

Sintering behavior of large size, Sm-doped ceria solid electrolyte disk

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The sinterability of a submicrometre-sized Sm-doped ceria solid solution powder (SDC, powder A) with a composition of $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ and a mechanically mixed submicrometre-sized Sm_2O_3 - CeO_2 powder (powder B) was studied at 1300-1550 °C in air in order to make a practical solid electrolyte disk of 150 mm diameter. No phase change was observed in powder A heated at 600-1550 °C. The Sm_2O_3 component in powder B dissolved into the CeO_2 powder at temperatures above 1500 °C. The sinterability of powder A was higher than powder B. The formation of SDC in powder B at 1500-1550 °C enhanced the sinterability. No cracks and no warps were observed in the small (10 mm diameter) and large (150 mm diameter) disks after sintering at 1300-1550 °C. The uniformity of microstructure was higher for the disk from powder A than from powder B.

Key words: Sm-doped ceria solid solution, Sintering, Density, Lattice parameter, Microstructure.

Introduction

Solid oxide fuel cells (SOFC) are candidates for highly efficient and clean electric generators. Recently SOFC with rare-earth-doped ceria (RDC) as a solid electrolyte has been widely studied because of the higher oxide ion conductivity of RDC than Y_2O_3 -stabilized ZrO_2 [1, 2]. This paper reports on the sintering of a large size Sm-doped ceria compact (150 mm diameter) as part of a process of developing a practical solid electrolyte. Usually, an increased scale of a powder compact is accompanied by the formation of cracks or warps due to the microstructural inhomogeneity after sintering. These defects need to be eliminated in a thin solid electrolyte with a large surface area to increase the electric power of a SOFC. In this paper, two types of starting powders were used: (A) a submicrometre-sized Sm-doped ceria solid solution (SDC) powder prepared by an oxalate co-precipitation method [3], (B) a mixture of submicrometre-sized Sm_2O_3 and CeO_2 powders. These powders were formed into disks of 10 and 150 mm diameters and sintered at 1300-1550 °C in air. The density, cracking, microstructures and phases produced during the sintering were studied for the two kinds of starting powders.

Experimental Procedure

The detailed powder preparation method of SDC with a composition $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ is reported in our previous paper [3]. The oxalate solid solution $(\text{Ce}_{0.8}\text{Sm}_{0.2})_2(\text{C}_2\text{O}_4)_3$ was produced at room temperature by adding the mixed nitrate solution (0.2 M) of Ce and Sm into 0.4 M oxalic acid solution. The formation of the solid solution was examined by X-ray diffraction (XRD, RAD-IIB, Rigaku Co., Japan) and thermogravimetric differential thermal analysis (TG 8110, Rigaku Co., Japan). The co-precipitated oxalate powder decomposed to a resultant polycrystalline oxide solid solution by heating up to 600 °C. The as-produced SDC powder was milled with alumina balls (3 mm diameter) at 80 rpm for 24 h in a dry process. After the milling, the specific surface area of the SDC was 41.7 m²/g, which corresponded to 20 nm diameter of equivalent spherical particles. On the other hand, the following commercial Sm_2O_3 and CeO_2 powders (Nihon Yttrium Co., Japan) were mixed in a molar ratio of Ce:Sm = 0.8:0.2 and milled with alumina balls (10 mm diameter) at 80 rpm for 60 h in a dry process: CeO_2 -chemical composition >99.99 mass%, the specific surface area 1.9 m²/g (438 nm diameter of equivalent spherical particles), Sm_2O_3 -chemical composition >99.99 mass%, the specific surface area 1.8 m²/g (455 nm diameter of equivalent spherical particles).

The as-produced Sm-doped ceria powder (powder A) and the mixed Sm_2O_3 - CeO_2 powder (powder B) were compacted to form two disks with different sizes (small

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disk: 10 mm diameter, 2 mm thickness, large disk: 150 mm diameter, 7 mm thickness) by uniaxial pressing (small disk) and isotropic pressing (large disk) at 196 MPa. The formed green compacts were sintered at 1300-1550 °C for 6 h in air. Both the heating and cooling rates were 100 Kh⁻¹. The bulk density of the sintered compacts was measured by the Archimedes method using distilled water. The phases produced were identified by X-ray diffraction (XRD, RAD-IIB, Rigaku Co., Japan) using a copper target (wave length 0.15405 nm) at a scan speed 2° minute⁻¹. The lattice parameter of SDC was measured by X-ray powder diffraction using NaCl as an internal standard substance (50 mass%) at a scan speed 0.5° minute⁻¹. The microstructures of the sintered compacts were observed using a scanning electron microscope (FE-SEM, JSM-6330F, Nihon Denshi Co., Japan) and an electron probe microanalyzer (EPAM, JXA-8621MX, Nihon Denshi Co., Japan). Samples were polished with 1 μm diamond paste and thermally etched for 1 h in air at 100 °C below the sintering temperature.

