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Sintering behaviour of $\text{CeO}_2\text{-Gd}_2\text{O}_3$ powders prepared by the oxalate coprecipitation method

P. DURAN, J.R. JURADO and C. MOURE

Instituto de Cerámica y Vidrio (CSIC), Electroceramics Department, 28500 Arganda del Rey, Madrid, Spain

ABSTRACT

The powder and compact characteristics as well as the sintering behaviour of two $\text{CeO}_2\text{-Gd}_2\text{O}_3$ compositions prepared by the oxalate coprecipitation method are studied as a function of the powder particle size and the pore-size distribution in the powder compacts. Shrinkage was measured at a constant heating rate and the results are compared with those obtained by isothermal sintering experiments. Grain growth and microstructural development on sintered samples were studied.

INTRODUCTION

Gadolinium-doped cerium dioxide could be considered like a good solid electrolyte for high-temperature fuel-cells in view of the optimal $\text{Ce}^{4+}/\text{Gd}^{3+}$ ionic radii ratio (1). Nevertheless many difficulties are to be found in obtaining research-quality ceramics with reliable and reproducible fabrication parameters.

In previous works carried out by Kudo y Obayashi (2), Dirstine et al (3) and Gerhard et al (4) it was established that the most promising composition seemed to be that containing about 20 mole% $\text{GdO}_{1.5}$, however the results attained for the different authors do not coincide. Although the electrical behaviour was exhaustively studied for the above mentioned authors, nevertheless such studies were done at a fixed frequency by which the results cannot give a real interpretation about the influence of other parameters on the total electrical behaviour of these ceramic materials. It must be mentioned that Riess et al (4) reported some suggestions about the influence of the inhomogeneities existing in the samples on the electrical behaviour. Most of the authors believed that the results discrepancies are a consequence of the following causes, a) Different raw materials, and b) Distinct processing procedures and fabrication methods.

The main objective of the present work was to prepare basically different solid electrolytes from ceria-gadolinia powders with different morphologies and to study their influence on the sintering and microstructural development.

EXPERIMENTAL PROCEDURE

$\text{Ce}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$ and $\text{Gd}(\text{NO}_3)_3$ were used as the starting materials. The suppliers analysis indicated the presence of several impurities in the $\text{Ce}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$, mainly Si, Ca, Fe, Na and K at several tens ppm. The impurity level of $\text{Gd}(\text{NO}_3)_3$ was not reported by the suppliers though that was at least 99.9% pure. $\text{Ce}(\text{NO}_3)_3 \cdot 4\text{H}_2\text{O}$ and $\text{Gd}(\text{NO}_3)_3$ in the appropriate amounts were dissolved in distilled water to give a stock solution which was diluted again with distilled water up to a 0.3 mole/l solution was attained.

The preparation sequence of the $\text{CeO}_2\text{-Gd}_2\text{O}_3$ precipitate was the following: The stock solution containing the required Ce-Gd composition Ce-4Gd (4 mole% Gd_2O_3) or Ce-8Gd (8 mole% Gd_2O_3) was added by dropping and blending to an aqueous oxalic acid solution containing 35 gr/l. During the coprecipitation a rigorous control of the pH (between 6.5 and 7) was kept by the dropwise addition of diluted ammonia. When the coprecipitation process was completed, a small amount of diluted NH_4OH was added to precipitate any rest of Ce or Gd which could remain in the solution. After filtering the precipitate was first washed with water, and then with isopropyl

alcohol. The precipitate was slowly dried in air at 70–80°C. Samples of the precipitates were studied by using SEM, X-ray diffraction, and DTA/TGA. After calcining at 800°C for 1h the powders were attrition-milled for 1h in isopropyl alcohol, dried and examined by X-ray diffraction, SEM and BET (nitrogen adsorption). The calcined powders were formed into a billet without binder, isostatically pressed at 200 MPa, and then air sintered in the temperature range of 1200 to 1600°C for 4h. The study of the sinterability of the Ce-4Gd and Ce-8Gd calcined powders was performed on the isopressed compacts by using a dilatometer. The heating and cooling rates were 5°C/min and the sintering temperature was 1550°C. Bulk densities were measured by the Archimedes method using water as the liquid medium. Fracture surfaces from several samples were examined by SEM, which also enabled the grain size determinations on chemically etched polished surface samples.

The determination of the lattice constant was carried out by using a vertical computer-automated X-ray diffractometer with computer analysis of the rate. Cu K_{α} radiation with Ni filter was utilized. Only those peaks with angle $2\theta > 70^\circ$ were scanned for these measurements.

RESULTS AND DISCUSSION

Powder Characteristics

As shown in Fig. 1, graphic b, X-ray diffraction pattern of the coprecipitated oxalate showed a crystalline phase whose diffraction lines could not be indexed neither as cerium oxalate nor as gadolinium one, indicating that such a crystalline phase is not a mixture of the oxalates but a complex salt with an unknown formula. For comparison, in the same figure is shown the X-ray diffraction patterns of the commercial cerium oxalate (graphic a) and that of the thoroughly washed coprecipitated oxalate (graphic c). As it can be observed the X-ray diffraction peaks of the coprecipitated oxalate were strongly weakened by an intensive isopropanol washing leading to an almost amorphous oxalate. The initial precipitate exhibited a rod-like structure having an irregular prismatic shape which

Fig. 1. XRD patters of different cerium oxalates

after calcining retained such a morphology. Calcining the coprecipitated powders at 800°C for 1h leads to a powder with a particle morphology as shown in Fig. 2(A) and (B). A powder with microcracked and porous particles retaining the prismatic shape was obtained, and their dimensions varied from 0.5 to 1.5 μm length and 0.01 μm thickness. Calcination of the coprecipitates converted these to a fluorite-structure material whose X-ray diffraction patterns showed weak and very broad diffraction maxima. An estimation of the crystallite size was made from the broadened diffraction maxima of the calcined powders. The crystallite size measured were 30 and 41 nm for Ce-4Gd and Ce-8Gd respectively.

