Microstructure, texture and crystallography in Ni-GDC and Co-GDC porous cermets obtained from directionally solidified eutectic ceramics

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Abstract

Lamellar NiO-GDC (Gadolinium-doped Ceria) and CoO-GDC Directionally Solidified Eutectic Ceramics (DSECs) were produced by the laser floating zone (LFZ) technique and subjected to reduction in order to obtain porous cermets of Ni-GDC and Co-GDC, which have potential applications as anodes in solid oxide fuel cells (SOFC). The reduction of these DSECs into porous cermets was studied at 650 °C in NiO-GDC and at 500 and 700 °C in CoO-GDC, all of them processed with similar reduction kinetics. In comparison to similar Ni-YSZ and Co-YSZ lamellar cermets previously studied, no sharp reduction front was observed. The interface between the reduced and non-reduced zones is broader, with pores homogeneously distributed in wide areas. Afterwards, the microstructure, texture and crystallography of the samples were studied by electron microscopy as well as by electron and X-ray diffraction when completely reduced. The single crystal NiO and CoO lamellae transformed into porous polycrystalline metallic lamellae. Moreover, microscopy observations revealed a porous nanostructure of Co particles obtained by reduction at low temperatures (500 °C). Many of the Co and Ni particles seemed to have roughly maintained the previous crystallographic orientation with respect to the GDC phase, although the disorder of the crystallographic orientation increased significantly. In addition, a significant amount of the Ni particles reoriented to form an epitaxial interface with the (100)-GDC surface.

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1. Introduction

Composite materials of metals and ceramics, also referred to as cermets, have been widely studied for their use in many applications, for instance as anodes for solid oxide fuel cells (SOFCs) [1]. The most commonly used anode material in high and intermediate-temperature SOFCs, which use yttria-stabilized-zirconia (YSZ) as the electrolyte [2], is the porous cermet of Ni and YSZ [3]. Cobalt can be used instead of nickel, since it provides similar electric conductivity, while enhancing the catalytic properties and sulfur tolerance of the anode [4]. Due to its lower activation energy for oxygen vacancy diffusion, Gadolinium-doped Ceria (GDC) is a better ionic conductor and may be used instead of YSZ for the cell to be operated at lower temperature (down to 500 °C) [5], allowing the use of cheap stainless steel for the bipolar plates, gaskets and balance of plant components. As the thermal expansion coefficients of the anode and electrolyte have to match, metal-GDC anodes are preferred for low-temperature cells with GDC electrolytes.

Cermet microstructure plays a key role in determining the electrochemical performance of the anode, mainly in the case of the anode-supported cells in which the anode is the structural component. The anode must present gas permeation and both electronic and ionic conductivity through the metal and ceramic components, respectively. To achieve this, a uniform distribution of small pores and metal and ceramic particles, in addition to a good connectivity of the three phases, is required. The length of the triple phase boundary, where the electrochemical reactions take place, has also to be high. For long-term operation this microstructure must be retained, however coarsening of the metal particles during cell operation tends to deteriorate the anode performance. The metal particle coarsening kinetics depends on the wettability between the metal and the ionic conductor [6], and lower interfacial energies lead to reduce the driving force for metal particle coalescence [7].

Metal-YSZ and metal-GDC porous cermets obtained through reduction of Directionally Solidified Eutectic Ceramics (DSECs) show less degradation than cermets obtained through traditional fabrication methods, which are based on mixing and sintering the constituent powders. The stability under SOFC operating conditions of cermets prepared from DSECs has been evaluated by the evolution of the electronic conductivity and porosity with ageing [8-11]. The origin of this improved performance lies on their

microstructural characteristics. NiO-YSZ, CoO-YSZ, NiO-GDC and CoO-GDC DSECs show a regular self-assembled lamellar or fibrous microstructure, with low-energy interfaces and strong adhesion between phases [12]. After reduction of the 3d transition metal oxide, NiO or CoO, the YSZ or GDC scaffold remains unaltered. Its role on the material stability is, on the one hand, as a physical barrier that prevents the coarsening in the direction perpendicular to the lamellae. On the other hand, the good metal-ceramic adhesion, enhanced by the presence of low-energy interfaces, slows down particle coarsening [7]. Hence, it is import to study the orientation relationships and interfaces in the cermets and in the DSECs they are obtained from.

