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Sinterability, microstructures and electrical properties of Ni/Gd-doped ceria cermets used as anode materials for SOFCs

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Abstract

The influence of Ni content in Ni–CGO cermets on their electrical conductivity was investigated in order to create the most suitable microstructure. Ni–CGO (50/50, 45/55 and 40/60 wt%) powder mixtures were prepared by the polymeric organic complex solution method using ethyleneglycol as a polymerized soluble alcohol in water. By heat treatment a composite of ultrafine nickel oxide homogeneously dispersed in the CGO ceramic matrix was attained. After sintering of NiO–CGO composites in air at 1350 °C for several times and reducing treatment in N_2 90%–H_2 10% atmosphere, the microstructures showed a uniform distribution of porous metallic Ni particles surrounded by microporous spaces with total porosity (closed and opened) of ≈20–25%. The electrical properties of Ni–CGO cermets sintered at 1350 °C for 2 h were studied using impedance spectroscopy in the temperature range from 500 to about 700 °C in argon atmosphere. The Ni–CGO cermets showed metallic behaviour over all the range at temperatures studied, indicating a uniform and fine-grained microstructure in which the Ni–Ni particle contacts were predominant.

Keywords: Powders-chemical preparation; Sintering; Microstructure-final; Electrical conductivity; Ni-CGO cermet

1. Introduction

The CeO_2-based materials are an upcoming alternative solid electrolyte to yttria stabilized zirconia (YSZ) in solid oxide fuel cell (SOFC) applications. They have higher ion conductivity and lower ohmic losses than YSZ, and can also operate at lower temperatures (600–800 °C). These electrolytes based on ceria require special electrodes with a high performance and thermomechanically and chemically compatible.

Ni has been commonly used as anode material for SOFCs due to its high catalytic activity for the dehydrogenation of hydrocarbons as well as a highly electronic conductivity. The introduction of Ni into the doped ceria matrix would be a way to acquire sufficient electronic conductivity in order to prevent lateral electrical losses, therefore cermets based on doped ceria may be preferred for a high performance of the electrodes. The important functions of the CGO particles in the Ni–CGO cermet would be to: (a) supply oxide ions to the TPB, (b) suppress the sintering of Ni, and (c) match the thermal expansion coefficients between the cermet and the CGO electrolyte.

The electrical properties of a Ni–CGO cermet can be explained by percolation theory where the role of the microstructure it is very important for a satisfactory behavior of the anode material. Ni particles in the cermet should be connected to CGO particles (oxide ion supplier) and also exposed to H_2 gas. Kawada et al. [1] have demonstrated that the preparation process is of importance in controlling the electrode stability and performance and it has been shown that optimization of the anode microstructure by decreasing the particle size of the Ni phase would increase the length of Ni–CGO triple phase boundaries, and thus improve the anodic performance. Recent studies[2–4] on Ni/rare-earth-doped ceria cermet preparation are focused towards achievement of a uniform distribution of fine Ni particles in the ceramic matrix using different preparation techniques. In the present work, a polymeric organic complex solution method was used to prepare NiO/$Ce_{0.9}Gd_{0.1}O_{1.95}$ (NiO–CGO) composites and the influence of Ni content in electrical conductivity was studied in order to identify the most suitable microstructure.

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2. Experimental

NiO/$Ce_{0.9}Gd_{0.1}O_{1.95}$ powders with three different proportions[5] (50–50, 45–55 and 40–60 wt%) were prepared by the polymeric organic complex solution method. Aqueous solutions of corresponding nitrates were mixed by stirring with nitric acid and ethylenglycol. The as-obtained solutions were treated thermally in three steps, 80 °C for 24 h, 120 °C for 4 h and 220 °C for 24 h in oven to obtain a black resin embedding the NiO–CGO particles. After milling in an Agatha mortar, the resin was calcined at 800 °C for 1 h and attrition milled for 2 h in ethanol with zirconia ball media. X-ray analysis was performed in order to identify the present phases using a diffractometer Siemens (model D-5000, Erlangen, Germany), with Cu Kα radiation and Ni filter, and the BET surface area of the calcined powder was measured using a Quantachrome Accusorb instrument. Thermal analysis (TG/DTA, Netzsch model STA-409, Germany) was used for further characterization of the powders.

