

Effect of Sintering Atmosphere and Particle Size on the Ionic Conductivity of Gadolinia-Doped Ceria

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The effects of sintering under oxidizing, inert and reducing atmospheres on the microstructure and ionic conductivity of gadolinia-doped ceria were investigated. Commercial powders with specific surface areas from ~ 7 to $210 \text{ m}^2 \cdot \text{g}^{-1}$ were used as received. The sintering experiments were carried out in air, nitrogen, argon and in a mixture of argon-4% hydrogen. Powder compacts were isothermally sintered at 1523 K for 2 h. After isothermal treatments the relative density of compacts sintered at several atmospheres ranged from 92-97%. The linear shrinkage in air of powders with different particle sizes behave differently, but after the isothermal treatment their microstructure is homogenized and no significant difference was observed, except for the compacts sintered under reduced atmosphere. The total ionic conductivity of specimens sintered under oxidizing and inert atmospheres is similar. The specimens sintered under reducing atmosphere exhibits larger grain size and lower total ionic conductivity.

Introduction

Gadolinia-doped ceria, GDC, has been extensively investigated over the last decades as promising electrolyte and electrode material for intermediate-temperature solid oxide fuel cells (1). One of the main concerns of this ceramic material is its relatively low sinterability, requiring temperatures higher than 1573 K to achieve good densification, even for chemically synthesized powders (2,3).

A considerable amount of work may be found in the literature on the sintering process of doped cerias under oxidizing atmosphere (see for example 4-8). In contrast, relatively few studies have been carried out in oxygen-lean atmospheres. Recently, it was shown that an accelerated densification occurs upon sintering gadolinia-doped ceria under reduced oxygen partial pressures (9). The observed change in the mechanism of sintering was attributed to the formation of oxygen vacancies, electronic defects and reduced gadolinium/cerium cation mismatch (10). To the best of our knowledge no systematic study may be found on the effect of inert atmospheres on the microstructure of gadolinia-doped ceria.

In this work, the effect of the sintering atmosphere, including oxidizing, inert and reducing, on the microstructure and ionic conductivity of 10 mol% gadolinia-doped ceria is investigated. The main purpose of this study is to optimize the sintering process for obtaining a dense material with controlled microstructure along with good ionic conductivity.

Experimental

Ceria containing 10 mol% gadolinia, $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-\delta}$, commercial powders (>99.5%, Fuel Cell Materials), with specific surface area ranging from 7.4 to 210 $\text{m}^2\cdot\text{g}^{-1}$ were used as starting materials. Cylindrical pellets were prepared by uniaxial and isopressing followed by sintering at 1523 K for 2 h under oxidizing (air) as well as oxygen-lean (nitrogen, argon and a mixture of argon-4% hydrogen) atmospheres.

The average initial particle size of the powders was evaluated by nitrogen adsorption (Quantachrome, NOVA 1200) using the BET method (t_{BET}) and transmission electron microscopy (Jeol, 2010), (t_{TEM}), and agglomerate sizes, (t_{LS}), by dynamic laser scattering (Brookhaven, ZetaPlus). Characterization of the sintered materials was carried out by density measurements, thermodilatometry (Anter-1161, Unitherm), field-emission scanning electron microscopy (FEI, Inspect F50) and impedance spectroscopy (HP4192A). The apparent density was determined by the immersion method in distilled water. The linear shrinkage curves of powder compacts were obtained in air with heating rate of 10 $\text{K}\cdot\text{min}^{-1}$ up to 1600 K. For microstructure observations the sintered specimens were polished and thermally etched. Silver was used as electrode material for impedance spectroscopy experiments. The ionic conductivity measurements were carried out in the 5 Hz to 13 MHz frequency range with 100 mV of applied signal.

Results and discussion

Table I lists the particle size for the several starting powders obtained by the BET and transmission electron microscopy methods.

Table I. Particle size of the starting powders determined by transmission electron microscopy and nitrogen adsorption methods, and agglomerate size determined by dynamic laser scattering.

Powder	t_{TEM} (nm)	t_{BET} (nm)	t_{LS} (μm)
A	70	112	32
B	20	23	20
C	4.5	4	10

The agreement between values obtained by TEM and BET for powders B and C reveals that they consist of nanostructured and single crystalline particles. In contrast, the large difference between those values for powder A indicates that it is composed by nanostructured and polycrystalline particles. The mean agglomerate size increases with increasing the particle size.