The orientation relationships and interfaces of NiO-GDC and CoO-GDC DSECs as well as other eutectics solidified at different growth rates were studied by EBSD in a previous work [13]. The microstructure is made up of alternating lamellae, except for the eutectic solidified at 10 mm/h, which is fibrillar. The lamellar microstructure is formed by ~50-100 μm -size slightly misaligned eutectic grains. Within the eutectic grains each phase behaves as a single crystal. The solidification rate determines the lamellar width according to Hunt-Jackson law [14], being 600 nm and 1000 nm for, respectively, NiO-GDC and CoO-GDC eutectics grown at 100 mm/h. Two orientation relationships were found:

- OR1: $(1\ 1\ 1)_{\text{NiO/CoO}} // (0\ 0\ 2)_{\text{GDC}}$ (interfacial planes) $[0\ 1; \bar{1}]_{\text{NiO/CoO}} // [0\ 1\ 0]_{\text{GDC}}$
- OR2: $(h\ k\ l)_{\text{NiO/CoO}} // (h\ k\ l)_{\text{GDC}}$ $[u\ v\ w]_{\text{NiO/CoO}} // [u\ v\ w]_{\text{GDC}}$ ‘cube-on-cube’

The growth directions, interfacial planes and orientation relationships in these materials have been discussed in previous papers in terms of the coincidence of the reciprocal lattice point model (CRLP) and ionic charge density balance at the interface between polar planes [13,15]. The ionic forces within each ceramic phase extend and are compensated across the interface, as required by Pauling’s second rule of ionic structures [16]. For this reason, the interfaces are made up of polar planes with ionic charge densities as similar as possible. We showed that the experimental interfacial planes, $(111)_{\text{NiO/CoO}} // (002)_{\text{GDC}}$, do correspond to the best possible ionic charge matching between the polar planes of the rock-salt structure (NiO and CoO) and the fluorite GDC structure.

Reduction kinetics have been studied previously for CoO-GDC [17] and NiO-GDC [V.M. Orera, *personal communication*] DSECs. Although the reduction rate was expected to increase with temperature, isochronal thermo-gravimetric experiments on CoO-GDC showed an anomaly. The reduction process was abnormally slowed down at temperatures around 700 °C. A similar phenomenon has been reported for CoO-YSZ when reduced at around 750 °C, but was not observed for NiO-GDC or NiO-YSZ DSECs, nor for the conventionally prepared cermets [18].

In this paper, we discuss the microstructure, crystallographic orientation relationships and interfaces in Ni/Co-GDC cermets obtained through reduction of directionally solidified eutectic ceramics by electron microscopy as well as electron and X-ray diffraction. Combining these different experimental techniques we analyze the material over different length scales. The samples were studied both at full and intermediate reduction stages to obtain a better understanding of the role of the interphase interfaces in the phase transformation process. With the aim of understanding the aforementioned reduction-kinetics anomaly, CoO-GDC reduction was studied at two different temperatures, 500 and 700 °C. The results are compared with those regarding NiO-YSZ and CoO-YSZ DSEC cermets elaborated in a similar way.

2. Materials and methods

Directionally solidified eutectics of NiO-GDC and CoO-GDC were prepared by the laser floating zone (LFZ) technique. GDC powder was obtained from inorganic salt precursors following the Pechini method [19] with 10% dopant concentration ($\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_x$). NiO powder was from Alfa Aesar (99%), and CoO powder was obtained by heating Co_3O_4 powder (99.7%, Alfa Aesar) in air at 1000 °C and quenching. Powders were mixed along with polyvinyl alcohol according to eutectic compositions (73 mol% NiO, 27 mol% GDC and 82 mol% CoO, 18 mol% GDC) [11], isostatically pressed under 200 MPa for 5 min and sintered at 1400 °C for 12h in order to obtain ceramic precursors. Directional solidification was done by the laser-assisted floating-zone method using a CO_2 continuous wave laser ($\lambda = 10.6 \mu\text{m}$; Blade600, Electronic Engineering, Firenze). Laser processing was carried out in two steps. In the first step, carried out at 200 mm/h, the powder precursor was densified to 100% density. Then, the final solidification was done at 100 mm/h. The thermal gradient at the growth front, G ,

was about $6 \cdot 10^5$ K/m. The final directionally solidified eutectic cylinders were 8 cm in length and 1.8-2.5 mm in diameter.