After attrition milling, the powder was pressed in pellets at 200 MPa and the shrinkage behaviour was studied using a dilatometer Netzsch (model 407/E, Selb-Bayern Germany) up to 1550 °C with a heating rate of 2 °C/min and a cooling rate of 5 °C/min. After sintering pellets in air at 1350 °C for 2 h, the samples were reduced using a N_2/H_2 (90–10%) atmosphere at 700 °C for 2 h. After polishing and thermal etching, the microstructures of the sintered samples (non-reduced and reduced) were examined by scanning electron microscopy in a Zeiss Microscope (model DSM 950, Oberkochem, Germany). Impedance was measured from 150 up to 700 °C in argon using a LF Impedance analyser (model HP-4294A, Hewlett-Packard).

3. Results and discussion

3.1. Characteristics of NiO–CGO powder

The simultaneous TG/DTA curves for the different prepared powders during heating of the dried polymeric gel between room temperature and 1000 °C, revealed the same thermal features in all cases and, for clarity, only that corresponding to the composite NiO–CGO 50 wt% is shown in Fig. 1. The TG curve shows a total weight loss of about 50% up to1000 °C, due to evolution of carbon compounds (CO or CO_2) and elimination of nitrates (N_2, NO and NO_2). According to DTA curve it is found that in a small range of temperature of about 280 °C takes place an abrupt exothermal peak, which is due to the autocombustion reaction from the decomposition of the polymeric gel. After combustion the material had a black colour which remained throughout all the powder processing.

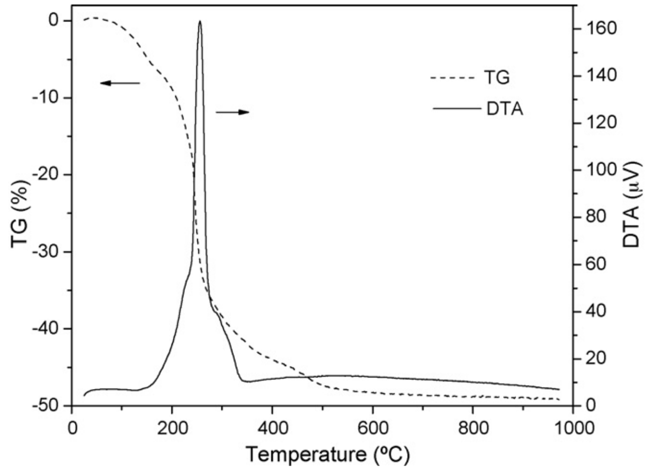

Fig. 1. TG and DTA curves corresponding to the gel precursor of the NiO–CGO 50 wt% composition.

