Flash sintering of one-step synthesized NiO-Ce$_{0.9}$Gd$_{0.1}$O$_{1.95}$ (NiO-GDC) composite

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Abstract

For the first time, the flash sintering process was successfully applied on NiO-Ce$_{0.9}$Gd$_{0.1}$O$_{1.95}$ (NiO-GDC) composite, satisfactorily obtained from a ‘one-step’ synthesis method, in the temperature range from 105 °C to 216 °C using an electrical field range from 130 to 40 V cm$^{-1}$. The use of a high electric field and high current densities increases the instability of the process, producing a high concentration of current in the material and presenting typical solidification microstructures, which is a sign of the high concentration of power under these conditions. The decrease of the electric field to 50 V cm$^{-1}$ allows highly densified samples to be obtained at temperatures as low as 200 °C using a current density of 260 mA mm$^{-2}$. The electrical conductivity of densified samples prepared at different current densities shows a high conductivity in the temperature range of 400–650 °C, in which it reaches up to 0.23 (Ω cm)$^{-1}$ at 650 °C.

Introduction

In recent years, an innovative sintering technique called ‘flash sintering’ has attracted much attention since it allows to obtain ceramic materials with high density in a few seconds at lower temperatures than those used in traditional processing techniques, under the effect of an external electric field [1–8]. Flash sintering is accompanied by an abrupt nonlinear increase in conductivity of the material under a threshold condition of temperature and an external applied electric field, which dramatically decreases both the time and temperature required for the densification of the material. The application of flash sintering has been reported in several oxides, including ionic conductors (yttria-stabilized zirconia [1–3], gadolinia-doped ceria [4, 5]), semiconductor ceramics (MnCo$_2$O$_4$ [6], La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_3$ [7]), and non-oxide materials (SiC [8]), among others.

The previous works have reported the flash sintering technique on two-phase materials (composites), by mixing a material susceptible to flash sintering with another that is essentially immune to the action of an electric field. Naik et al [9] studied the effect of an electric field on a biphasic material formed by alumina and yttria-stabilized zirconia (YSZ), in which the composite exhibited a flash sintering behavior close to the single-phase of YSZ. The composite was flash sintered with an electric field of 150 V cm$^{-1}$ at 1060 °C, while single-phase YSZ powders were flash sintered at 750 °C. In contrast, undoped alumina did not experience flash sintering at this field, requiring very high electric fields of around 1000 V cm$^{-1}$. Accordingly, Gaur et al [10] reported that the presence of the conductive MnCo$_2$O$_4$ phase allowed a decrease in the sintering temperature of CeO$_2$ from 1240 °C (using an electric field of 40 V cm$^{-1}$, without MnCo$_2$O$_4$) to 560 °C by applying an electric field of
Therefore, the presence of a secondary conductive phase, even in a small amount, can help significantly the electric field-assisted sintering process.

Despite various composite materials have been already prepared by flash sintering [11–14], the use of electric field to sinter Solid Oxide Fuel Cell (SOFC) anode precursor materials was punctually studied [15] to prepare NiO-YSZ composites and no report was found for NiO-GDC (NiO-Gd doped ceria) composites. The most common SOFC anode material is the cermet based on Ni and YSZ. However, its performance is poor at operating temperatures below 800 °C [11, 12]. In this regard, cermets containing Gd-doped ceria (GDC) as a ceramic component are preferred materials for operating temperatures below 800 °C due to higher ionic conductivity of GDC with respect to YSZ. In addition, the partial reduction of Ce⁴⁺ to Ce³⁺ under typical anode conditions increases the GDC electronic conductivity, thus improving its electrochemical performance. Moreover, GDC exhibits an ability to suppress the formation of carbon in methane-rich atmospheres [16–18]. Macedo’s research group has studied the relationships between composition, processing conditions, structure, microstructure, and electrical properties of NiO-GDC composites obtained by a one-step synthesis method and further processed by conventional sintering [19–23].

To our best knowledge, this work is the first report on the flash sintering of one-step synthesized NiO-GDC composites. The powders were flash sintered following a typical route at a constant heating rate. Different electric fields were applied under isothermal conditions. The effect of the current density on microstructure and electrical properties is discussed in detail.