For obtaining the porous cermets, rods of both eutectics were reduced in a tubular furnace with a mobile quartz tube to facilitate quenching the samples. Rods of NiO-GDC DSEC were partially (30% oxygen mass loss) and completely reduced at 650 °C, while CoO-GDC reduction was performed at 500 °C and 700 °C, with 42% and 56% oxygen mass loss, respectively, for the partially reduced samples. The reducing atmosphere was 5% H₂/N₂.

All the microstructural characterization was performed on transverse cross-sections of the eutectic rods. To this end, slices (~1 mm thick) were cut with a diamond saw from the as-grown, partially reduced and completely reduced samples. Then, the specimens were grounded and polished using SiC abrasive papers and diamond suspensions. As surface effects had been previously reported in the crystallographic behavior of Ni-YSZ cermets prepared in a similar way [7], the observed cross-sections were prepared after grinding the slice more than 500 µm. Scanning electron microscopy (SEM) observations and EBSD experiments were carried out in a Merlin Field-Emission SEM (Carl Zeiss, Germany) with an integrated EBSD system (HKL model from Oxford Instruments, United Kingdom). In the EBSD experiments, the sample was tilted 70° at a working distance of 14.5 mm away from the pole piece. The accelerating voltage was 15 kV and the probe current, 800 pA. The Channel5 software was used to process the EBSD data. Details of sample preparation for SEM and EBSD are explained elsewhere [13]. TEM observations were performed in JEOL 2000FXII, and JEOL 2010F microscopes (Tokyo, Japan). The specimens were prepared by wedge mechanical polishing. Ion milling (Model 600Dif, Gatan, Warrendale, PA) was subsequently applied at liquid nitrogen temperature in order to avoid artifacts, such as further reduction of the fluorite phases by radiation damage, previously observed in NiO-YSZ when ion milled at room temperature [7].

X-ray diffraction experiments were performed on samples polished following the same procedure as for SEM and EBSD. Texture measurements were performed using a Bruker D8 Discover diffractometer equipped with Cr Twist tube, V filter, parallel-beam PolyCapTM system (divergence of 0.25°), UBC (Universal Beam Concept) device collimator and a 1-D LynxEye detector (active length in 2θ 2.7°). The sample was

mounted on an Eulerian Cradle with computer controlled X-Y-Z stage. Data were collected for three non-equivalent reflections using a fixed mode and time per orientation of 20 s: (111), (311) and (420) for GDC; (200), (220) and (311) for NiO and CoO; (111), (200) and (220) for Ni and Co. The data, in standard mode, was acquired for over the range of 0-360° in increments of 5° in Phi (ϕ) and 0-75° in increments of 5° in Psi (ψ) range, yielding 2079 total sample orientations. Multex 3 software from Bruker AXS was used to develop the component analysis of the pole figures and represent the calculated pole figures of the three main {200}, {220} and {111} independent reflections of the cubic systems (all the crystallographic phases involved belong to the $Fm\bar{3}m$ space group).