The linear shrinkage curves obtained under oxidizing atmosphere (Fig. 1) show that good densification of gadolinia-doped ceria is attained depending on the initial size of the powder particles.

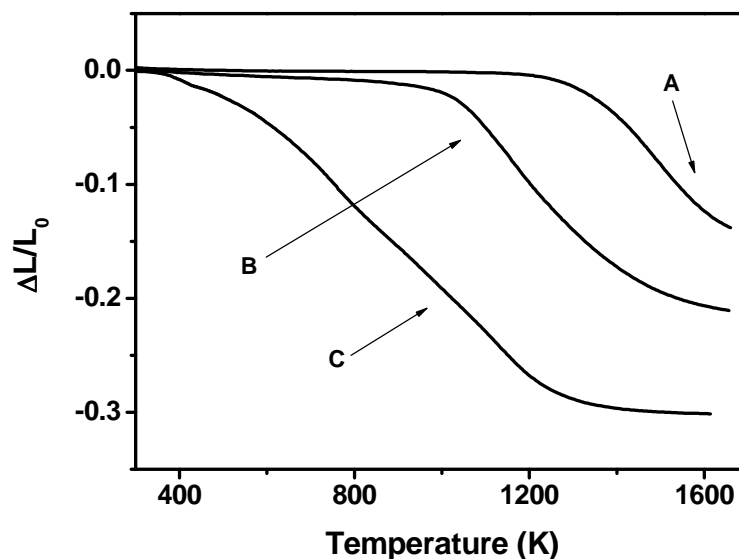


Figure 1. Linear shrinkage curves of powder compacts in air.

The larger is the average particle size, the lower is the linear shrinkage level at a given temperature. The temperature at which the shrinkage starts decreases with decreasing the particle size. However, for powder C, the onset temperature of the linear shrinkage is higher than that in Fig. 1, because this material undergoes mass loss (not shown here) up to 870 K. Then, in this case, the onset temperature may be considered to be higher than 870 K.

Table II shows relative density values for powders compacts sintered under different atmospheres.

Table II. Values of relative density of specimens prepared with powders A, B and C and sintered at 1523 K for 2 h under different atmospheres.

Atmosphere	A (%)	B (%)	C (%)
Air	93.2	95.6	96.8
Nitrogen	95.4	96.5	95.1
Argon	95.0	96.0	96.9
Ar/4% H ₂	92.1	92.3	93.1

Surprisingly, after isothermal treatments at 1523 K for 2 h all sintered specimens attained relative densities in excess of 92%. This means that the powder with small particle size possesses an accelerated grain growth.

For the sake of brevity only results obtained with specimens prepared with powder B will be shown hereafter. A full account on the effect of the particle size including all three powders will be published elsewhere.

The microstructure of the powder compacts changes according to the sintering atmosphere. Fig. 2 shows, as an example, scanning electron microscopy micrographs of specimens prepared with powder B after sintering at 1523 K for 2 h.