Results and Discussion

Phases produced in heated powders

Figure 1 shows the X-ray diffraction patterns for powder A heated at 600-1500 °C. Only ceria solid solution was detected in the starting and heated powders. A com-

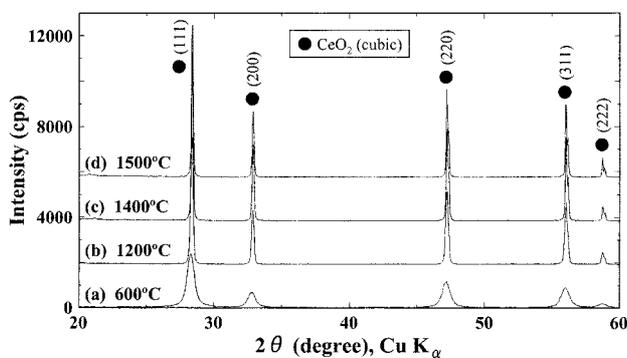


Fig. 1. X-ray diffraction patterns of powder A heated at 600-1500 °C.

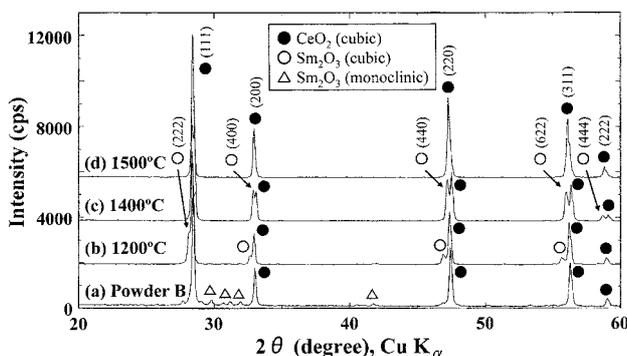


Fig. 2. X-ray diffraction patterns of starting powder B and powder B heated at 1200-1500 °C.

plete Sm-doped ceria solid solution was produced from the co-precipitated oxalate precursor. Figure 2 shows the X-ray diffraction patterns for powder B heated at 1200-1500 °C. The as-mixed powder B contained cubic CeO₂ and monoclinic Sm₂O₃. Two crystalline phases of cubic Sm₂O₃ and cubic CeO₂ were identified in powder B heated at 1200-1400 °C. However, the heating at 1500 °C gave the X-ray diffraction pattern of only the CeO₂ solid solution. This result indicates that the Sm₂O₃ in powder B dissolved into the CeO₂ on heating at 1500 °C.

Figure 3 shows the lattice parameters of SDC in powders A and B as a function of heating temperature. In Fig. 3, half the lattice parameter of Sm₂O₃ identified in powder B is also plotted. Powder A provided a constant lattice parameter of 0.5435 nm over the wide heating temperature range from 600 °C to 1500 °C. The lattice parameter of SDC with a composition of Ce_{1-x}Sm_xO_{2-x/2} is fitted by Eq. (1) [4].

$$a = \frac{4}{\sqrt{3}} [xr_1 + (1-x)r_2 + (1-0.25x)r_3 + 0.25xr_4] \cdot 0.9971 \quad (1)$$

where a is the lattice parameter, r_1 , r_2 , r_3 and r_4 are the radii of the samarium ion (0.1079 nm), the cerium ion (0.097 nm), the oxygen ion (0.138 nm) and the oxygen vacancy, respectively. Hong and Virkar [5] proposed a value of 0.1164 nm for r_4 . The correction factor, 0.9971, was introduced from the ratio of the lattice parameter measured for pure ceria (0.5411 nm; JCPDS No. 43-394) to the calculated value 0.5427 nm based on the ionic radii. The measured lattice parameter for SDC in powder A was substituted into Eq. (1) to determine the Sm content. The value obtained, x , was 0.19 and agreed well the mixing ratio of the starting metals in the mixed nitrate solution.