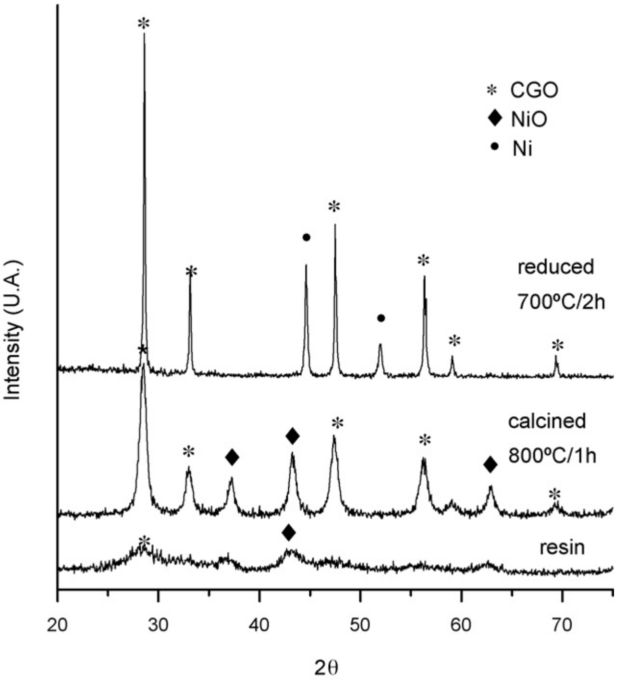

Fig. 2. XRD patterns of NiO–CGO 50 wt% (a) resin, (b) calcined at 800 °C/1 h and (c) alter reduction in 90% N_2–10% H_2 at 700 °C for 2 h.

Fig. 2 shows XRD patterns of NiO–CGO resin, calcined and reduced composite powder. It is possible to appreciate that the polymeric resin is a composite organic matter that should contain metallic cations and this resin stayed like this up to 280 °C, whose XRD analysis is not shown here. After calcination the synthesized powder was a composite consisting of NiO and $Ce_{0.9}Gd_{0.1}O_{1.95}$ crystalline phases and after reduction only Ni metal and $Ce_{0.9}Gd_{0.1}O_{1.95}$ phases were present, i.e., NiO traces were not identified.

The powders calcined at 800 °C for 1 h were highly sinterable and in all cases showed high specific surface areas, especially in the composition NiO–CGO 50 wt%. In all cases an average agglomerated particle size calculated by BET ($D = 50\%$) was $\sim 1.5 \pm 0.7\ \mu m$. The calculated equivalent particle diameter, taking into account the BET analysis and using the equation $d_{BET} = 6/S\rho$, where ρ is theoretical density and S specific surface area, are smaller in all cases, $\approx 0.04 \pm 0.02\ \mu m$. These results indicate: (a) a certain agglomeration level of particles, and (b) powders obtained are nanometric and consequently highly sinterable. Specific surface and particle diameter of powders containing 50, 45 and 40 wt% NiO after calcination at 800 °C for 1 h in air are shown in Fig. 3.

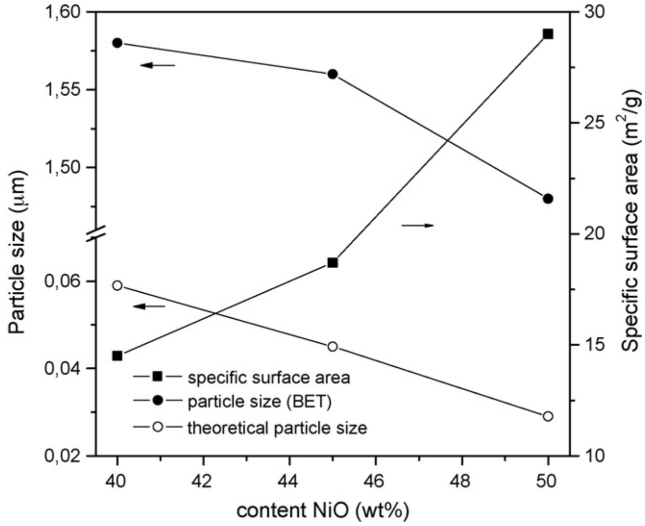

Fig. 3. Particle size and specific surface evolution as a function of NiO content within NiO–CGO powders calcined at 800 °C in air.