**Experimental procedure**

NiO-Ce₀.₉Gd₀.₁O₁.₉₅ (NiO-GDC, 50 wt% NiO) composite powder was prepared by a ‘one-step’ synthesis method and further calcined at 700 °C for 2 h, as previously reported by Cela et al and Araújo et al [20, 22, 23]. Afterwards, the powder was mixed with 3 wt% of polyvinyl alcohol (PVA, Sigma-Aldrich) as a binder and distilled water. The mixture was dried in an oven at 80 °C overnight and then ground in an agate mortar. The powder was uniaxially pressed at 200 MPa into a dog bone shaped die, having a gauge length of 12 mm and a rectangular cross section of 3.3 × 1.58 mm. The samples were pre-sintered at 600 °C for 1 h in order to remove the binder. The pre-sintered samples were suspended in the center of a horizontal tubular furnace (Lenton Thermal Designs, UK) by means of two platinum electrodes attached to the handles of the dog bone specimen and filled with silver paste (Sigma-Aldrich) to improve the electrical contact. After that, the power source (Sorensen DLM 300-2) and two multimeters were connected to measure the change of the current (Keithley 2110) and voltage (Tektronix DMM 4050). The set-up used in the flash sintering process is shown in the figure 1.

The crystalline phases were identified by x-ray diffraction (XRD, Bruker AXS D4 Endeavor) using Cu-Kα radiation, in the 2θ range of 20°–80°. The diffraction peaks were indexed using the space group Fm-3m (225) of the sodium chloride-type crystal structure of NiO (JCPDS card: 47–1049) and fluorite-type cubic structure of Ce₀.₉Gd₀.₁O₁.₉₅ (JCPDS card: 75–0161). The microstructures of the flash sintered composites were analyzed by scanning electron microscopy (SEM, JEOL 6460 LV) equipped with energy dispersion spectroscopy (EDS). After the flash sintering, dog-bone samples were cut into bar-shaped samples. The electrical conductivity was
measured by the two probe DC method in the temperature range of 400 °C–600 °C and current range –10 to 10 mA using an external power source (Sorensen DLM 300-2).

**Results and discussion**

**Power dissipation**

Arrhenius plots of the measured input power dissipation versus the reciprocal absolute temperature at different applied electric fields are shown in figure 2. The power is normalized with respect to the volume of the presintered sample. The flash sintering phenomenon is observed above 40 V cm$^{-1}$, being characterized by an abrupt increase in power dissipation [2, 6]. At 30 V cm$^{-1}$ one can observe a sudden increase in power dissipation followed by a plateau at a predefined current. For 20 V cm$^{-1}$, the flash phenomenon is not observed. The onset of the instability occurs at the same power density level of around 5 mW mm$^{-3}$ for all electric fields. Before the onset of instability, the power dissipation shows almost a linear dependence on the furnace temperature for all electric fields. This is the expected behavior for NiO-GDC composites, whose electrical conductivity increases with increasing temperature [20]. On the other hand, it is remarkable to note the low temperatures at which the flash sintering occurs. The phenomenon is observed between 105 and 216 °C, under electric fields ranging from 130 to 40 V cm$^{-1}$. For comparison, under similar electric fields, some ionic conductor ceramics require higher temperatures to cause flash sintering. For example, flash phenomena begin at 850 °C under 120 V cm$^{-1}$ for YSZ [1] and at 475 °C with 130 V cm$^{-1}$ for GDC [4]. Both of them are well known ionic conductors, differing from each other in that the ion conduction mechanism for the GDC are activated at lower operating temperatures [24, 25]. The flash sintering is also observed at low temperatures. This is the case of the MnCo$_2$O$_4$ spinel in which the flash sintering was around at 120 °C–250 °C, under 7.5–17.5 V cm$^{-1}$ [6]. Although the temperature range is close to those shown in figure 2, lower electric fields are required to obtain flash sintering. In this case, a semiconductor-type conduction behavior prevails, which would explain the requirement for a low electric field.

**Microstructure**

Although the sudden increase of conductivity is observed in a wide range of electric fields, it does not mean that uniform densification occurs successfully. Figure 3 shows the evolution of the specimens at different electric fields and $j = 260$ mA mm$^{-2}$. The samples under electric fields of 130 and 110 V cm$^{-1}$ are particularly affected by the intensity of the applied field, with a lot of cracks along the samples. Moreover, high brightness areas are observed under these conditions along the specimen and around the electrode holes. From 90 V cm$^{-1}$ down to 40 V cm$^{-1}$, there is a progressive improvement in the appearance of the samples, which decreases both the number of cracks and the bright phase areas, with an improvement in densification of the center zone of the samples.

