



Instability of supercritical porosity in highly doped ceria under reduced oxygen partial pressure

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The thermomechanical behavior and microstructural evolution of low relative density (~ 0.40) gadolinium-doped ceria are characterized under oxidative and reducing conditions at high temperatures. The electronic defects generated in the structure by Ce^{4+} to Ce^{3+} reduction play an important role on all mass diffusion phenomena, including densification and grain growth. Thermodynamically stable porosity (supercritical porosity) is dominant for isothermal sintering treatments in air. Conversely, the facilitated diffusion of ions through the lattice in reducing conditions results in a nearly full densification.

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Due to its high oxide ion conductivity, catalytic properties and chemical stability under diverse operating conditions, ceria and doped ceria are considered among the most relevant materials for energy systems and chemical conversion [1–7]. These materials are used both as dense layers, e.g. as electrolytes in solid oxide fuel cells, and as highly porous systems for gas conversion and catalytic substrates [6,8,9]. Full control of the microstructural features both during the fabrication and operation is essential in order to improve performance in the final application [10].

In porous materials with very low relative density, the large porosity is stable and usually cannot be annihilated by sintering. Kingery and Francois [11] have demonstrated that, where the ratio between the pore size and the particle size is the same as or above a critical value, the porosity does not shrink during sintering. In randomly packed materials, the presence of supercritical porosity, i.e. pores with size above the critical value, depends on the density of the green body before sintering, and Chen and Chen [12,13] showed that the critical ratio of pore size to particle size for thermodynamical sinterability in CeO_2 is 0.46. In other cases the large porosity is formed by the use of pore formers with a larger size than the starting particle. Supercritical porosity can greatly influence densification and grain growth mechanisms, and it has been widely reported that large porosity agglomeration acts in Ce–Gd–O (CGO) as a densification inhibitor [14–16]. In previous work, we

showed that the reduction of Ce^{4+} to Ce^{3+} and the related change in oxygen vacancy concentration have a significant influence on the sintering kinetics [17]. The experimental observations showed that grain growth of CGO was limited in air due to solute drag phenomena at the grain boundaries in highly doped ceria [17–19], while the effect of a thermal treatment in 9% H_2/N_2 on CGO pellets resulted in rapid grain growth, from ~ 250 nm to ~ 10 μm , and in very few residual porosities [17,20].

Since CGO plays an important role in several technological applications operating both in reducing and oxidative conditions [3–5,21], in this study we gave great relevance to the combined effect of chemical reduction and temperature on the densification mechanism and microstructure properties of low relative density gadolinium-doped ceria.

Commercial CGO ($\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95-\delta}$) powder from Rhodia (France) with a specific surface area of 5.2 m^2 g^{-1} , named ultralow surface area (ULSA), was used for tape casting [8]. In order to obtain tapes with low green density, graphite (V-UF1 99.9, specific surface area: 16.4 m^2 g^{-1} ; Graphit Kropfmühl, Germany) was used as a pore former. This forms pores that are 10–100 times larger than the starting particles, ensuring the presence of supercritical porosity in the ceramic body [14]. After drying, the tapes were laminated and cut into 10 mm \times 4 mm rectangular bars, with a thickness of 3 mm. Relative density of the CGO tape was around 40% after debinding. In such conditions, the presence of thermodynamically stable porosity is thus expected [12,13] and CGO densification is inhibited [14]. The densification process was performed with a high-precision thermomechanical analyzer (TMA; 402 F1

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Hyperion, Netzsch, Germany) which operates as a contact dilatometer at high temperatures (up to 1550 °C). The samples were fired continuously in air at a heating rate of 0.33 °C min⁻¹ from room temperature to 400 °C and held for 4 h to ensure the burn-out of all organics. After binder burn-out, the samples were fired at the same heating rate to 800 °C and held for 2 h to remove the graphite pore former. The samples were then cooled down, followed by sintering at heating rates of 0.33, 1 and 5 °C min⁻¹ from room temperature to 1400 °C. Different heating rates were performed for the sintering kinetics evaluation. Temperature sweeps, from room temperature to 1400 °C, were performed in a flow of 60 ml min⁻¹ in air ($p_{O_2} = 0.2$ atm) or in dry 9% H₂/N₂ ($10^{-24} < p_{O_2} < 10^{-12}$ atm, depending on temperature). The uniaxial viscosities of the samples were measured with a thermomechanical analyzer performing cyclic loading dilatometry, as reported in Ref. [22]. For this characterization, the samples were sintered at a heating rate of 1 °C min⁻¹ from room temperature to 1400 °C, in air and under reducing conditions, respectively. Microstructures were determined using scanning electron microscopy (SEM; Carl Zeiss field emission microscope (SUPRA 35) for high-resolution imaging) on mechanically polished cross-sections of the samples sintered for 1 and 60 h at 1450 °C, both in air and under reduced oxygen partial pressure. Isothermal sintering for 1 and 60 h were adopted to analyze the combined effect of holding time and different atmospheres on the densification and microstructure evolution. The relative densities of the samples after sintering were estimated by SEM image analysis using freeware software ImageJ®.