3. Experimental results and discussion

3.1. Microstructure of the partially and fully reduced NiO-GDC and CoO-GDC samples

SEM and TEM micrographs of the NiO-GDC and CoO-GDC partially reduced samples can be seen in Fig. 1 and 2 respectively. The reduction process differs somewhat from the one observed in the case of the NiO-YSZ and CoO-YSZ DSECs [18], both in the way the reduction front advances from the surface of the sample towards the center of the cylinder axis, as well as how each lamella of NiO and CoO reduces into Ni and Co. There is not a clear reduction front in the GDC eutectics as in the YSZ eutectics. In the first stages of the reduction process (up to 30% weight loss of the sample), pores appeared distributed throughout the whole transverse cross-section. Then, when the weight loss exceeded 50 wt%, there was a fully reduced zone at the outer part of the rod, while reduced and non reduced NiO or CoO coexisted in the remaining areas. However, in NiO-YSZ and CoO-YSZ eutectics there were very distinct reduced and non-reduced regions and a small partially reduced area between them that was usually limited to only one or two lamellae [18]. In the Ni-YSZ and Co-YSZ lamellar cermets, as well as in Ni-CaSZ (calcium stabilized zirconia) lamellar cermets [20], the reduction process seemed to follow a model where the oxygen anions left the NiO/CoO through their interface with the doped zirconia, which is an ionic conductor, and from the zirconia to the atmosphere, while the electrons traveled through the Ni or Co metallic phase and reunited with the oxygen at the surface. Thus, the reduction started on the sample surface and then advanced inwards, as metal routes were established. The Ni or Co particles nucleated at the YSZ interface were continuous, forming a path for electron transport.

The reduction process for NiO/CoO-GDC eutectics is distinct from the YSZ and CaSZ counterpart. This could be due to the mixed electronic and ionic properties of GDC in comparison with YSZ, which is a pure ionic conductor. Under low oxygen partial pressure conditions, Ce^{4+} cations from the GDC phase tend to reduce to Ce^{3+} , according to Eq. 1 (written in Kröger-Vink notation) [21],

giving rise to electronic conduction. According to Steele [5], electronic contributions to total conductivity is as important as the ionic conductivity contribution for oxygen partial pressures of approximately 10^{-28} bar at 500 °C or 10^{-20} bar at 700 °C, and more important for lower oxygen partial pressures. As there is an extra path for the electrons leaving NiO or CoO, with no need of any metal connection to the surface, it could be easier for the reduction process to start anywhere within the material. This also would result in the nucleation of discontinuous metal particles at the metal-GDC interface (Fig 2b and 2e).

In CoO-GDC samples, when the sample is reduced at low temperature, this microstructure evolves towards the sponge-like nanostructure shown in Fig. 2b for the partially reduced at 500 °C. In CoO-GDC samples reduced at 700 °C, the beginning of the reduction (Fig. 2d) is similar to the one observed when reduced at 500 °C. However this microstructure evolves towards coarser grains (Fig 2e), without forming the nanostructure shown in Fig 2b. In NiO-GDC samples partially reduced at 650 °C, the nanostructures are rarely observed, generally coexisting with a coarser microstructure (Fig 2f). This microstructure tends to coarsen at higher temperatures or longer reduction times, as the small crystals coalesce and form larger grains with less specific surface area, reducing the contributions of interfacial energy to the total system free energy.

When the reduction is completed, the final microstructure depends on the reduction temperature. As can be observed in Fig 3, the metal particles in the Ni-GDC cermet reduced at 650 °C and the Co-GDC cermet reduced at 700 °C are thicker than in the Co-GDC cermet reduced at 500 °C. The microstructure shown in Fig 3b (Co-GDC reduced at 500 °C) is an evolution of the nanostructure shown in Fig 2b after the reduction is completed.

3.2. Crystallography and orientation relationships in Ni-GDC and Co-GDC porous cermets

Crystallographic orientations during the reduction process were first studied locally by selected area electron diffraction (SAED) in the TEM, with a spatial resolution of about 0.5 μm . Afterwards, orientation relationships in Ni-GDC and Co-GDC porous cermets were studied by EBSD and X-ray diffraction pole figures. EBSD experiments provide local crystallographic information, with a spatial resolution about 50 nm, and can be utilized to analyze large areas, on the order of mm^2 , of bulk materials [22]. X-ray diffraction pole figures provide average orientation information from transverse cross-section of the eutectic rod. The probe size used was 1 mm, with the spot size including 90% of the incoming energy, while the diameter of the samples was about 2 mm. Thus, TEM, EBSD and X-ray diffraction techniques provide complementary information.

