could be eliminated if large aligned microstructures are avoided. We varied the growth parameters and sample composition to achieve optimal sample quality (homogeneous eutectic microstructure, absence of cracks and no segregation of primary phase). The best growth conditions to produce a fine and homogeneous microstructure are pulling speeds of $R = 100$ mm/hr, a counter-rotation of precursor and sample of 10 rpm, and laser powers of about 40 W during growth. Rod diameters must be less than 1.5 mm to avoid cracks. In terms of the G/R parameter that better describes the condition of the eutectic growth, we obtain $G/R = 2 \times 10^{10} \, ^{\circ}\text{C} \, \text{s/m}^2$. The selected composition of the precursor ceramics are (in mol%): 75 NiO-23.1 ZrO$_2$-1.9 Y$_2$O$_3$.

This eutectic lamellar microstructure consists of 20 to 80 µm eutectic grains with NiO lamellae ($\approx 0.5$ µm thick) alternating with YSZ lamellae ($\approx 0.4$ µm). The interlamellar spacing ($\lambda \approx 0.9$) is compatible with the empirical relationship rate $\lambda^2 \, R = 10^4 \, \text{mm}^3/\text{hr}$ given by Dhalenne et al. for the NiO/ CaSZ eutectic (13). We analyzed the final composition of the eutectic samples by 2D image analysis. The result in vol% is: $56.5 \pm 1.7$ NiO—$43.5 \pm 1.7$ YSZ. The content of the calculated transition metal oxide by this method is lower than the precursor composition due to the solubility of transition metal oxide in the YSZ, as we confirm in a later section.

**Reduced Samples**

Reduction was done at temperatures above 600°C. The composition of the resulting material has been determined by X-ray powder diffraction, indicating that all the transition metal oxide is fully transformed into metal and pores. Because the external dimensions of the sample do not change during the reduction process and cracks are not observed, we can obtain the final composition of the samples according to the results obtained by image analysis of the non-reduced samples. It corresponds in vol% to $43.5 \pm 1.7$ YSZ—$33.1 \pm 1.0$ Ni—$23.4 \pm 0.7$ pores. After reduction, the YSZ matrix remains apparently intact. Note that the resulting materials consist of $\approx 41\%$ porous Ni between the YSZ lamellae and that alignment of the structure along the growth direction ensures a good connection between phases (see below).

To obtain some insight into the reduction process of the oxide-oxide eutectics, some not-fully reduced samples were analyzed by SEM. The reduction mechanism is complex. As shown in Figure 2 (left), the oxygen ions leave the NiO toward the YSZ lamellae and diffuse easily along the YSZ lamellae to the external surface. The electrons required to maintain electronegativity move most likely along percolating Ni particles. In our samples, this anisotropic behavior is averaged out in transverse cross sections by the grain structure. The transverse cross section of the Ni-YSZ cermet after complete reduction is shown in Figure 2 (right).

For long-term stability of the material, it is important to notice that the YSZ skeleton sustains the Ni particles and pores. Moreover, in the eutectic growth, low-energy interfaces are expected between metallic Ni and the ceramic YSZ phase. We performed TEM experiments in NiO- YSZ and Ni-YSZ transverse-cross sections to study the bonding between the phases. In the as-grown sample (NiO-YSZ), both phases are well bonded.
Figure 2. SEM micrographs of transverse cross sections of (L) a NiO-Ni-YSZ rod (polished section) showing the beginning of the reduction process (light phase - Ni, light grey - YSZ, dark grey - NiO) and (R) a completely reduced cermet of Ni-YSZ (fractured view) (light phase - Ni, grey - YSZ, black - pores).

by low energy interface planes $\langle 111 \rangle_{\text{NiO}} // \langle 002 \rangle_{\text{YSZ}}$. Electron diffraction experiments confirmed that during the NiO reduction there is a topotactic process wherein the NiO crystallographic orientation is maintained $\{hkl\}_{\text{NiO}} // \{hkl\}_{\text{Ni}}$. This process leads directly to the formation of $\langle 111 \rangle_{\text{Ni}} // \langle 002 \rangle_{\text{YSZ}}$ interfaces. In addition, in some cases in our samples the Ni particles undergo a crystallographic reorientation to present $\langle 002 \rangle_{\text{Ni}} // \langle 002 \rangle_{\text{YSZ}}$ interfaces, which are probably even more stable than the $\langle 111 \rangle_{\text{Ni}} // \langle 002 \rangle_{\text{YSZ}}$ interfaces. In fact ab initio density functional theory calculations on $\langle 002 \rangle_{\text{Ni}} // \langle 002 \rangle_{\text{YSZ}}$ interfaces reported a strong metal-ceramic bonding (14). These two types of well-bonded interfaces are expected to act as a barrier to the growth of metallic particles, ensuring good microstructural stability during anode operation.

