Colloidal processing and sintering of porous percolative Ni-YSZ layers
Isabel Gonzalo-Juan, Begoña Ferrari, María T. Colomer, A.J. Sánchez-Herencia*
Instituto de Cerámica y Vidrio – CSIC, C/Kelsen, 5, 28049 Madrid, Spain

A R T I C L E   I N F O
Article history:
Received 14 November 2009
Accepted 28 January 2010
Available online 4 February 2010

Keywords:
Percolation
Porosity
Sintering
Electrophoretic deposition
Rheology

A B S T R A C T
Electrocatalytic applications of metal–ceramic composites (CerMet), such as Ni-YSZ materials, require processing adjustments to ensure the structural integrity of porous structures. In this paper, the fabrication of a porous Ni-YSZ (50/50, v/v) material through colloidal processing of Ni particles with a thread like shape is presented. Phase segregation and similar deposition rates for both powders are achieved by milling the suspension and adding a binder. Suspension parameters such as viscosity and homogeneity of dispersed powders are controlled before shaping 500 μm thick self-supported layers by electrophoretic deposition. A thermal treatment that includes an oxidation step at 1100 °C and a reduction step at 800 °C was designed through the thermal and microstructural characterization of Ni-YSZ specimens. The maintenance of the thread like shape of the nickel particles allows the fabrication of percolative and mechanically stable materials with structural density > 80% and porosity > 65%.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Electrocatalytic applications of metal–ceramic composites (CerMet) require processing adjustments to ensure the structural integrity of porous structures. In fact, effectiveness in applications such as solid oxide fuel cells electrodes, electrofilters or membrane reactors is based on the stable conjunction of metal conductivity and ceramic resistance. In this sense nickel is one of the most active catalysts employed, and nickel-zirconia CerMets (Ni-YSZ) are commonly used in methane reforming or oxidation as well as in solid oxide fuel cells. Apart from their electrical properties, the use of zirconia with low concentration of Lewis acid sites results in enhanced catalyst activity, lower coke deposition rate and therefore in more stable catalysts, while the presence of the metal phase confers large sustainability to the porous structure [1–3].

Among the requirements for such applications, the effective use of electrical and ionic conductivities depends on the ceramic and metal percolation throughout the porous structure. In this sense percolation of the phases has been tackled by different design strategies [4] such as the employment of different particle sizes of the insulating and conductive materials [5,6], using particles with thread like morphologies [7] or, more recently, designing the morphology and composition of synthetic particles [8–12]. The processing requirements for the fabrication of this microstructural designs have two critical factors: compaction of green pieces or layers with biphasic powders with nanometric size or thread like particles, and control of the structure development during its consolidation.

Most of the work done in the processing of Ni-YSZ CerMet deals with mixing and shaping studies of ceramic powders (NiO and YSZ powders) and their further sintering and reducing behavior during thermal treatments [13,14]. Both NiO and Ni have a face centered cubic lattice having lattice parameters 4.1769 and 3.5238 Å, respectively. The theoretical densities of NiO and Ni are 6.806 and 8.907 g/cm³, respectively. Hence the reduction of NiO/YSZ composite to Ni/YSZ CerMet is associated to a decrease of the structure volume or an increase of porosity due to the loss of oxygen and crystallographic change. For this reason one of the main problems associated to this processing strategy is the structural stability of the CerMet after reduction, which limits its porosity. During firing, YSZ particles must form a three-dimensional continuous net to assure the functionality of the structure, while withstandng contraction pressures during the reduction of NiO to Ni [15]. Moreover, studies of the Ni-YSZ structure evolution under reduction atmospheres showed the strong tendency of Ni particles towards agglomeration and growth during the NiO to Ni reduction. In these processes, although the volume reduction associated to the NiO to Ni evolution leads to an increase in porosity, it also enhances the decreases in three phase boundaries [16,17].