TEM electron diffraction patterns acquired over partially reduced NiO and CoO, at 500 and 700 $^{\circ}\text{C}$, revealed the presence of multiple small crystals (Fig. 2c), in contrast to the single crystal Ni and Co phases reported for NiO-YSZ and Co-YSZ DSECs which appears to be a topotactic interface reaction [7,9]. This experimental finding, which was observed in all reduced areas, regardless of the microstructure morphology, also suggests a different reduction mechanism.

3.2.1. Ni-GDC porous cermets

We performed X-ray diffraction and EBSD experiments on NiO-GDC and fully reduced Ni-GDC samples. X-ray diffraction pole figures for the as-grown and fully reduced NiO-GDC samples are shown in Fig. 4. The NiO-GDC sample is made up of many eutectic grains that show little deviation from each other. This is easily discerned as the poles of the as-grown samples are relatively sharp, which indicates little mosaicity. In fact, only two similar crystal orientations can be distinguished. Also, we note that, although the as-grown and completely reduced specimens come from locations separated several millimeters away in the same eutectic rod, the GDC pole figures in the NiO-GDC and Ni-GDC are almost the same. This implies that NiO-GDC DSEC rods solidify like a monolith. The poles figures can be properly fitted using only a few sphere-type texture components. The isotropic fractions are near 30% for GDC and 40% for NiO. Only one orientation relationship between the phases appears: $(1\ 1\ 1)_{\text{NiO/CoO}} // (0\ 0\ 2)_{\text{GDC}}$ and $[01;\bar{1}]_{\text{NiO/CoO}} // [0\ 1\ 0]_{\text{GDC}}$, i.e., OR1, the majority orientation

relationship previously found by EBSD [13]. The cube-on-cube orientation relationship was not discernible in the pole figures, thus it is under the detection threshold of this technique, which can be around 5 vol%. As explained in the introduction, an interface made up of polar planes, as in OR1, compensates the ionic forces and improves its stability. While the cube-on-cube orientation relationship is a favorable orientation relationship from a geometric point of view [15], it lacks good matching of polar interface planes, which could be the reason why this appears rarely in comparison with OR1.

Observing the pole figures of the Ni:GDC cermet (Fig 4b), a Ni crystallographic reorientation process is evident. GDC pole figures before and after reduction are almost identical, but Ni pole figures have evolved towards two different sphere-type texture components. One corresponds to an orientation relationship originated by a reduction process in which the Ni particles maintain the same crystallographic orientation (OR1) as before the reduction process: $(111)_{\text{Ni}} // (002)_{\text{GDC}}$ and $[01; \bar{1}]_{\text{Ni}} // [010]_{\text{GDC}}$. This is the expected behavior for NiO isolated grains. NiO reduction usually takes place according to a topotactic process in which oxygen departure from the NiO phase leaves the structure and crystallographic orientation of the Ni sublattice unaltered [23-24]. However, this behaviour can be modified by the presence of the (100)-GDC interfaces. In fact, the other texture component represent a crystallographic reorientation of the Ni particles to form a cube-on-cube orientation relationship: $[001]_{\text{Ni}} // [001]_{\text{GDC}}$ and $[100]_{\text{Ni}} // [100]_{\text{GDC}}$. Analogous behavior was reported for Ni-YSZ [7,25] cermets obtained by reduction of DSEC, although the reorientation behavior found in NiO:GDC was not exactly the same as in NiO-YSZ. On that occasion, NiO-YSZ DSECs showed two different reorientation processes, the same we have just reported for Ni-GDC (called OR4 in that paper) and OR3: $(002)_{\text{Ni}} // (002)_{\text{YSZ}}$ and $[100]_{\text{Ni}} // [110]_{\text{YSZ}}$, which was predominant (we will maintain the same notation for the crystallographic reorientation in this paper). In fact, it was estimated that 30 vol.% of NiO reoriented according to OR3 at 800° C. However, this reorientation has not been found in Ni-GDC. It is not easy to obtain quantitative information from the X-ray pole figures. However, we can approximately state that about 10 vol% of the Ni particles reoriented according to OR4, 40 vol% maintained the same orientation relationship as before reduction and the remainder of the particles can be categorized in the isotropic fraction.