The combination of high electric field and high current density increases the probability of the preferential current flow paths occurs. This in turn produces locally hotter zones which become also more conductive, increasing local current and power dissipation. Consequently, the sample becomes increasingly hot and conductive (in the zones of preferential current path) and therefore the densification contraction is also different, which induces the formation of cracks along the material. This problem is related to the so-called hot-spot, which has been reported for different ceramics [26–28], producing a preferential current flow path and thus leading to a microstructural inhomogeneity.

![Figure 2. Arrhenius plots of power dissipation under different electric fields for NiO-GDC.](image-url)
The specimen flash sintered at 130 V cm\(^{-1}\) and 260 mA mm\(^{-2}\) was specially affected by the intensity of the power dissipation. The area close to the positive electrode of this sample was selected since the energy concentration of such magnitude is able to evaporate part of the material in this zone, as shown in figure 4(a). The microstructure evolution around this area is shown in figure 4(b), where a eutectic solidification evolution is observed. An irregular lamellar eutectic can be seen in figure 4(b.1), next to the area that was evaporated. The route towards areas furthest from the edge towards the interior of the material, i.e., far from the focus of electric power concentration, shows that the microstructure is becoming ordered, from a lamellar eutectic type (figure 4(b.3)) until the typical microstructure of sintering (figure 4(b.5)), with two transition areas (figures 4(b.2) and (b.4)). This solidification microstructure was expected because the NiO-GDC composite has a eutectic composition of around 54 wt% NiO-46 wt% GDC\(^29\), similar to that used in the present work. The study of this system by using laser floating-zone technique, reveals lamellar microstructure\(^30\), similar to that shown in the figure 4(b.3). The evolution from solidification to densification microstructure in a narrow area of the specimen is a sign of both high localized thermal gradient and high cooling rates. After the flash sintering, when the power supply is turned off, it generated a high temperature difference between the specimen and the interior of the furnace. By using the black body radiation model for Joule heating\(^31\), a first approximation of the sample surface temperature \(T_s\) can be calculated by equation (1):

\[
T_s = (T_0^4 + W/A\sigma\varepsilon)^{1/4}
\]

where \(T_0\) is the furnace temperature, \(W\) is the electrical power dissipation (W), \(A\) is the surface area of the sample \((m^2)\), \(\sigma\) is the Boltzmann constant \((5.67 \times 10^{-8} \text{ Wm}^{-2}\text{K}^{-4})\) and \(\varepsilon\) the emissivity of the ceramic (0.9 for oxides). According to equation (1), by considering a \(T_0 = 105^\circ\text{C}\) and at maximum power density of \(~2\text{ W mm}^{-3}\) (in the transient), the sample temperature is around 1860\(^\circ\text{C}\). This temperature surpasses those required to densify NiO-GDC composites\(^21, 22\). However, the instability of the process due to the high electric field generates preferential current path which increases the local temperature, producing local melting around the hole of positive electrode and in some region along the specimen, as shown in the figure 4(a). Localized melted region is a defect that appears in flash sintered samples under severe conditions of flash sintering\(^26, 32\). According to model proposed by Dong\(^33\), who identified the conditions that lead to the hot spot formation, there is a critical defects size, above which a small temperature perturbation will be magnified and hot spot will be generated. In practice, such defects could come from inhomogeneity in the microstructure, like non-uniform powder packing (difference in the green density) or electrical loading, like non-uniform contacts between electrodes and the sample.