To improve the metallic phase percolation reducing its concentration in the CerMet, different Ni-YSZ processing approaches have been proposed. Those include several synthesis routes such as sol–gel [8], high-energy milling [9], combustion [15], electroless plating [10,11,18], etc., leading to complex particles [11,12] or infiltrate structures [18]. In this way improvements related to the metallic phase content have been done, achieving percolation lim-
its around 20 vol.% of Ni [18] and increasing the porosity up to 40% without using a pore-former [11].

Regarding the shaping of the metal–ceramic compacts in the green stage, colloidal processing of metals has proved to be a valid tool for the fabrication of metal–ceramic composites [4,19–25]. Processing of metallic powders in a liquid media allows the application of a wide number of shaping techniques, already developed for ceramic suspensions, to fabricate complex shaped samples, or to design complex microstructures like dispersion of second phases or fabrication of multilayers and coatings by tape casting, electrophoretic deposition or dip coating [26–28]. These special microstructures are useful for electrochemical applications where an intimate metal–ceramic joining is required as well as phase distributions which enable the electrical and ionic conductivity. On the contrary the sintering of CerMet structures is a complicated step since pure metal diffusion mechanism starts at relatively low temperatures if compared with ceramic oxides [21]. For that reason sintering cycles have also to be designed to keep the phase percolation in the final structure [20,29].

The objective of this work has been the fabrication of porous metal–ceramic layers with percolative phases shaped by electrophoretic deposition, controlling the sintering behavior of the porous composite to obtain an interconnected metal structure throughout the film. The employment of nickel particles with a thread like morphology as starting material is a key factor in the present study. Nickel oxide cannot be employed because of its poor mechanical properties and brittleness which make materials lose the shape factor during the processing steps. All the mentioned processing steps, such as milling, shaping and sintering, have been optimized to take advantage of nickel high shape factor.

2. Experimental

Nickel (Ni, Nickel 210H, INCO, Canada) and cubic ZrO2 stabilized with 8 mol% Y2O3 (8YSZ, TOSOH, Japan) submicronic powders were used as starting materials. Particle size distributions and specific surface areas of the powders were measured with a laser analyzer (Mastersizer S, Malvern, UK) and by one point N2 adsorption (monosorb, Quantachrome, USA), respectively. Ni powders have a mean particle size of 1.75 μm and a specific surface area of 4.0 m² g⁻¹, while YSZ powders have a mean particle size of 0.35 μm and a surface area of 4.7 m² g⁻¹. Powder densities were determined with a He-multipicnometer (Quantachrome, USA), being 8.3 and 6.0 g/cm³ for Ni and YSZ, respectively [21].

A commercial polyacrylic acid based polyelectrolyte (Duramax D–3005, Rohm and Haas, USA) and a commercial carboxymethylcellulose (CMC, OPTAPIX PA4G, Zschimmer–Schwarz, Germany) were employed as dispersant agent and binder, respectively.

Aqueous suspensions of a Ni/YSZ mixture (50/50, v/v) with solid contents of 10 wt.% (50Ni50Z) were prepared by mixing the powders with water containing 1 wt.% of dispersant (D–3005) referred to solids. The slurry was maintained at pH=10 with tetramethylammonium hydroxide (HTMA) during all the process. Agglomerates were broken off by sonication, using a 400 W probe (Hielscher UP400S, Germany) for 2 min. This slurry was named as “50Ni50Z”. A milling process was also carried out in a 250 mL mill using 15 nylon balls with 5.66 g and 17.27 mm of weight and diameter, respectively for 20 h. The slurry obtained after the milling process was named as “50Ni50Z + M”. Finally, the binder was added to the milled slurry and stirred for 30 min. The latter slurry was named as “50Ni50Z + M + CMC”.