3.2. Sintering behaviour and microstructure developing

As it can be observed in Fig. 4a, the shrinkage rate curves of samples were similar for composites NiO–CGO 45–55 and 40–60%, in these cases the sintering process takes place with the appearance of two maximum shrinkage peaks: a small one at about 875 °C, and a higher at about 1350 °C. Between them an inflexion point at approximately 1000 °C occurred, i.e., the densification of the composites NiO–CGO takes place in a two-stage process. When the NiO content increases up to 50 wt%, the first peak slightly shifted to higher temperatures with broader distribution, indicating a more gradual densification, although reaches the maximum of densification rate (second peak) at a similar temperature, 1350 °C. Although that temperature corresponding to the maximum densification rate does not depend of NiO content, the shrinkage rate is dependent and increases with the NiO content by a factor of 4–6. The linear shrinkage of the samples as a function of the temperature as well as relative density is shown in Fig. 4b. The sintering shrinkage of all samples begin at a relatively low temperature (800 °C), but a lower end point temperature was achieved for the NiO–CGO 50 wt% samples, and a higher density was attained, 96.8% relative density versus 93.80 and 92.07% relative density, for 45 and 40 wt% NiO, respectively. The difference in the shrinkage behavior between them, can be due to the higher sintering characteristics of the NiO powder, i.e., NiO particles have a higher contraction and this phenomenon allow a normal sintering process of the CGO ceramic phase with trapped NiO particles into.[5]

Fig. 5 shows the evolution of the density and grain size of CGO phases for the samples sintered at 1350 °C in air as a function of the sintering time. The relative density increases with sintering time. The grain size of CGO does not depend on sintering time (CGO grain size increased only up to about 0.3–0.4 μm at 1350 °C for 2 h), these results indicate that the presence of NiO grains intergranularly located retard the grain growth of CGO

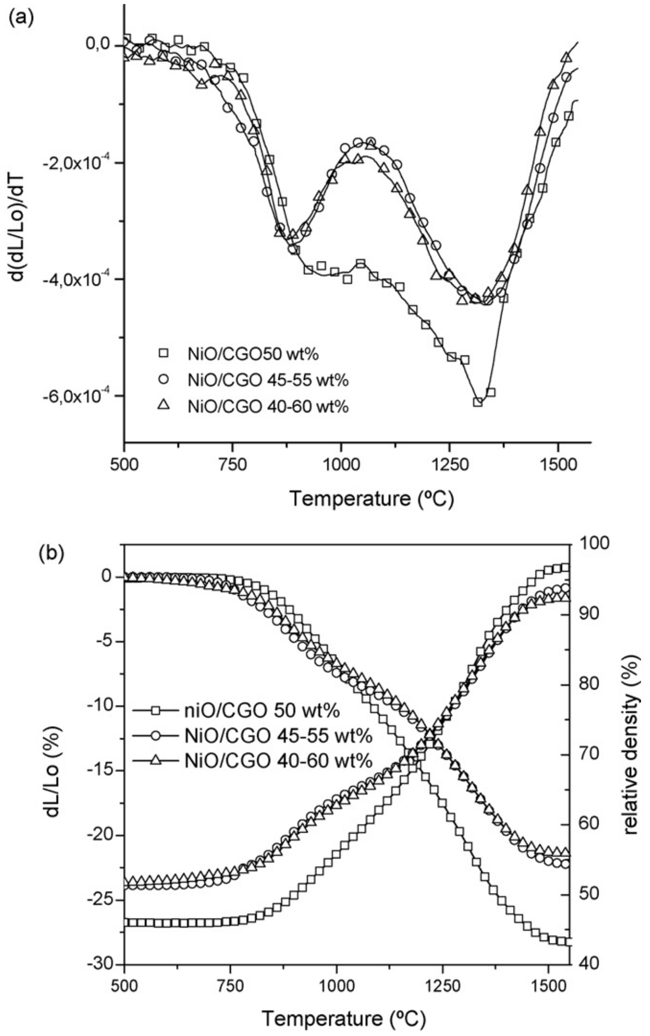

Fig. 4. (a) Shrinkage rate spectra and (b) linear shrinkage behaviour of NiO–CGO composites vs. sintering temperature.