The reorientation process was also monitored by EBSD. An EBSD orientation map of Ni-GDC covering $10\ \mu\text{m} \times 45\ \mu\text{m}$ and the associated pole figures are presented in Fig 5. The GDC lamellae display a very homogenous purple color, which means all the GDC in the map is oriented in the same way. This is also evident in the GDC pole figure of the reduced sample (Fig. 5b). In contrast, the Ni particle orientations are more random although they appear fiber-textured, revolving around the interface plane of OR1, $(111)_{\text{Ni}} // (002)_{\text{GDC}}$, which has been preserved through the Ni reorientation process for many of the particles. The quantitative estimation from the EBSD experiments was in good agreement with the X-ray experiments. About 40% of the NiO volume transformed to Ni following a topotactic process, which leaves Ni roughly oriented in the way NiO was before. Another $\sim 10\ \text{vol}\%$ of Ni particles evolved to the new OR4 and the rest of the particles were oriented more randomly, albeit with a fiber texture about the $(111)_{\text{Ni}} // (002)_{\text{GDC}}$ interface plane normal.

It is interesting to compare the reorientations in Ni-YSZ versus Ni-GDC cermets. The dominant coincidence cells in Ni-YSZ epitaxial interfaces were experimentally studied and theoretically analyzed by Dickey and co-workers by electron diffraction and the Near Coincident Site Lattice (NCSL) theory [26]. According to the coincidence cells described in reference [26], the lattice mismatch for the Ni-YSZ cermets in both orientation relationships is similar: $\delta_{\text{Ni-YSZ}}=2.85$ for OR3 and $\delta_{\text{Ni-YSZ}}=3.0\%$ for OR4 ($a_{\text{Ni}}=3.524\ \text{\AA}$ [27], $a_{\text{YSZ}}=5.127\ \text{\AA}$ [18]), although the size of the coincidence cell is much larger for OR4. Both orientation relationships are experimentally found in cermets prepared from DSEC [7] and in Ni films deposited over zirconia substrates [26]. However, in the case of the Ni-GDC cermet, the lattice parameter of GDC is $\sim 6\%$ larger than in YSZ ($a_{\text{GDC}}=5.418\ \text{\AA}$) [28]. Thus, the lattice mismatch, represented in Fig 6 using the same coincidence cells as in reference [26], is now worse for OR3 ($\delta_{\text{Ni:GDC}}=8.4\%$) and better for OR4 ($\delta_{\text{Ni:GDC}}=2.5\%$) and, in fact, only the reorientation corresponding to OR4 has been experimentally observed.

We believe that, as in the case of Ni-YSZ cermets prepared from DSECs, this crystallographic reorientation occurs because the Ni particles reorient during reduction to form an epitaxial interface with the GDC lamellae. The crystallographic reorientation is possible because the oxygen atoms leave the composite through the GDC phase. These interfaces would provide lower interfacial energy and, consequently, better

adhesion between the phases of the cermet, from which we may expect an improved microstructural stability for long-term operation. In the analogous studies about crystallographic reorientation of Ni particles in Ni-YSZ cermets [7], we showed that the fraction of reoriented particles varied with the reduction temperature. It is expected that we could also increase the amount of reoriented particles in Ni-GDC cermets adjusting this temperature. In addition, with respect to the fiber-textured Ni particles, although they do not form epitaxial interfaces, in any case they are bonded to a polar GDC surface. Theoretical calculations show that adhesion between metal and polar ceramic surfaces is stronger than in the case of non-polar surfaces. The electronic charge at the polar surface is not compensated, resulting in a high surface reactivity and consequently a good adhesion with the metal surface [29].