The particle size distributions in the slurries were determined by a laser analyzer (Mastersizer S, Malvern, UK). The rheological characterization was made at the three different preparation stages by control rate (CR) tests using a rotational rheometer (Haake RS50, Germany) with a double cone-plate measurement system. The shear rate was incremented from 0 to 1500 s⁻¹ in 3 min for all the slurries. Fits to rheological models were performed employing the Rheowin 3 data manager program. Layers of 50Ni50Z + M + CMC were shaped by electrophoretic deposition (EPD) performed under galvanostatic conditions applying current densities of 3.8 mA/cm² during 300 s with a power source AMEL (551, UK). Commercial graphite foils (Carbone Lorraine, France) were used as work and counter-electrodes. Substrates were stainless steel (Fe22Cr, chemical composition: 22.3 wt.% Cr, 0.34 wt.% La, 0.48 wt.% Mn, 0.16 wt.% Si, 0.31 wt.% Ti) round plates of 1 cm diameter attached to the work electrode (one of the graphite foils) that were completely dipped in the suspension during the EPD process. Both electrodes were separated a distance of 2 cm from each other. EPD equipment was provided with a lift in order to guarantee a constant withdrawal rate of 7.5 mm s⁻¹. During the deposition process mechanical stirring was maintained at 275 rpm [21].

Green compacts of pure Ni and Ni/YSZ (50/50, v/v) mixture with dimensions of 50 mm × 50 mm × 10 mm were obtained by casting the 10 wt.% suspension used in EPD (50Ni50Z + M + CMC) onto a plater mold. Green densities of the cast compacts were determined by the Archimedes method in mercury. These compacts were used for thermogravimetric (TG) and dilatometric analysis. Thermogravimetric tests were performed with a Perkin-Elmer TGA7 equipment using a heating rate of 5 °C/min from 25 to 900 °C and an air flow of ~60 mL min⁻¹. Dynamic sintering tests were performed on Ni and 50Ni50Z bulk pieces. A push-rod dilatometer (Netzsch, Germany) was used under flowing atmospheres of Ni₂/10 vol.% H₂ or air. Tests were recorded at temperatures up to 1400 °C at a heating rate of 5 °C/min.

A tubular furnace with flowing atmosphere (Severn Furnaces Limited, UK) which uses an Eurotherm programmer was employed for sintering. When it was necessary the sintering atmosphere was purged prior to heating by applying vacuum to the sealed tube and filling it with the desired gas. During the thermal cycle the gas flow was maintained. Gases employed were Ni₂/10 vol.% H₂ and argon. All the gases were high purity standards.

XRD patterns were collected in a D5000, Siemens, Germany diffractometer employing a Kα, radiation (λ = 1.54051 Å) with a Ni filter at room temperature over a range of 30° ≤ 2θ ≤ 70° at a step scan rate of 2° s⁻¹.

Density of the structural skeleton and open porosity for the Ni–YSZ sintered specimens was determined comparing the density measured by helium piconetry (He-multipiconeter, Quantachrome, USA) with theoretical density calculated by the rule of mixtures and the apparent density obtained by the Archimedes method in Hg, respectively. Pore diameter distribution and the mean pore size of the Ni/YSZ (50/50, v/v) specimens were measured using a Hg-porosimeter (Poromaster, PM-338, Quantachrome Instruments, USA). Microstructural observations were made in fracture surfaces by scanning electron microscopy with energy dispersive X-ray spectroscopy analyzer (SEM-EDS) (SEM, Zeiss DSM–400, Germany).

A voltammetry (WTW, LF320, Germany) has been employed to check if the samples are metallic conductors.

3. Results and discussion

3.1. Shaping of the Ni–YSZ layers by colloidal routes

The as-received Ni powder is characterized by a thread like morphology as can be observed in Fig. 1. This shape factor plays a critical role in order to achieve the percolation of the metallic phase in the porous samples with as low as possible amount of Ni and, conse-
quent particle morphology has to be kept during the fabrication process. Also, to ensure Ni percolation a homogenous distribution of the phases in the slurry first and in the compacted layer later has to be achieved.