Figure 3. Evolution of samples under different electric fields at 260 mA mm\(^{-2}\).
The first idea after seeing the brightness phase (as shown in figure 4(a)) is the presence of metallic phase under severe conditions of flash sintering. In order to elucidate the phases present under different electric field, x-ray diffraction was performed in the center zone of the dog bone specimen, with a spot size of 10 mm in the samples with no crack along the surface and 4 mm for samples under high electric field. Due to the presence of more cracks in the samples at high electric field (130 and 110 V cm$^{-1}$), the current density was limited to 130 mA mm$^{-2}$. Although the current limit was reduced, the brightness phase is still visible at high electric field. Figure 5 shows the XRD patterns of the samples under different electric fields and of the calcined powder, in which the latter showed the formation of NiO-GDC nanoparticles from the oxidation of the precursor powder. The presence of NiO and GDC phases is corroborated under all the electric fields herein studied. The appearance of new phases is not detected. NiO-GDC showed diffraction peaks at 37.1°, 43.1°, 62.6°, 75.2°, and 79.1° (2θ) corresponding to (111), (200), (220), (311), and (222) crystal planes of the NiO phase. The peaks of the
The effect of the limit current density on the microstructure and electrical properties of the NiO-GDC composite was studied applying two different values: 130 and 260 mA mm$^{-2}$, keeping constant both the electric field and the temperature, which were 50 V cm$^{-1}$ and 200 °C, respectively. The sample was heated at 200 °C and then the power supply was turned on. The electric field and temperature were selected in order to ensure that the flash event occurs and to decrease the number of defects on the sample. The amount of defects is minimal at a field of 50 V cm$^{-1}$ (see figure 3(e)) and the onset temperature of the flash event under these conditions is around 200 °C, as are shown in the power dissipation curve of figure 2. In this way, by imposing this electric field, it is ensured that the current in the specimen rises abruptly, until the predefined limit value is reached, as shown in the power density curve of figure 7(a). In the flash sintering, the power supply is quickly switched from voltage control to current control upon reaching a preset value of the current. The transition between voltage and current control produces the spike in the curve of power dissipation, which is a sign of flash sintering. The peaks of power densities reached values of 584 and 1132 mW mm$^{-2}$ for the lowest and highest limit current density, respectively. This difference can affect the densification process, as reveals the remarkable difference in the microstructure in figure 7(b). The specimen that reaches 130 mA mm$^{-2}$ shows poor densification, with a large remaining porosity and inhomogeneity between grain sizes of GDC phase (white $\rightarrow$ higher atomic weight) and NiO phase (dark $\rightarrow$ lower atomic weight), where the NiO phase had a greater grain size. On the other hand, the sample that reaches 260 mA mm$^{-2}$ had a high degree of densification, although it is also possible to observe a larger grain size for the NiO phase.

The different conduction mechanisms between single-phases (NiO and GDC) would influence the microstructure, since single-phase NiO is a p-type semiconductor while GDC is an ionic conductor. Considering the low temperature used (200 °C) and the low applied electric field of 50 V cm$^{-1}$, it is probable that the preferred current path will occur by the NiO phase instead of GDC. A limit current density of 130 mA mm$^{-2}$ at these threshold conditions would be not sufficient to overcome the associated activation barriers of GDC but it would be sufficient to NiO, which could explain the superior densification and grain size of this phase observed in figure 7(b) left, compared to GDC. In addition, raising the limit current density to 260 mA mm$^{-2}$ (figure 7(b) right), it seems to favor the densification of the composite, decreasing significantly the remaining porosity. It is interesting to note that the NiO-GDC composite was flash sintered at 200 °C under 50 V cm$^{-1}$. For GDC, flash sintering, the power supply is quickly switched from voltage control to current control upon reaching a preset value of the current. The transition between voltage and current control produces the spike in the curve of power dissipation, which is a sign of flash sintering. The peaks of power densities reached values of 584 and 1132 mW mm$^{-2}$ for the lowest and highest limit current density, respectively. This difference can affect the densification process, as reveals the remarkable difference in the microstructure in figure 7(b). The specimen that reaches 130 mA mm$^{-2}$ shows poor densification, with a large remaining porosity and inhomogeneity between grain sizes of GDC phase (white $\rightarrow$ higher atomic weight) and NiO phase (dark $\rightarrow$ lower atomic weight), where the NiO phase had a greater grain size. On the other hand, the sample that reaches 260 mA mm$^{-2}$ had a high degree of densification, although it is also possible to observe a larger grain size for the NiO phase.

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Sintering is observed at temperatures above 600 °C at 50 V cm⁻¹ [5], although is not observed at this same field in the samples made by tape casting [4]. This can be attributed to the difference in the initial green density. In any case, according to these previous data, it is not possible to obtain flash sintered specimens of single-phase GDC at 200 °C and 50 V cm⁻¹, which means that the presence of NiO phase favors the GDC sintering mechanism at a current density of 260 mA mm⁻². Similar behavior has been reported for the alumina-YSZ composite [9]. These phases separately have a different behavior under an electric field. For example, at 150 V cm⁻¹, undoped alumina does not experience flash phenomena, while single-phase of 3YSZ sinters at 750 °C. In alumina-3YSZ, with the same field, the composite sinters near to fully density at 1060 °C. Apparently, there is an improvement in alumina-related kinetics along the interface of the two phases and, similarly, this approach can also be inferred for the GDC kinetics at the NiO/GDC interface. The positive effect of the GDC phase on the sinterability of NiO-GDC composites has also been reported by Grilo et al [34], and reported that the addition of 10 wt.% of GDC to NiO leads to a relative density of 90% (for conventional sintering at 1400 °C), against 65% for single-phase NiO. Besides, the composites with 10–60 wt.% of GDC achieved over 95% relative density (against 70% for NiO) after sintering at 1500 °C. The remarkable sinterability of the NiO-GDC composites in comparison to NiO is most likely due to the minor cationic impurities from the GDC phase.