3.2.2 Co-GDC porous cermets

In a previous paper, Ortega-San-Martin *et al.* hypothesized that the anomaly observed in the reduction kinetics of CoO-GDC and CoO-YSZ could be related to the appearance of the spinel phase Co_3O_4 at the interface between Co and GDC or YSZ [9]. Via extensive TEM and SAED analysis, we were not, however, able to find residual Co_3O_4 at the Co-GDC interface for any of the reduction conditions. HRTEM and electron diffraction patterns from the residual CoO areas in the partially reduced CoO-GDC samples (both at 500 and 700 °C), as well as in the as-grown eutectic, showed the coexistence of the rocksalt CoO and spinel Co_3O_4 phases. Even though Co_3O_4 spinel phase was widespread throughout the samples, X-ray diffraction experiments did not detect its presence. Although in some compounds rocksalt and spinel phases cannot be distinguish because the symmetry overlaps in averaged diffraction patterns [30], this is not the case of CoO and Co_3O_4 phases, which can be fully discriminated in powder X-ray diffraction experiments. This suggests that it could be a surface effect or a phase transition induced by the interaction with the TEM electron beam. With regard to the origin of the anomaly in the CoO-GDC reduction kinetics, while rocksalt NiO is the only binary nickel oxide, cobalt possesses many oxidation states and may form different oxide phases, such as the cubic spinel Co_3O_4 [31], a wurtzite CoO (hexagonal) [32-33] and even a transition from ordered to disordered Co_3O_4 spinel has been reported to take place at around 830 °C [34-35]. If that were so, it would be reasonable to conclude that such a phase change could happen to a different extent for 500 and 700 °C and exert

some influence on the reduction kinetics. However, our experiments to-date are not extensive enough to confirm the aforementioned hypothesis.

In the EBSD experiments on partially and fully reduced CoO-GDC samples, the Kikuchi patterns of Co lamellae appeared diffuse and could not be indexed. Since multiple attempts at refining the sample preparation procedures did not improve the quality, we surmise that the phase coexistence between the rock-salt and spinel phases within the diffraction volume is the most likely origin of the poor pattern quality. Thus, the analysis is based on the X-ray pole figures, which are represented in Fig. 6 for the as-grown and fully reduced at 500 °C CoO-GDC samples. No significant differences were discerned between samples reduced at 500 °C or 700 °C. Pole figures from the CoO-GDC samples are more diffuse and not as well ordered as in the NiO-GDC pole figures. Apart from the various sphere-type texture components that appear as scattered spots in Fig 4a, texture components forming rings centered on the rod axis can also be observed in the pole figures. These fiber-type components indicate the presence of CoO-GDC eutectic grains with the normal vector of the interfacial planes at random orientation within the plane perpendicular to the growth direction. Thus, the directionally solidified CoO-GDC rods cannot be considered as monoliths, as in the case of NiO-GDC rods.

As for the Co-GDC cermets, from the observation of the pole figures in Fig. 4b, it can be concluded that some fraction of the Co particles tend to maintain, after reduction, the original parallelism $(111)_{\text{CoO}} // (002)_{\text{GDC}}$ of the interfacial planes (marked in red in Fig 4b), indicating a possible topotactic reduction process in which $\{hkl\}_{\text{CoO}} // \{hkl\}_{\text{Co}}$. However, it was not possible to estimate this fraction from the pole figures. Moreover, the disorder of the crystallographic orientation has increased. In fact, the isotropic fraction in the pole figure fitting increased from about 50% in the CoO case to approximately 70% in the Co one. The cermet microstructure was made up of small, ~80-500 nm size, crystals oriented in many directions. The differences between CoO and Co pole figures are not more significant than those between the GDC pole figures in the as-grown and after reduction pole figures, and they are within the range of variation existent between any two slices from the same eutectic cylinder.

4. Conclusions

The reduction process in NiO/CoO-GDC DSECs into Ni/Co-GDC porous cermets with potential applications as anodes in SOFC has been studied by SEM, TEM, EBSD and X-ray pole figures.

The reduction mechanism found is different from the previously reported for analogous NiO/CoO-YSZ DSECs. The reduction process develops in a manner with more spatial homogeneity, without the sharp reduction front found in the YSZ analogs and the metallic particles nucleated at the interfaces are discontinuous. This different behavior is attributed to the partial electronic conductivity of GDC in reducing atmosphere. TEM observations revealed a porous polycrystalline (~40-200 nm) microstructure at intermediate reduction stages of CoO-GDC samples reduced at 500 °C, and this nanostructure can be maintained to full reduction at 500 °C with pores with sizes ~80-500 nm. Coarser microstructures are observed at higher-temperature reduction in both CoO-GDC and NiO-GDC reduction.