In recent studies, the authors of the present work reported on mass diffusion mechanisms for CGO powders of diverse morphologies sintered under low oxygen partial pressure ($p_{O_2} < 10^{-12}$ atm) [17]. Such phenomena are activated by the reduction of Ce⁴⁺ to Ce³⁺, which, increases the mass diffusion coefficient compared to the oxidized form by several orders of magnitude, leading to full densification and rapid grain growth at low temperatures [17]. Consequently, dramatic changes in the microstructure are observed. Shrinkages and shrinkage rates of highly porous CGO layers measured under different heating conditions, in air and in 9% H₂/N₂, are reported in Figure 1a and b. In particular, Figure 1a shows the shrinkages of CGO as a function of temperature during sintering in reducing conditions and in air at different heating rates.

Under reducing conditions, the onset temperatures of highly porous CGO, where the shrinkage became evident, was as low as 850 °C, which is at least 150 °C lower than that in air. The densification of CGO in 9% H₂/N₂ was thus significantly enhanced at lower temperatures. At temperatures above 900 °C, due to the reduction of Ce⁴⁺ to Ce³⁺ resulting in increased oxygen non-stoichiometry and the formation of oxygen vacancies, the diffusion of cations through the lattice was facilitated, and this resulted in enhanced densification of CGO [18,23]. Assuming an isotropic shrinkage behavior during sintering, the relative densities were calculated as a function of temperature from the linear shrinkage data:

$$\rho(T) = \rho_0 e^{-3\varepsilon} \quad (1)$$

where ρ_0 is the relative density of green bodies and ε is the linear shrinkage [15]. After debinding in air, the relative density of CGO was 0.40. The relative densities of CGO in air and under reducing conditions are showed in the inset

of Figure 1a. The final relative densities of CGO sintered at 1400 °C (at a heating rate of 1 °C min⁻¹) in air and 9% H₂/N₂ were about 64% and 82%, respectively (Fig. 1a, inset). Figure 1b shows the shrinkage rates, which are the derivatives of the data in Figure 1a with respect to time. The maximum shrinkage rates for CGO sintered in 9% H₂/N₂ were always found at lower temperatures (at least 150 °C) with respect to that sintered in air. At a certain temperature, the lower heating rate resulted in increased diffusion time for densification [24]. In particular, for samples sintered both in air and under reducing conditions, as the heating rates increased, the shrinkage rates increased and shifted toward higher temperatures.

During sintering, the viscosity of ceramic materials changes in line with the mass diffusion phenomena which are activated in the process. These strongly depend on the temperature, the atmosphere and the microstructural features of the materials (i.e. relative density, grain size, and porosity) [20,25–28]. Uniaxial viscosities of the porous CGO were calculated as a function of sintering temperature both in air and under reduced oxygen partial pressure, as shown in Figure 2. As reported by Bollina and German [29], the uniaxial viscosity decreases with increasing mass diffusion during the preliminary and intermediate stages of the sintering. The viscosities decreased to around 10 GPa s and to 5 GPa s for CGO sintered in air and 9% H₂/N₂, respectively. The different viscous behaviors can be attributed to different sintering mass diffusion mechanisms at the grain boundaries, and also to an incipient diversification of the microstructure under the two different sintering conditions [20]. In the later stage of the sintering, the grain growth greatly influenced the viscosity of CGO treated under reducing conditions. Figure 2 shows that, at temperatures above 1000 °C, the viscosity of CGO treated in 9% H₂/N₂ increased due to the change in the microstructures in the sample, from a highly porous body to a quasi-dense continuum. At the end of the heat treatment at 1400 °C, the viscosity of CGO treated under reducing conditions reached a constant value higher than that for the sample in air. Such phenomena can be attributed to the considerable enhancement of densification and grain growth under reducing conditions [20]. Conversely, the slight increase in viscosity values for CGO sintered in air was mainly due to the annihilation of small pores and the rearrangement of large pores, as reported for the same material by Ni et al. [14].

The combined effects of holding time and sintering atmosphere on microstructure evolution of porous CGO were studied at 1450 °C, as shown in Figure 3 for samples treated in air (Fig. 3a and b) and in 9% H₂/N₂ (Fig. 3c and d). After sintering in air at 1450 °C for 1 h, the relative density of CGO was as low as 70%, as shown in Figure 3a. Increasing the holding time considerably (to 60 h) did not improve the relative density substantially, reaching a value of only 75%, as shown in Figure 3b. Conversely, the CGO sintered under reducing conditions showed a much higher densification; the relative density was estimated to be 85% after just 1 h of isothermal sintering at 1450 °C (Fig. 3c). After a dwell time of 60 h at 1450 °C under reducing conditions, a relative density of 95% was achieved (Fig. 3d). The results shown in Figure 3 are also consistent with the previous experimental observations that grain growth of highly doped ceria is limited in air due to solute drag phenomena at the grain boundary [14,17,20], while the effect of a prolonged thermal treatment in 9% H₂/N₂ resulted in very

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