The YSZ skeleton determines the thermomechanical behavior of the porous cermet. In fact, we have measured the thermal expansion coefficient (within the 20° to 900°C range), which is $10.8 \times 10^{-6} \, \text{K}^{-1}$ for the Ni cermet. The same value holds for the bulk 8YSZ ($10.8 \times 10^{-6} \, \text{K}^{-1}$). This is an important property for achieving good thermomechanical integration with the YSZ electrolyte.

**YSZ Matrix**

We characterized the YSZ phase of the cermet as follows. After total reduction, all the transition metal phase was removed by reaction with diluted nitric acid, thus obtaining the isolated and porous YSZ matrix. XRD experiments reveal only the cubic phase of the YSZ (space group: $Fm\bar{3}m$), indicating that all the metal has been removed. From Rietveld refinements we obtained the lattice parameter for the Ni-YSZ ($5.127 \pm 0.001 \, \text{Å}$), which is the same as was found by Ingel in 8YSZ (15).

The emptied YSZ skeleton, although fragile, has enough mechanical resistance to be handled. The amount of NiO dissolved in the YSZ matrix was quantified by EDS
microanalysis in the TEM. In this way, spurious signals coming from the transition metal lamellae that could be activated by bremsstrahlung x-rays produced in the TEM condenser aperture are avoided (16). The results obtained are (mol%) 7.45 ± 0.12 Y₂O₃ and 1.99 ± 0.06 NiO dissolved in the YSZ. These results correspond to the solubility of the transition metal in 8YSZ at the eutectic temperature (~1800°C). The latter coincides with that given by Linderoth et al. in their study of the effect of NiO-Ni transformation in the 8YSZ matrix (9). However, these authors reported a decrease of the YSZ lattice parameter with the Ni content, which we did not observe. NiO dissolved in the YSZ produces an increment in charge to compensate for oxygen vacancies. The final composition for the YSZ matrix is Zr₀.₈₃Y₀.₁₅Ni₀.₀₂O₁.₉₁. For further comparisons, our sample contains the same amount of oxygen vacancies as YSZ with 10 mol% of Y₂O₃.

To determine whether the transition metal impurity was diluted to the atomic scale in the YSZ matrix and to obtain an insight into the impurity ion environment, we performed a spectroscopic study using the diffuse reflectance of the "emptied" sample. The optical properties correspond to the presence of transition metal oxide dissolved in the YSZ matrix. We compare the measured diffuse reflectance with the optical absorption spectra measured for a single crystal of YSZ grown by the "skull method" and slightly doped with Ni(II). The diffuse reflectance spectra measured for the Ni sample gives two bands at 423 and 525 nm. These bands were assigned, according to the work of Kunz et al. (17), to the transitions ³A₂ (F) → ³T₁ (P) and ³A₂ (F) → ¹T₂ (D), respectively. Similar results were obtained for the measured absorption spectra of the YSZ:Ni single crystal, giving also an octahedral crystal field for the Ni²⁺.

**Reaction Kinetics During the Reduction Process**

Reduction kinetics has been studied by monitoring the weight loss during isothermal reduction experiments given by Mt/M₀, (the ratio between the actual mass loss and the loss when the sample is totally reduced) as a function of time (Figure 3, left). Cylindrical samples of approximately the same size were partially reduced at different temperatures, then quenched to room temperature, weighed, and placed back into the furnace until transition metal oxide reduction was completed. This weight loss is due to the reduction of the transition metal oxide to the metal and agreed with the amount of transition metal oxide phase.

Isochronal experiments, where weight loss was measured for a given period of time at different temperatures, show that for the Ni-YSZ cermet the reduction process is clearly temperature-activated within the complete temperature range explored (600° to 900°C).

The study of the progression of the reduction front indicates that the reduction takes place via a diffusion-limited process. This means that the kinetics of the reduction reaction

\[
\text{NiO} + \text{H}_2 \rightarrow \text{Ni} + \text{H}_2\text{O (g)} \tag{1}
\]

could be dominated by the diffusion of the same species, presumably that of oxygen ions through the YSZ matrix. The electrons are easily transported by the metallic phase.

We now analyze the kinetic curves in the thermally activated range given in Figure 3 (left). The mathematical theory of diffusion in isotropic substances is based on the
Figure 3. (L) Mass reduction fraction versus time for the Ni-YSZ cermet; experimental points and fitting curves use Eq. 4; in the insets, temperatures are in °C; (R) D(T) versus 1/T for 10YSZ (E_a = 1.04 eV) (20) and NiO-YSZ (E_a = 1.16 eV).

Hypothesis that the rate of transfer of the diffusing substance through a unit area of section is proportional to the concentration gradient measured normal to the section, according to Fick’s Law:

\[ \vec{F} = -D \nabla C \]  \hspace{1cm} [2]

where \( \vec{F} \) is the flux of the diffusing substance, \( C \) its concentration, and \( D \) the effective diffusion coefficient.