After reduction of NiO and CoO, Ni and Co particles are oriented with respect to the GDC phase more or less in the same way as NiO/CoO was prior to reduction. In the case of CoO-GDC samples, no differences in crystallography were observed between the samples reduced at 500 °C or 700 °C. However, a fraction of the Ni particles reorient to form an epitaxial interface with the GDC surface ($[001]_{\text{Ni}} // [001]_{\text{GDC}}$ and $[100]_{\text{Ni}} // [100]_{\text{GDC}}$). The formation of low-energy interfaces would enhance the metal-ceramic adhesion and might be in the origin of the improved long-term material endurance of these materials at high temperatures [10]. Regardless of the presence of reorientation phenomena, the metal-ceramic interfaces are formed, in all the cases, between metal particles and polar ceramic surfaces, which have stronger adhesion than in the case of non-polar surfaces, promoting microstructure stability. Further high-resolution TEM observations and theoretical calculations of the Ni-GDC epitaxial interfaces described in this paper are in progress.

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Figure Captions

Fig. 1. SEM micrographs of transverse cross-sections of NiO-GDC (a) and CoO-GDC (b) partially reduced samples (at 650 °C the NiO-GDC samples and a 500 °C the CoO-GDC samples). Pores appear distributed throughout the cross-section and no sharp reduction front can be identified. (Pores: black; Light grey: GDC; Dark grey: NiO, Ni, CoO and Co).

Fig. 2. a) SEM micrograph of the reduction process in the NiO-GDC sample reduced at 650 °C. b) TEM micrographs showing the beginning of the reduction process in the CoO-GDC sample reduced at 500°C. c) TEM micrograph displaying the nanoporous microstructure (40-200 nm pore size) of Co particles in the sample reduced at 500 °C. d) Selected area electron diffraction pattern showing the polycrystalline nature of the Co particles that are nucleating. e) TEM micrograph showing the beginning of the reduction process in the CoO-GDC sample reduced at 700 °C. f) TEM micrograph showing the evolution of the reduction process in the CoO-GDC sample at 700 °C.

Fig. 3. a) SEM micrograph of the fully reduced Ni-GDC cermet obtained by reduction of the eutectic at 650 °C b) fully reduced Co-GDC sample reduced at 500 °C. c) fully reduced Co-GDC sample reduced at 700 °C

Fig. 4. X-ray diffraction pole figures for a) as-grown NiO-GDC and b) Ni-GDC. Particles oriented according OR1 are marked in (a) in red, $(002)_{\text{GDC}}// (111)_{\text{NiO}}$, and blue, $[020]_{\text{GDC}}// [0\bar{1}1]_{\text{NiO}}$. Particles reoriented according to OR4 are marked in white in the {200} pole figure.

Fig. 5. a) EBSD Orientation map of Ni-GDC. The color of each pixel stands for the crystal orientation at that precise point. Purple lamellae are made up of GDC, while Ni is distributed in small particles with different orientation, thus different color. Pores are colored black; b) Ni and GDC pole figures. Interfacial planes from OR1, $(111)_{\text{Ni}} // (002)_{\text{GDC}}$, are highlighted in red. The $[0\bar{1}1]_{\text{NiO}} // [010]_{\text{GDC}}$ relationship from OR1 is marked in green. OR4 relationships are marked in blue and black, $\{200\}_{\text{Ni}}//\{200\}_{\text{GDC}}$.

Fig. 6. Lattice site coincidences at the interface between $(002)_{\text{Ni}}$ Ni atoms and $(002)_{\text{GDC}}$ oxygen ions in OR3 and OR4 for Ni-GDC. The lattice mismatch is 8.4% for OR3 and 2.5% for OR4.

Fig. 7. X-ray diffraction pole figures for a) as-grown CoO-GDC and b) Co-GDC reduced at 500 °C. The interfacial planes, $(002)_{\text{GDC}}// (111)_{\text{CoO}}$ and $(002)_{\text{GDC}}// (111)_{\text{Co}}$, are marked in red.

Conflict of interest

The authors state that there is no conflict of interest that could potentially influence or bias the submitted work.