To promote the homogeneous distribution of the phases the 50N50Z slurry with a solid content fixed at 10 g/L was ball milled during 20 h. Particle size distributions of the suspensions before and after the milling process are shown in Fig. 2. It can be observed that a bimodal distribution curve is obtained before milling, with particle sizes ranging from 1 to 100 μm due to a high agglomeration degree of the powders in the suspension, even after the sonication process. After the milling process a monomodal curve with a narrower particle population is obtained. In the latter case, the curve shows a negative bias distribution since the medium value of 1.53 μm is obtained. In the latter case, the curve shows a narrow mode of the statistical population, 1.7 μm, is the same that the average particle size (Dv50) of the Ni and the value of Dv10 < 0.3 μm in the asymmetrical distribution curve verifies the presence of the dispersed YSZ particles. Those data indicate that after the milling process the achieved suspension is a mixture of Ni and YSZ particles homogeneously dispersed.

During the packing of the particles to form the final shaped green sample there are possibilities of phase segregation, inhomogeneities, sedimentation, or other phenomena associated to the different densities of the metal and ceramic phases. To ensure the homogenous distribution of the compounds during the forming process the rheological behavior of the slurries has been characterized at different stages. Fig. 3 shows the viscosity versus shear rate curves registered in control rate for the sonicated slurries (50N/50Z), sonicated and milled (50N/50Z + M), and after addition of the binder (50N/50Z + M+CMC). In the three cases a shear thinning behavior is observed. Shear thinning, or pseudoplasticity, is characterized by a decreasing viscosity as the shear rate increases, being specially important the viscoelastic transition zone at the lower shear rates [30]. This shear thinning has been previously observed in aqueous nickel and nickel-alumina slurries employed for colloidal processing [22,31].

Shear thinning of fluids can be fitted to the Cross model in order to obtain the values of a zero-shear viscosity and infinite-shear viscosity [32]. Zero-shear viscosity (η0) is the extrapolation of viscosity for non-Newtonian liquids to zero shear and determines the behavior of the just consolidated body. On the other side of the shear thinning curve is the infinite-shear viscosity (η∞) which is defined as extrapolation of viscosity for non-Newtonian liquids to infinite shear. Cross model is described by the formula:

$$\frac{\eta - \eta_{\infty}}{\eta_0 - \eta_{\infty}} = \frac{1}{1 + (K \dot{\gamma})^m}$$  \hspace{1cm} (1)

where K has the dimensions of time, and m is dimensionless. When this model is used to describe the non-Newtonian behavior of suspensions, the degree of shear thinning is associated to the value of m. Values of m tending to zero are achieved for Newtonian fluids while the most shear thinning liquids present values of m tending to unity [32]. The rheograms presented in Fig. 3 were fit to the Cross model achieving for all the cases a r² > 0.999. Table 1 summarizes the parameters obtained with these fits.

Sonicated slurry (50N50Z) presents a η0 value of 1.17 Pa s−1 and an infinite-shear viscosity, η∞, of 5.33 mPa s−1. The milling process increased the value of η0 to 2.23 Pa s−1 but decreased the value of η∞ to 4.12 mPa s−1. The increment in the value of η0 is due to the increment of the surface area during the milling process and the breaking of the agglomerates which allows higher interactions between particles in the stationary slurry. The decrease in η∞ is a consequence of the reduction of the size of the particles and
their homogeneous dispersion. Finally, as expected, the addition of the 1 wt.% CMC to the milled slurry as binder increases both the zero-shear viscosity and the infinite-shear viscosity of the suspension. This fact ensures that after consolidation the samples will preserve the layer thickness and shape. It is also remarkable that "m" value is high in all the cases, indicating that processes associated to the shear thinning behavior are not depending on the processes or additives employed to fabricate the slurry. The use of a short chain CMC did not have any dispersing effect because the slurry is already dispersed by the polyacrylate used for milling and it only affected the rheology by increasing the viscosity of the suspension.