If the diffusion coefficient is constant, and for an infinite cylinder of radius \( a \) with a constant surface concentration of diffusing species \( C_0 \), the solution for Eq. 2 is

\[ \frac{C(r,t) - C_i}{C_o - C_i} = 1 - \frac{2}{\alpha} \sum_{\alpha n} \exp(-D\alpha_n^2 t)J_0(\alpha_n r) \]

where \( J_0(\alpha) \) are the Bessel function of the first kind, \( C_i \) is the initial concentration inside the cylinder, and \( \alpha \alpha_n \) are the positive roots of \( J_0(\alpha) \) (18). In terms of the measured \( M/M_\infty \) quotient this equation can be transformed into

\[ \frac{M(t)}{M_\infty} = 1 - \frac{2}{\alpha} \sum_{\alpha n} \frac{4}{\alpha_n^2} \exp(-D\alpha_n^2 t) \]

where \( \alpha \) are the positive roots of \( J_0(\alpha) \) (18). In terms of the measured \( M/M_\infty \) quotient this equation can be transformed into

\[ \frac{M(t)}{M_\infty} = 1 - \frac{2}{\alpha} \sum_{\alpha n} \frac{4}{\alpha_n^2} \exp(-D\alpha_n^2 t) \]

In Figure 3 (left) we plotted the results of the isothermal reduction studies performed in Ni-YSZ. We used long enough samples (≈6 mm) compared with diameter (≈1.4 mm) to use Eq. 4. The experimental data are well described by this equation leaving as a fitting parameter the effective diffusion coefficient \( D \).

Effective diffusion coefficients for this compound follow an Arrhenius type law:

\[ D(T) = D_0 \exp(-E_a/kT) \]  \hspace{1cm} [5]
In Figure 3 (right) the effective diffusion values, which control the thermally activated reduction process in NiO-YSZ, are compared with the oxygen diffusion coefficient obtained from conductivity measurements for YSZ (10 mol% Y2O3, single-crystal). The comparison corroborates that the diffusive species in the NiO-YSZ eutectic is very likely the oxygen ion. The oxygen readily diffuses through the eutectic matrix, 5 to 10 times faster than in bulk YSZ. This is probably a consequence of oxygen diffusing through a combination of oxide ions along YSZ and O2 gas along pores. The value for the activation energy ($E_a = 1.16$ eV for the NiO-YSZ) is also a little higher than in pure 10YSZ ($E_a = 1.04$ eV). We believe that this increase in activation energy in the YSZ can be caused by the presence of the transition metal ion impurities dissolved into the YSZ matrix and their associated charge compensating oxygen ion vacancies. This increase in the oxygen vacancy concentration lowers the diffusion coefficient and increases the activation energy in cubic YSZ beyond the optimum vacancy concentration corresponding to the 8YSZ composition (19).

**Aging Experiments; Conductivity Measurements and Hg Porosimetry**

We performed aging experiments under a continuous flow of H2/N2 for 300 hours at 900°C. SEM images taken before and after this treatment showed no evidence of Ni particle coarsening or evolution of the pores. TEM experiments confirmed that the above-mentioned Ni-YSZ interfaces are stable and that they do not present any kind of transformation or evolution after the aging treatment. The connectivity between Ni particles and the size distribution of pores were tested by electrical conductivity and Hg porosimetry measurements respectively. We measured the electrical conductivity of the same sample at RT before and after aging using the DC four-point technique and it showed no signs of degradation. The electrical conductivity of these samples is $(8.9\pm0.9)\times10^5$ S/m, a value about two times higher than in other isotropic cermets previously reported (21,22). This is a consequence of its lamellar microstructure.

We determined the size distribution of pores in the 1.4-mm-diameter samples by Hg porosimetry that averages 200 nm. There are no significant differences between 0 and 300 hr, indicating that there was no evolution of pores, due in part to the lamellar microstructure of the cermet and also to the good bonding between the Ni and YSZ phases, as previously described. Note that the pores are located only in the metal channels, so the open porosity (14.8 vol% from total, 27 vol% from metal channels) is high enough to ensure gas permeation (3).

**CONCLUSIONS**

We produced dense and crack-free rods of NiO-YSZ eutectics by the LFZ method. Growth rate, composition, and diameter were adjusted to achieve a homogeneous eutectic microstructure with interface spacing of about 1 μm. These eutectic rods have been used to study the reduction process of NiO to Ni. The transition metal oxide is transformed to porous metal during reduction, producing a porous microstructured cermet consisting of alternate porous lamellae of Ni (electronic conductor) sustained by the YSZ skeleton (ionic conductor). Diffusion of the O2− ions takes place preferentially along the YSZ phase with activation energies slightly larger than pure 8YSZ due to the presence of Ni2+
doping ions. The interfaces formed during the eutectic growth and maintained during the reduction process give the material a long-term stability.

The electrical conductivity of the reduced eutectics is higher (by a factor of 2) than other isotropic cerments reported in the literature. Open porosity is good enough to ensure permeation of gas. Both properties present no degradation up to 300 hr under work atmosphere at high temperatures.

The thermoelastic properties of the cermet are dominated by the YSZ skeleton, which makes the material very promising as an anode substrate for YSZ thin film electrodes.

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