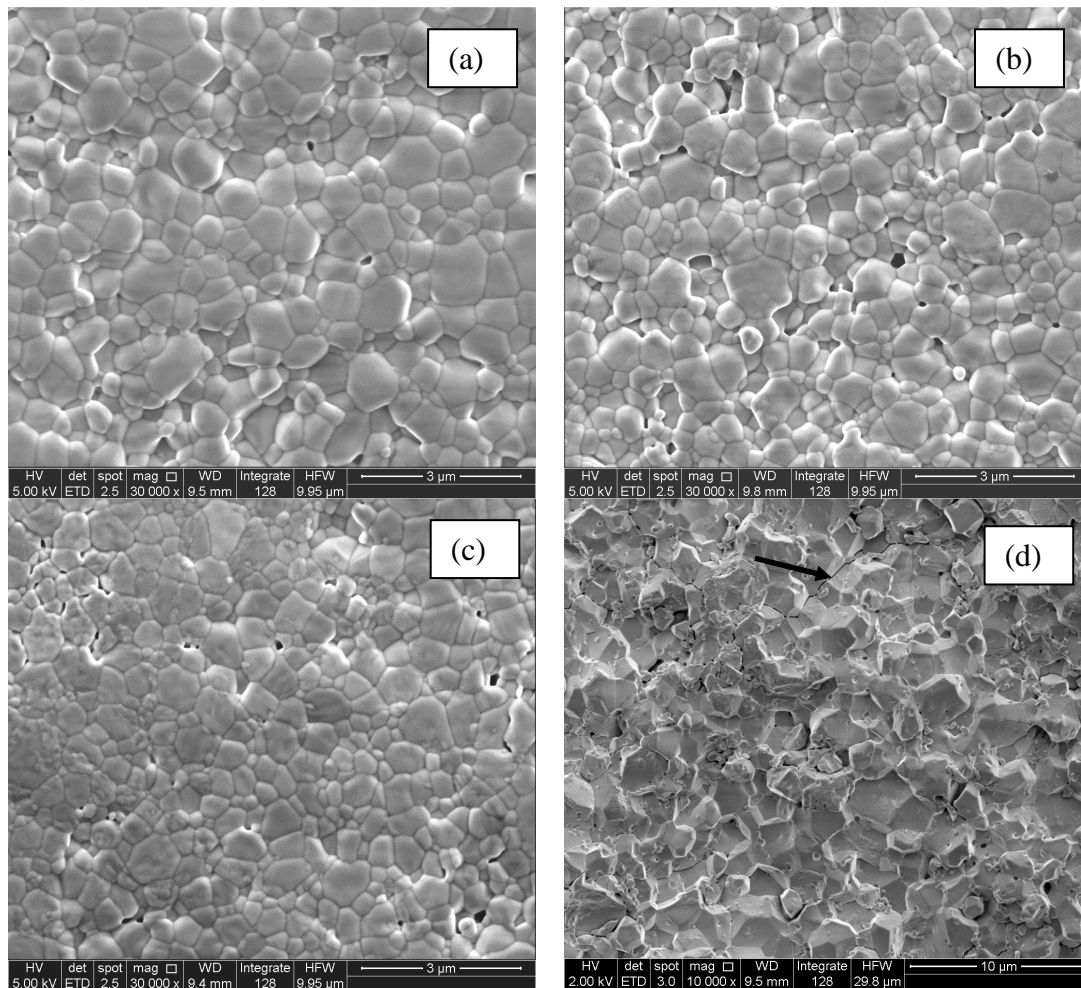


Figure 2. Representative scanning electron microscopy micrographs of powder compacts prepared with powder B and sintered at 1523 K for 2 h in: (a) air, (b) nitrogen, (c) argon and (d) argon-4% hydrogen.

The microstructure of the specimen sintered in air (Fig. 2a) shows polygonal grains and reduced porosity. The pores are preferentially found at the triple grain junctions and the grain size distribution is comparatively broad. The powder compacts sintered under inert atmospheres of nitrogen (Fig. 2b) and argon (Fig. 2c) show similar mean grain size compared to the specimen sintered in air ($\sim 0.7 \mu\text{m}$). In contrast, the specimen sintered in a mixture of argon-4% hydrogen (Fig. 2d) exhibits large grain size (note the different scale bar) and extensive porosity. In this case, the pores are found inside the grains (intragranular) and along the grain boundaries (intergranular). The intragranular porosity evidences an accelerated kinetics of grain growth, where the pore mobility is lower than the grain mobility. The formation of intergranular pores indicates that gaseous species might have been trapped along the boundaries, possibly due to a low solubility of these species in the matrix or due to some reaction of the gaseous species with impurities at the boundary region. As a consequence, microcracks (one of them is indicate by the arrow)

along the grain boundaries were observed to occur, in a clear demonstration of boundary weakening.

The ionic conductivity of sintered specimens was determined by impedance spectroscopy. Fig. 3 shows the impedance plots at 500 K of specimens prepared with powder B and sintered in different atmospheres. In these plots the impedance was normalized for sample dimensions. In the frequency range of measurements the impedance plots exhibit two well-resolved semicircles and a low-frequency spike.