The layers were fabricated from 50N50Z+M+CMC suspensions by EPD onto stainless steel substrates applying a current density of 3.8 mA/cm² during 300 s. During the deposition process the suspension was stirred at 250 rpm, which corresponds to a shear rate of 770 s⁻¹. Stirring avoids the Ni settling due to its elevated density and consequently the phases segregation in the suspension during the EPD process. Moreover, it also maintains the viscosity values out of the viscoelastic zone and, consequently, ensures stable viscosity values during the EPD improving its reliability. Fig. 4 shows the microstructure of a green stage deposit obtained by EPD, where the white, grey and dark areas represent the nickel, YSZ, and pores, respectively. The thread morphology of the Ni powders homogeneously mixed with the YSZ is evident in the micrograph. Also, this micrograph confirms that the milling process contributes to the particles dispersion and to the mixture homogenization in the suspension if it is compared with the materials prepared under similar conditions but using an unmilled suspension [21]. Additionally, it proves that after milling Ni and YSZ powders keep their initial morphology. The homogeneous packing of Ni and YSZ points out that electrophoretic movement of particles has been continuous and independent under the selected dispersing conditions.

### Table 1

<table>
<thead>
<tr>
<th>Slurry</th>
<th>( \eta_0 ) (Pa s⁻¹)</th>
<th>( \eta_\infty ) (Pa s⁻¹)</th>
<th>( \eta_r ) (s)</th>
<th>( K )</th>
<th>( m )</th>
<th>( r )</th>
</tr>
</thead>
<tbody>
<tr>
<td>50N50Z</td>
<td>1.16</td>
<td>0.005333</td>
<td>3.493</td>
<td>0.894</td>
<td>0.9996</td>
<td></td>
</tr>
<tr>
<td>50N50Z+M</td>
<td>2.23</td>
<td>0.004127</td>
<td>3.49</td>
<td>0.816</td>
<td>0.9988</td>
<td></td>
</tr>
<tr>
<td>50N50Z+M+CMC</td>
<td>12.54</td>
<td>0.02122</td>
<td>0.119</td>
<td>0.881</td>
<td>0.9990</td>
<td></td>
</tr>
</tbody>
</table>

Values of zero-shear viscosity \( \eta_0 \), infinite-shear viscosity \( \eta_\infty \), and characteristic constants \( K \) and \( m \) obtained by fitting of the viscosity versus shear rate curve to the Cross model. The correlation coefficient \( r \) is also indicated.

In order to maintain the nickel morphology while promoting neck growth between particles at high temperature, oxidation of nickel has been performed by thermal treatments in air. Fig. 5 shows the thermogravimetric (TG) curves for pure Ni and 50N50Z+M+CMC green compacts in air. In the 50N50Z+M+CMC curve it can be observed a first mass loss of about ~2 wt.% between 250 and 300 °C. This is associated to the burning out of the dispersant and binder CMC added during the compact preparation. As the pure nickel samples have been prepared without additives no weight loss is observed for them. After this first process, a weight gain of 18.9% in the Ni compact and 11.4% in the 50N50Z+M+CMC compact can be observed. This weight increase is due to the oxidation of Ni in both cases. As expected the maximum value for the 50N50Z+M+CMC compact is close to half of the one recorded in the pure nickel curve. In fact, if removal of organic is taken into account, the final weight gain for 50N50Z+M+CMC compact is 20.15%. The theoretical weight gain associated to the total oxidation of pure Ni to NiO is of 27.3 wt.% and the lower value recorded in the sample can be explained by the presence of a remaining metallic nickel core in the oxidized particles. The calculated amount of remaining nickel is around 15%. Except for the organic removal, the temperature of the maximum oxidation rate and the temperature where the maximum oxidation value is achieved are similar.