The average particle size of Ce-4Gd and Ce-8Gd powder samples after calcination at 800°C for 1h, as measured by Sedigraph were 3 and 1.5 μm about respectively. Differences in the particle size measured by SEM observations and that from the sedimentation technique arise as a consequence of the

particle agglomeration state. It is believed that the average particle size measured by using the sedimentation technique is rather an average of the agglomerate size. The surface area values as measured by the BET method were 55 and 64 m^2g^{-1} for the Ce-4Gd and Ce-8Gd calcined powders respectively.

Isothermal Sintering

The two calcined powders Ce-4Gd and Ce-8Gd isostatic-pressed at 200 MPa presented similar green density values, ($\sim 40\% D_{\text{th}}$). However microstructure of the green compacts was more uniform in the case of the Ce-8Gd samples, as it can be seen in Fig. 3(A) and (B). Figure 4 shows the isothermal sintering studies (4h cycle) for the $\text{CeO}_2\text{-Gd}_2\text{O}_3$ powder compacts. In the case of the Ce-4Gd samples a densification as high as 91% was achieved at 1300°C, while only a 88% was obtained in the Ce-8Gd samples. Above that temperature the sintering process occurred very rapidly for that samples which were 98% dense at 1400°C, and almost fully dense at 1500°C. In that temperature range the densification process for Ce-4Gd was much more slow, thus at 1400°C the samples were 95% dense and only 98.5% dense at 1500°C. Above that temperature the density of the Ce-8Gd sintered samples slightly decreased and the density of the Ce-4Gd samples still increased. The lattice parameters calculated

Fig. 2. SEM of calcined powders (A) Ce-4Gd, and (B) Ce-8Gd

on the 1550°C Ce-4Gd and Ce-8Gd sintered samples were 0.5416 and 0.5418 ± 0.0005 nm respectively in good agreement with those measured by Bevan et al (5) and Etsell and Flangas (6). From these lattice parameters values and the composition of the two samples, the theoretical densities were calculated to be 7.22 and 7.24 gr cm^{-3} respectively. Therefore the 1550°C sintered samples were 99.9 and 99.4% dense respectively. These results points out that the sinterability of Ce-8Gd powder, as previously stated, was higher than that of the Ce-4Gd one.

Shrinkage Behaviour

Figures 5 and 6 show the shrinkage and shrinkage rate of the powder compacts. Shrinkage of the Ce-4Gd compacts starts at about 400°C with a first maximum rate at 700°C in which a shrinkage of 12% was reached. A second and higher maximum rate was present at 1330°C, and an end point was not achieved above 1500°C for a shrinkage of approximately 23%. In the case of the Ce-8Gd compacts the shrinkage starts at about the same temperature (360°C) than that for Ce-4Gd compacts, however the first maximum rate was located at 660°C and a shrinkage of about 10%.

The second maximum rate was present at about 1460°C for a shrinkage of about 22%, and the end point was attained at about 1530°C. The density of the compacts after this experiment was 6.93 and 7.13 g cm^{-3} for the Ce-4Gd and Ce-8Gd samples respectively. In the temperature range of 700°C and about 950°C, the shrinkage rate significantly decreases. Such a decreasing could be associated, according to the XRD results, with the solid solution $\text{Ce}_{1-x}\text{Gd}_x\text{O}_{2-\frac{x}{2}}\Pi_{x/2}$ (Π is an oxygen vacancy) reaction formation. Effectively at this temperature range a transition from the almost amorphous phase to a polycrystalline one took place. This solid solution reaction formation does not apparently modify the volume porosity. When such a phase reaction formation is complete (at 1150°C and 1250°C respectively), the densification of the compacts progress and the shrinkage rate increases again attaining a maximum at 1330°C and 1460°C for Ce-4Gd and Ce-8Gd ceramic compacts respectively. In both maxima the sintering rate of the respective cubic solid solutions is maximum. At those temperatures the densities of the samples were ~ 90% and 97% dense respectively which are in good agreement with the isothermal sintering results.

Fig. 3. SEM of fracture surface for Ce-4Gd (A) and Ce-8Gd (B) compacted green bodies

Fig. 4. Isothermal sintering of Ce-4Gd and Ce-8Gd samples

Fig. 5. Shrinkage and shrinkage rate of Ce-4Gd samples.

Fig. 6. Shrinkage and shrinkage rate of Ce-8Gd samples

Microstructural Development

Figure 7 shows the microstructure evolution at 1400°C to 1600°C. Comparatively both kinds of sintered samples has the same aspect and presents grain sizes ranging from 1 to 7 μm and from 0.6 to 8 μm for Ce-4Gd and Ce-8Gd samples respectively.

Fig. 7. Microstructure of Ce-4Gd and Ce-8Gd samples sintered at 1400°C to 1600°C

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