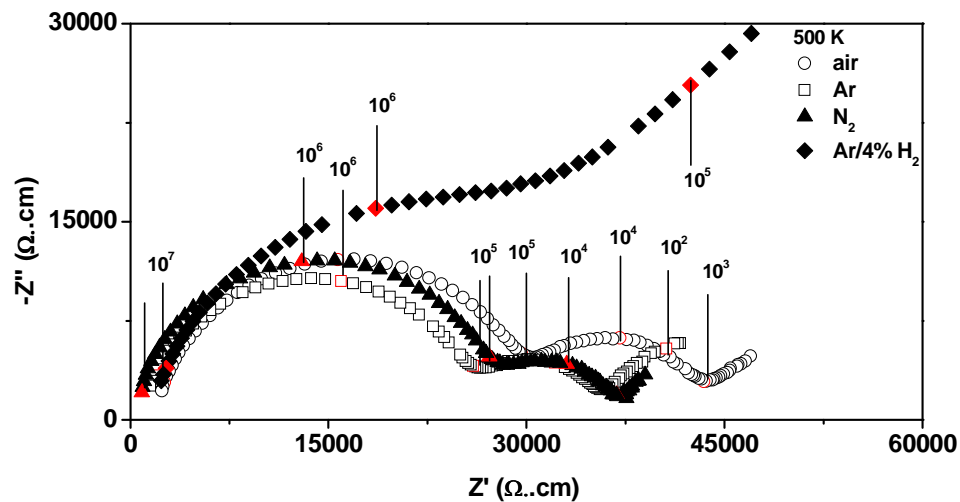


Figure 3. Impedance spectroscopy diagrams of specimens prepared with powder B and sintered at several atmospheres. Temperature of measurement = 500 K.

The main feature in this figure is the variation of the grain boundary blocking effect. The blocking of charge carriers at the grain boundaries is higher for specimens sintered in reducing (Ar/4% H₂) atmospheres than those in inert (N₂ and Ar) and oxidizing (air) atmospheres.

The Arrhenius plots of the total conductivity of specimens prepared with powder B and sintered at several atmospheres are shown in Fig. 4.

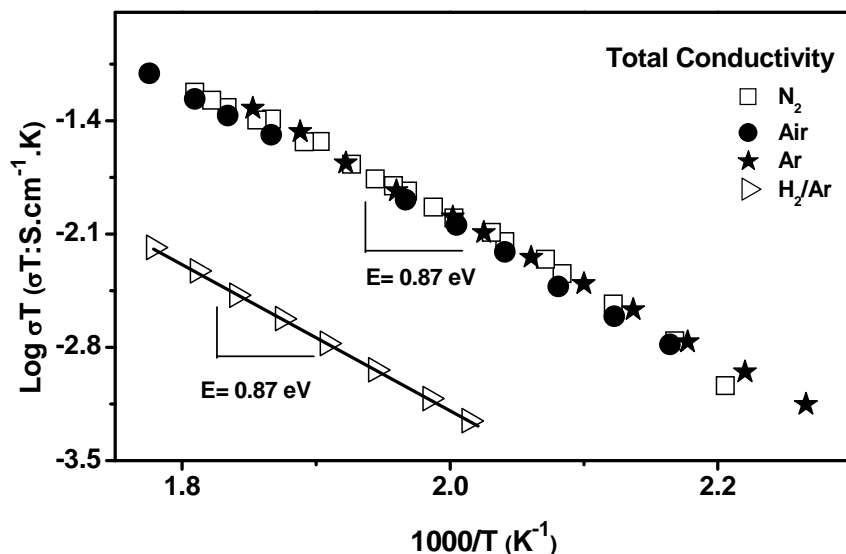


Figure 4. Arrhenius plots of the total ionic conductivity of $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-\delta}$ ceramics sintered in diverse atmospheres.

The ionic conductivity value of specimens sintered under oxidizing as well as inert atmosphere is approximately the same. It is remarkable the decrease of the total conductivity of $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-\delta}$ sintered under reducing atmosphere. This effect may be attributed to the extensive porosity (Fig. 2) and to microcracks. The activation energy for conduction determined from the slope of these straight lines is 0.87 eV.

Conclusions

All investigated properties changed to some extent with the sintering atmosphere and the initial particle size of the starting powders. The particle size influences the linear shrinkage in air. The powder with the lower particle size exhibits about 30% of linear shrinkage up to 1300 K. After isothermal treatment for 2 h at 1523 K dense specimens were obtained when sintered in air and inert atmospheres. Specimens sintered under reducing atmosphere exhibit extensive porosity and intergranular microcracks. The overall microstructure seems to be more homogeneous for specimens sintered under inert atmospheres. The activation energy for conduction is similar for all specimens and amounts 0.87 eV.

Acknowledgments

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