3.2. Thermal characterization of Ni-YSZ layers and design of the sintering cycle

Fig. 6 shows the XRD spectra recorded for the processed samples of pure Ni (Fig. 6a–c) and 50N50Z+M+CMC (Fig. 6d and e) in the green stage and after thermal treatment at 1100 °C in air. In addition, the sample of oxidized Ni was crushed in an agate mortar and the XRD pattern registered (Fig. 6c). In plots 6a and 6d, which correspond to the green samples, it can be observed the presence of metallic nickel without any evidence of oxidation during the shaping process. Spectra shown in plots b and c correspond to samples after the thermal treatment. In these samples no evidence of metallic nickel was detected indicating a complete oxidation of nickel particles. However, these data are not in agreement with the TG curves that suggest the presence of a remaining metallic nickel fraction. The presence of this metallic nickel is confirmed in the XRD pattern of the crushed sample presented in plot c. In this figure the peaks corresponding to both Ni and NiO are observed. The TG and XRD results showing the presence of metallic and oxidized nickel after crushing indicate that at 500 °C the compact is formed by a core of metallic Ni (26 wt.% of the initial Ni) covered by...
a ceramic crust of NiO (74 wt.% of the initial Ni). No further oxidation is expected due to the shield effect of the NiO crust.

Dynamic sintering studies (Fig. 7) were performed under both air and N₂/10% H₂ atmospheres for 50N50Z + M + CMC and Ni composites, both of them prepared by slip casting. Green samples showed a green density around 30 th.% which is a very low value for a slip casting process. This low density is a consequence of the high viscosity and the low solids content of the slurry and it is necessary to achieve a high porosity after the sintering process. It can be observed that the pure nickel compact under reductive atmosphere starts to sinter close to 120 °C and has the maximum shrinkage rate around 450 °C. As expected this characteristic temperatures are lower than those recorded for compacts processed by a similar route with bigger nickel particles [21,22]. Densification finishes around 1000 °C with a final shrinkage close to 50%. This high shrinkage is a consequence of the low green density of the compact and the high atomic mobility of nickel. In the curve recorded for the nickel compact in air it can be observed that nickel oxidation inhibits the sintering process. At low temperature, densification starts at 200 °C but as the expansion associated to oxidation makes the sample to recover its dimensions only a small peak centered at 325 °C is observed. The sintering of the nickel oxide crust (described in the XRD discussion) starts at 610 °C having its maximum rate at 825 °C. Densification process finishes at 1130 °C and only shrinkage of 8.6% is achieved. As the starting packing density is very low and mobility of oxide is also very low, densification of the sample does not go forward.

These data obtained for the pure nickel samples are going to be useful to discuss the sintering behavior of sample 50N50Z + M + CMC where a different sintering behavior under reductive or oxidative atmosphere is observed. Under the reductive one densification starts at 200 °C as diffusion between nickel particles joins them. This process stops at 595 °C where the zirconia takes control of the sintering behavior of the compact [17]. Densification resumes at 920 °C as zirconia particles start to sinter reaching a maximum rate of shrinkage at 1335 °C. At the final temperature of the experiment (1400 °C) the samples have shrunk a 33%. It should be noted that at this temperature the densification process has not finished yet. The dilatometry recorded for the 50N50Z + M + CMC composite sintered in air shows characteristic behaviors of both Ni in air and composite in reductive atmosphere. As it happens for the Ni compacts in air, nickel particles start to sinter at low temperature (215 °C) but oxidation of nickel inhibits the densification and recovers the dimensions of the sample showing a small peak centered at 400 °C. The sintering process stops at 450 °C and does not restart until 920 °C are reached. It should be noted that the presence of the zirconia inhibits any sintering process of nickel (nickel oxide actually) at 610 °C as was observed at this temperature in the sintering curve of nickel in air. This different behavior at this intermediate temperature is due to the high atomic mobility of metallic nickel that overcomes the blocking effect of the zirconia. Finally at temperatures higher than 920 °C zirconia particles control the densification process in a similar way to that observed in the 50N50Z + M + CMC composite under reductive atmosphere. The maximum shrinkage rate is achieved at 1375 °C and finally the sample shrinks a 20%. As previously observed for reductive atmosphere, at the maximum temperature of the experiment (1400 °C) densification of the sample has not finished.