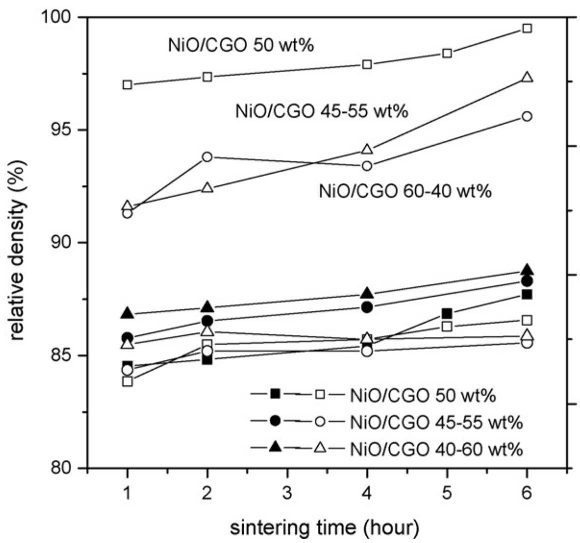

Fig. 5. Relative density and average grain size as a function of the sintering time for NiO–CGO composites sintered at 1350 °C in air.

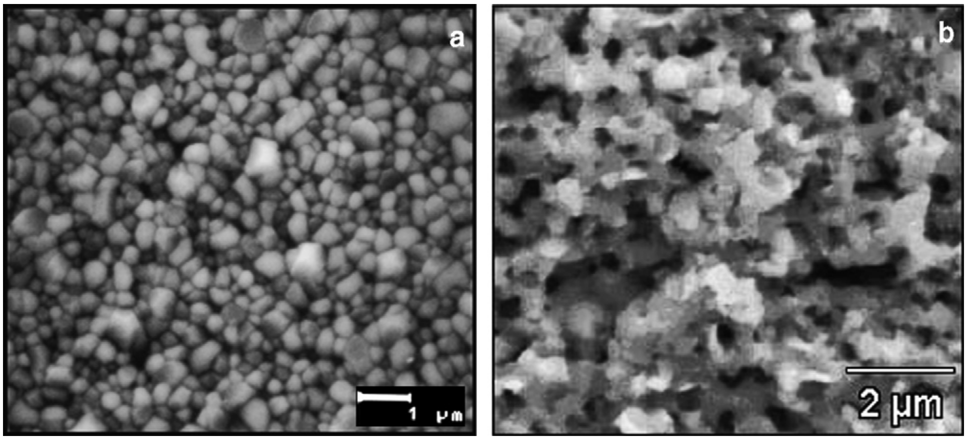

Fig. 6. SEM micrographs of composite NiO–CGO 50 wt% sintered in air at 1350 °C for 2 h (a) before reduction and (b) after reduction.

Table 1
Main characteristics of the cermets sintered at 1350 °C for 2 h

NiO content (wt%)	Ni content after reduction (wt%)	Total porosity after reduction (%)	σ_T (700 °C) (S/m)	E_a (kJ/mol)
40	29.91	23.6	51.87	4.73
45	34.37	24.7	63.46	3.81
50	39.03	25.1	68.07	3.15

grains, it is the phenomenon namely known as pinning effect. A similar suggestion was reported by Dees et al.[6] for cermets based on Ni/YSZ.

In all cases microstructures were similar, for clarity, only the corresponding to NiO–CGO 50 wt% is shown. Fig. 6a shows the microstructure after sintering at 1350 °C for 2 h before reduction. Although the contrast between nickel and CGO is low because of the small difference in average atomic weight, it was possible to distinguish with relative clarity between two kinds of grains, by using back-scattered electrons, darkish and brighter. EDX analysis revealed that the darkness grains were NiO, and brighter-looking grains were CGO. The microstructures were dense and fine-grained, with a homogeneous distribution of the two NiO and CGO phases. After reduction (700 °C/2 h using a N_2/H_2 (90–10%) atmosphere), Fig. 6b shows the fracture of Ni–CGO cermets with a uniform distribution of porous/spherical Ni particles surrounded by CGO particles. Such as microstructures present good connections between Ni–Ni, CGO–CGO, and Ni–CGO grains and high-interconnected porosity, which is essential to improve the triple phase boundary (TPB) area where reaction takes place, between gas, Ni and ceramic. The Ni particles present a similar average grain size as before reduction, which indicate that a grain growth process does not take place during reduction process. The obtained microstructures could enhance significantly the performance characteristics of Ni–CGO anode cermet, because, as it is known, that depends strongly of the Ni particles distribution in the ceramic matrix, increasing the number of active sites at the boundary between Ni (electronic conductor), CGO (ionic conductor) and H_2 gas (fuel). A similar phenomenon was observed in the case of Ni–YSZ cermets.[7]