The lattice parameter of the CeO₂ in the heated powder B was smaller than that of the SDC in the powder A and was 0.5415 nm in the temperature range below 1400 °C. This value corresponded to $x=0.02$ in Eq. (1), indicating little dissolution of Sm₂O₃ into CeO₂ during the heating. However, the lattice parameter

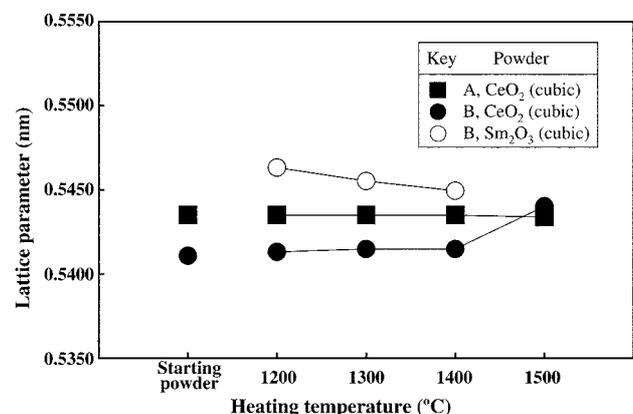


Fig. 3. Lattice constants of CeO₂ and Sm₂O₃ in powders A and B as a function of heating temperature.

(0.5440 nm) of the CeO_2 heated at 1500°C was close to that of the SDC in powder A. The lattice parameter corresponded to $x=0.23$ in Eq. (1), which was close to the mixing ratio of CeO_2 and Sm_2O_3 in powder B. On the other hand, the lattice parameter of Sm_2O_3 in powder B decreased gradually with increasing heating temperature. This result is explained by the dissolution of the CeO_2 component into Sm_2O_3 at $1200\text{--}1400^\circ\text{C}$ [6]. After the heating at 1500°C , no Sm_2O_3 was identified in the powder X-ray diffraction pattern (Fig. 2). This result indicates the dissolution of Sm_2O_3 into CeO_2 at 1500°C .

Sintering of Sm-doped ceria powder and $\text{Sm}_2\text{O}_3\text{-CeO}_2$ mixed powder

Figure 4 shows the bulk density of disks formed from powders A and B as a function of sintering temperature. The theoretical density (D) of SDC was calculated by the following vacancy model [7],

$$D = \frac{4xM_S + 4(1-x)M_{\text{Ce}} + 4(2-x/2)M_{\text{O}}}{N_A a^3} \quad (2)$$

where M_S , M_{Ce} and M_{O} are the atomic weights of samarium, cerium and oxygen, respectively, N_A is the Avogadro's number, and a the lattice parameter determined by X-ray diffraction pattern. The x value is the Sm content determined by Eq. (1). The relative density for powder A was based on the theoretical density 7.139 g/cm^3 which was calculated by Eq. (2). In powder compact B, the theoretical density was approximated by the mixing rule of the densities of SDC and Sm_2O_3 .

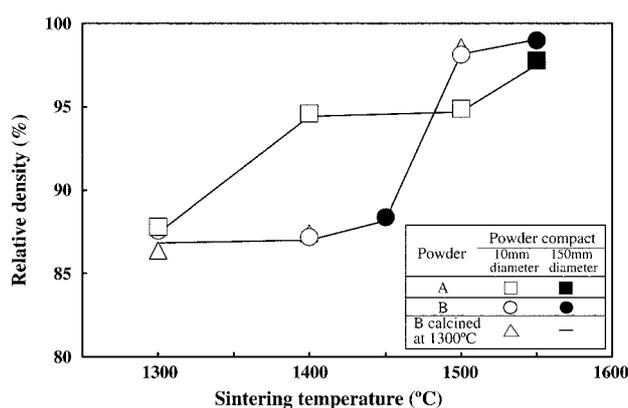


Fig. 4. Relative density of powders A and B sintered at $1300\text{--}1550^\circ\text{C}$.

As shown in Fig. 4, powder A was sintered highly at $1400\text{--}1550^\circ\text{C}$. The large disk with 150 mm diameter of powder A was also highly sintered, above 98% relative density at 1550°C . No cracks or no warps were observed in the small and large disks after the sintering. The sinterability of powder B was low at temperatures lower than 1450°C but was enhanced at $1500\text{--}1550^\circ\text{C}$. During the sintering at $1500\text{--}1550^\circ\text{C}$, the Sm_2O_3 component in powder B dissolved into CeO_2 . That is, the formation of SDC promoted the densification. The above interpretation also explains the high sinterability of SDC in powder A. In addition no cracks and no warps were produced in the dense large solid electrolyte disk (~ 150 mm diameter) from powder B.