Electrical conductivity was measured by the two-probe method (d.c. electrical conductivity) along the sample, in the temperature range between 400 and 650 °C in air atmosphere. The conductivity was calculated using equation (2).

\[
\sigma = \frac{1}{RS}
\]
Figure 7. (a) Power density for samples under 50 V cm\(^{-1}\) at 200 °C, limit current density of 130 and 260 mA mm\(^{-2}\), (b) Backscattering SEM images of the NiO-GDC composite.

Figure 8. Electrical conductivity at different temperatures (a) and Arrhenius plots for samples under different electrical limits currents densities: 130, 200 and 260 mA mm\(^{-2}\) (b).
where $l$ is the length, $R$ is the electrical resistance and $S$ is the cross-sectional area. Figure 8 shows the electrical conductivity values (a) and the Arrhenius plots of the total conductivity as a function of the reciprocal absolute temperature (b). Figure 8(a) depicts the results for three different specimens flash sintered at limited current densities of 130, 200 and 260 mA mm$^{-2}$. As expected, the total conductivity increases with temperature, reaching a maximum value at 650 °C for all samples. The sample under 130 mA mm$^{-2}$ has slightly lower conductivity values compared to the others, which may be due to the high remaining porosity (figure 7(b) left). On the other hand, the samples at 200 and 260 mA mm$^{-2}$ exhibit near conductivities in the temperature range of 400 °C–650 °C.

The total conductivities values at different temperatures were plotted against the reciprocal absolute temperature in figure 8(b). The total activation energy for electrical conductivity is given by the equation (3):

$$\sigma = \frac{(A/T)}{\exp (-E_a/RT)}$$

(3)

Where $A$ is a pre-exponential factor and $E_a$ is the activation energy for electrical conduction. It can be seen that there is an overlap between curves of 200 and 260 mA mm$^{-2}$, which was expected by the similar conductivity values obtained under both regimes and, therefore, the same activation energy was calculated. There is a wide range of activation energy and conductivity values for NiO-GDC samples reported in the literature. It is expected since powders are prepared by different synthesis methods and the sintering conditions might strongly influence the formation of defects and the densification [34–36]. Under the measuring temperature range of 500 °C–650 °C, one-step synthesized NiO-GDC composites conventionally sintered at 1500 °C showed an activation energy $E_a$ of around 0.2 eV for similar compositions [34]. The composition plays an important role in the conductivity of NiO-GDC composite. It has been reported that over the percolation limit of 40% mol NiO, the conductivity is predominantly electronic, confirming that total conductivity is governed by the NiO phase [19, 35]. The low activation energies of 0.20 and 0.23 eV obtained in the present work are related to the NiO-NiO contacts. Therefore, it is worth mentioning the similar electrical performance of NiO-GDC composites flash sintered at 200 °C and NiO-GDC composites conventionally sintered at temperatures as high as 1500 °C.

**Conclusions**

The flash sintering technique was applied successfully on NiO-GDC composite. The high values of electric field in combination with high current densities produce inhomogeneity of densification which allows decreasing the applied electric field for a constant current density. By using an electric field of 50 V cm$^{-1}$ and a current density of 260 mA mm$^{-2}$, it was possible to flash sinter the NiO-GDC composite to obtain dense samples at a temperature as low as 200 °C. The densification was not reached at 130 mA mm$^{-2}$, although the electrical conductivity under the same condition was slightly less than the measured values for the specimen flash sintered at 200 and 260 mA mm$^{-2}$. The electrical conductivity values present a noticeable improvement with respect to those reported in the literature, which must be examined in greater detail, requiring in the future work the application of the electrochemical impedance spectroscopy (EIS) technique to elucidate the influence of grain boundaries on the global conductivity of the material.

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