3.3. Electrical properties

The function of nickel phase in the composite material is to serve as an electrocatalyst for hydrogen oxidation and to provide the anode with high electrical conductivity. To satisfy these conditions, the Ni phase must become continuous, in this case nickel grains can act as a continuous metallic medium allowing the electrons to migrate throughout the material. This requires an appropriate microstructure which depends on cermet morphology and a threshold value of Ni content, from our studies not presented here, is considered that the boundary between an essentially ionic and essentially electronic conduction is located

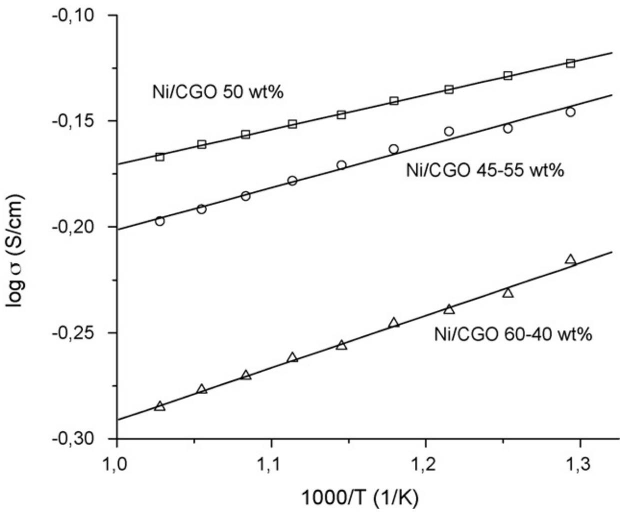

Fig. 7. Arrhenius plot for the total electrical conductivity of the Ni–CGO cermets.

about 29 vol.% NiO. The easiest way to verify the continuity of the nickel phase is to measure the electrical conductivity of the cermet. According to the impedance measurements, all samples are electronically conducting. The relatively high value of electrical conductivity at 700 °C which is close to the conductivity of pure metallic nickel (70 S/m at 700 °C) proves that the nickel phase is continuous (see Table 1). The temperature dependence of the conductivity (σ) can be described by the Arrhenius equation: $\sigma = \sigma_0 \, e^{E_a/T}$. The activation energies (E_a) for the samples are given in Table 1. From the Arrhenius plot (Fig. 7), it can be seen that the equation fits the data over the temperature range studied and that the electrical conductivity decrease with increasing temperature (besides for lower Ni content), which is characteristic from a pure metallic electronic conductor. This behaviour verifies again the continuity of the nickel phase, with predominant Ni–Ni contacts, demonstrating that there is not sintering of Ni particles.

4. Conclusion

Nanometric powders NiO–$Ce_{0.9}Gd_{0.1}O_{1.95}$ with highly sinterizable characteristics were prepared by the polymeric organic complex solution method. Sintered composites NiO–CGO exhibit adequate microstructures and after reducing Ni–CGO cermets present a uniform distribution of spherical particles Ni surrounded by a pore space and by the CGO particles. Such microstructures could improve the TPB area between gas (H_2), Ni (electronic conductor) and CGO (electrolyte with a high ionic conductivity). The mixed oxygen ion-electronic conduction with ≥40 wt% NiO content is governed by the electronic metallic conduction, suggesting predominant Ni–Ni connectivity. To enhance electronic conductivity, the cermet should have a NiO content higher than 50 wt%.

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