Figure 5 shows the microstructures of sintered SDC disks with 10 mm diameter. Both the disks sintered

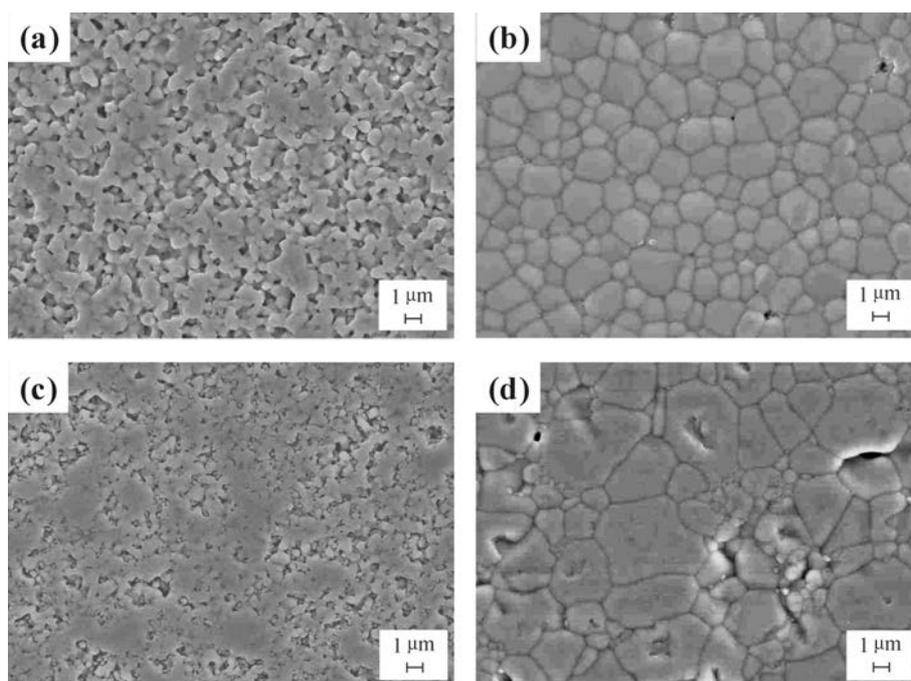


Fig. 5. Microstructures of Sm-doped ceria sintered from powder A (a, b) and powder B (c, d) at 1300°C (a, c) and 1500°C (b, d) in air.

from powders A (a) and B (c) at 1300°C showed porous microstructures with grains smaller than 1 µm. With an increase of sintering temperature to 1500°C, the SDC grains of 1-2 µm were sintered densely in the disk from powder A. Powder B provided a wider grain size distribution (0.1-2.5 µm) in the dense microstructure. Therefore, the microstructural uniformity of the disk from powder A was superior to that from powder B. EPMA analysis of the microstructure of the disk from powder A indicated that the Ce and Sm elements were uniformly distributed. In the disk from powder B, Ce and Sm elements were separately distributed at a sintering temperature lower than 1400°C. However, a uniform distribution of Ce and Sm elements was measured in the disk sintered at 1500°C, indicating the formation of SDC from powder B.

Conclusions

A Sm-doped ceria solid solution powder (SDC, powder A) and a mechanically mixed Sm₂O₃-CeO₂ powder (powder B) were formed into disks of 10 and 150 mm diameters and sintered at 1300-1550°C to produce a solid electrolyte with a composition of Ce_{0.8}Sm_{0.2}O_{1.9}.

(1) Only Ce_{0.8}Sm_{0.2}O_{1.9} was detected in powder A heated at 600-1550°C. Sm₂O₃ reacted with CeO₂ in powder B at 1500-1550°C to form a solid solution of Ce_{0.8}Sm_{0.2}O_{1.9}. Both the phases Sm₂O₃ and CeO₂ were identified in the powder compact B sintered at 1200-1400°C.

(2) Powder A showed a higher sinterability than powder B at the sintering temperatures of 1300-1450°C. The formation of SDC in powder B disk enhanced the sinterability at 1500-1550°C. No decrease in the sintered density, no cracks and no warps were measured for the large disks with 150 mm diameter from both the powders A and B.

(3) The dense microstructure with a narrower grain size distribution (1-2 µm) was achieved after the sintering at 1500°C in the disk from powder A than from powder B.

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