These results indicate that the oxide shell surrounding the nickel core of thread like particles (verified by TG and XRD analyses) makes the metal-containing samples sinter as a ceramic–ceramic composite. Even more, ceramic characteristic of both components holds up the sintering at the beginning of the shrinkage process providing the sample with porosity and strength enough for its further applications. Based on these dilatometric results a thermal cycle has been designed to fabricate porous materials while maintaining the percolative characteristics of nickel. The cycle starts in air by a 5 °C/min heating ramp in air up to 1100 °C where sample is kept for 1 h and continues with a 5 °C/min cooling ramp down.
Fig. 8. Thermal cycle designed to keep the percolative characteristics of nickel after sintering in the 50N50Z + M + CMC composite.

Fig. 9. SEM pictures of the 50N50Z + M + CMC CerMet after sintering at 1100 °C for 1 h in reductive atmosphere. Ball shaped grains with a diameter around 1–2 μm are metallic nickel and small grains with diameter lower than 0.5 μm are YSZ.

Fig. 10. Micrographs on the fractured surfaces of the 50N50Z + M + CMC composite after the thermal cycle. (a) General view of the layer; (b) close up to observe the open porous structure; (c) closer view where nickel threads and zirconia particles have been identified.

to 800 °C. In this first part the nickel oxidizes and the NiO/ZrO₂ composite starts to form necks, as it can be inferred from Fig. 7. Later, at 800 °C the sintering chamber is purged with an Argon flow for 1 h and the flowing atmosphere is changed to a reductive one (N₂/10 vol.% H₂). Sample is kept under this atmosphere and temperature conditions for 1 h and then cooled down to room temperature at 5 °C/min maintaining the reductive atmosphere. During this step the NiO shell is expected to be reduced to metallic nickel [29].

For comparative purposes 50N50Z + M + CMC layers were also sintered at 1100 °C for 1 h under a flowing N₂/10 vol.% H₂ atmosphere with cooling and heating rates of 5 °C/min. Fig. 9 shows the microstructure of this specimen. It can be observed that porosity of the sample is maintained, but at this sintering temperature the metallic nickel particles have lost the shape factor to adopt a spherical morphology that is thermodynamically more stable than the linear one. The random and homogeneous distribution of 1 or 2 μm in diameter Ni grains mixed with the YSZ ones inside the porous matrix does not allow the percolation of Ni. Consequently this sample does not show the electronic conductivity throughout the film required for both catalytic and mechanical applications such as SOFC cathodes or electrofilters. In this case, the neck formation between YSZ particles confers mechanical stability to the structure.

For samples treated with the thermal cycle designed to maintain the percolation paths of the metallic nickel the electron micrographs show different microstructures to those observed in samples sintered under reductive atmosphere. Fig. 10a–c presents different magnifications of the fracture surface of a 50N50Z + M + CMC layer processed by EPD after the thermal treatment indicated in Fig. 8. Micrograph in Fig. 10a shows the cross-section of the 500 μm thick layer shaped by EPD, while Fig. 10b and c shows deeper details on the microstructure. Microstructure presented in Fig. 10b shows that there is no significant evolution in the sense that both Ni and YSZ phases maintain their “green” morphology after the thermal treatment. This point can be more clearly appreciated if this microstructure is compared to the green one showed in Fig. 4. The sole difference between both materials is due to the formation of necks between particles. These necks have been developed from the oxide particles keeping the open structure, maintaining the starting shape and providing the sample with enough strength for handling. A closer vision of the microstructure (presented in Fig. 10c) shows that phases are interlinked and create a continuous web throughout the whole material.

The chemical analysis (EDX) performed on this sample confirms that the white and grey areas correspond to Ni and YSZ respectively and it shows that metallic part retains the thread morphology. The strong influence of the thermal cycle on the microstructure can be
pointed out if micrograph shown in Fig. 10c is compared with that observed in Fig. 9.

The percolation of the nickel particles within the sample has been confirmed by means of a rough electrodeity test measured with a voltammeter. In the sample thermally treated in pure reductive atmosphere (Fig. 9) the nickel arrangement in spheres avoids the percolation of Ni and no electrical signal was detected throughout the film. Conversely, the samples calcined according to the thermal treatment depicted in Fig. 8 present electrodeity, thus indicating that Ni percolative paths have been kept. Cross sections were cut and tested in order to ensure that electrical conductivity is not only a surface phenomenon. Once the thermal cycle has been optimized to maintain the cross-linked structure of Ni throughout the sample, further and deeper studies are required in order to evaluate the range of film conductivities and determine the lowest amount of Ni needed to ensure its percolation throughout the whole structure.

Theoretical density calculated by the rule of mixtures considering densities of 6.0 and 8.2 g/cm³ for YSZ and Ni powders, is 7.1 g/cm³. The density of different Ni-YSZ specimens was measured by He picnometry and the Archimedes method in Hg. Results show that the structure skeleton of the Ni-YSZ porous specimens has a density of 5.9 ± 0.4 g/cm³, whereas apparent density is 1.7 ± 0.2 g/cm³. That means that the obtained Ni-YSZ structure in the porous layer has a density >80% of that calculated from the rule of mixtures and a porosity >65%. Pore size distribution for this material is presented in Fig. 11. A monomodal distribution with an average porous diameter of 0.5 µm and with minimum and maximum pore diameters of 0.2 µm and 4 µm, respectively, is observed. Within a pore diameter range between 5 and 10 µm also three small peaks can be observed. All the peaks are considered to be in the open macroporous range.

Summarizing, by keeping the thread morphology of Ni particles, the percolation of the metallic phase within the sample and the high degree of open porosity (>65%) in a stable structure can be ensured. Consequently, these materials meet the requirements for catalytic applications, where keeping the intrinsic and electronic conductivity as well as the catalytic triple points (nickel, zirconia and gas) during the sintering process is a critical point.

4. Conclusions

The employment of metallic nickel particles with a high shape factor strongly affects the properties of metal/ceramic composites and allows the fabrication of structurally stable porous materials.

The shape of the powders determines the processing steps and the final performance in use. It has been proved that controlling the slurries, a high dispersion of nickel particles with a thread like morphology in the ceramic matrix can be achieved and shaped by EPD to obtain homogeneous percolative porous metal–ceramic layers 500 µm thick.

Sintering of these composites in reductive atmosphere makes the nickel lose its shape factor and consequently the electrical conductivity throughout the structure. Nickel percolation can be achieved by maintaining the particle shape through the design of a thermal treatment based on thermogravimetric and sintering studies. The cycle consists of three steps: previous oxidation of the nickel particles, neck formation between particles at high temperature and further reduction of nickel oxide to the metallic form. The final stable material consists of a structure formed by a continuous three-dimensional (3D) network of Ni, YSZ and pores where, the Ni/YSZ skeleton has a density of 80 th. % and the open porosity is close to 65 vol. %. This layer should allow the ionic (electrolyte) and electronic (metal) charge transport as well as gas-phase transport.

Acknowledgements

This work has been supported by Spanish Administrations under contracts MAT2006–01038, MAT 2009–14448–C02–01 and CCG08–CSIC/MAT–3811.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.memsci.2010.01.060.

References


Fig. 11. Pore size distribution of the 50N50Z + M + CMC after the thermal treatment.


