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Improvement of sinterability of gadolinia-doped ceria via a high-energy ball milling process

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Abstract High-energy ball milling process has been applied to gadolinia-doped ceria system. The sinterability of gadolinia-doped ceria was significantly enhanced by the high-energy ball milling process. A comparison was also made of the sintering behavior of milled powders doped with gallia as a sintering aid. Dense $Ce_{0.8}Gd_{0.2}O_{1.9}$ ceramics with 97% of the theoretical density could be obtained by sintering the milled mixture with 0.5 mol% Ga_2O_3 addition at 1,250 °C for 5 h.

Introduction

Ceria-based ceramics have been considered as one of the most promising electrolytes for intermediate temperature solid oxide fuel cells because their electrical conductivity is higher than that of yttria-stabilized zirconia [1]. However, ceria-based ceramics are difficult to be densified below 1,600 °C [2]. This makes them difficult for manufacturing ceria-based electrolytes, which can be used for solid oxide fuel cells system because ceria-based electrolytes and other components such as cathode and anode cannot be cofired at high temperatures.

In order to lower the sintering temperature, other methods utilizing fine starting powders and additives as sintering aids have been exploited. The preparation of ultra fine ceria-based ceramic powders has been studied by many investigators [2–9]. Most of the investigators have studied for the preparation of ultra fine ceria-based ceramic powders by chemical routes such as coprecipitation and sol–gel process. Recently, it has been reported that Ga_2O_3 [10–12], Al_2O_3 [13], MnO_2 [14], Fe_2O_3 [15], Co_3O_4 [16], and CoO [17] are effective sintering aids for the densification of ceria-based ceramics.

The chemistry-based wet routes are indeed advantageous over the conventional solid-state reaction one because they can synthesize ultra fine powders with atomic or molecular scale homogeneity. However, there are still problems for these chemical routes. It is difficult for these routes to control the process. They are also non-economical routes due to the expensive precursors and limits of the yield.

It is, therefore, desirable to find a simple, economic way to improve the sinterability of commercial powders. The ball milling process is superior to chemistry-based wet process for several reasons, such as the use of low-cost and widely available oxides as the starting materials, the convenience in process, and the possibility to produce large quantities. In addition, the high-energy ball milling process can produce submicron-sized powders or nano-sized powders and mix multi-component system homogeneously. Furthermore, the mechanically derived powders possess a high sinterability.

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In this study, gadolinia-doped ceria powders are prepared by the high-energy ball milling process using commercially available powders. The powder characteristics and sintering behavior of the high-energy ball-milled powders are investigated, and compared with those of conventionally milled powders. In particular, we investigated the effect of gallia doping on the sintering behavior of milled powders.

Experimental procedure

Figure 1 shows a schematic flow diagram of experimental procedure. Conventional ball milling technique and high-energy ball milling technique were applied to gadolinia-doped ceria system. Mixtures having a composition corresponding to $(Ce_{0.8}Gd_{0.2}O_{1.9})_{1-x}(Ga_2O_3)_x$ (x = 0–0.07) were milled using each technique. High purity commercial CeO_2 (99.9% purity, Aldrich Chemical Co., USA), Gd_2O_3 (99.9% purity, Aldrich Chemical Co.), and Ga_2O_3 (99.99% purity, Aldrich Chemical Co.) powders were used as starting materials.

The CeO_2 powders consisted of particles having a size of approximately 1 μm as shown in Fig. 2a. Figure 2 shows the SEM micrographs of commercial powders. The Gd_2O_3 powders consisted of particles having a size of approximately 3 μm. The Gd_2O_3 particles, however, contained more cracks. The Ga_2O_3 powders used as additives had the morphology of coarse elongated particles with a high aspect ratio.

The mixtures were conventionally ball-milled or high-energy ball-milled. A conventional ball milling process was carried out in ethanol for 24 h using a plastic jar and zirconia balls. A high-energy ball milling process was carried out in ethanol for 10 h using a Fritsch Pulverisette 6 planetary ball milling system with a zirconia bowl and zirconia balls as a milling medium.

After milling the mixtures, the powders were dried at 120 °C for 10 h. The dried powders were screened to –325 mesh. The sieved powders of –325 mesh size fraction were uniaxially dry-pressed at 196 MPa into pellets having a diameter of 12 mm and a thickness of 4 mm. After compaction, the compacts were sintered at 1,250 °C for 5 h. The heating rate was fixed to 10 °C/min.

The particle sizes and morphologies of the milled powders were measured by using a scanning electron microscope (SEM) (Model S-2400, Hitachi).

The sintered densities were measured by using the Archimedes method with water and/or calculated from the weights and the dimensions of the specimens. It was found that both methods used for obtaining the density provided almost the same value. An average value obtained from the five specimens was taken.

For microstructural investigation, the specimens were Au-coated and examined with a SEM. The elemental distribution was detected utilizing energy dispersive X-ray analysis spectroscopy (EDX) (Model Sigma MS3, Kevex).

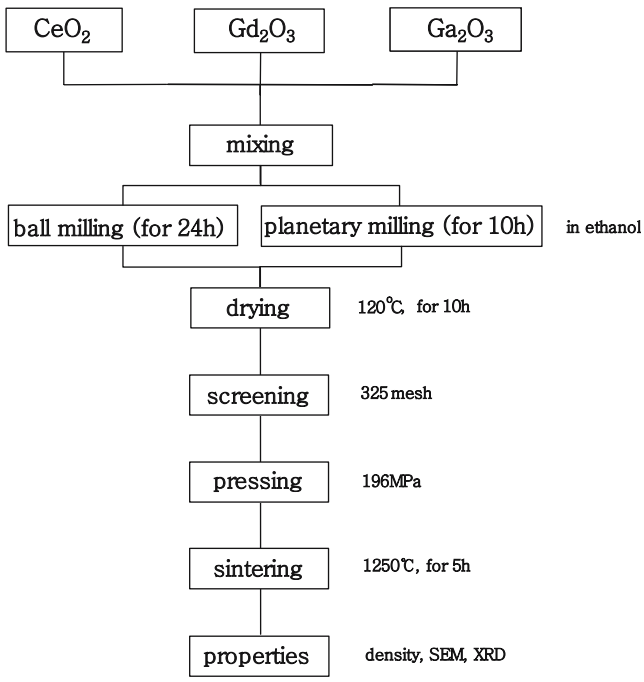

Fig. 1 Flow chart of experimental procedure

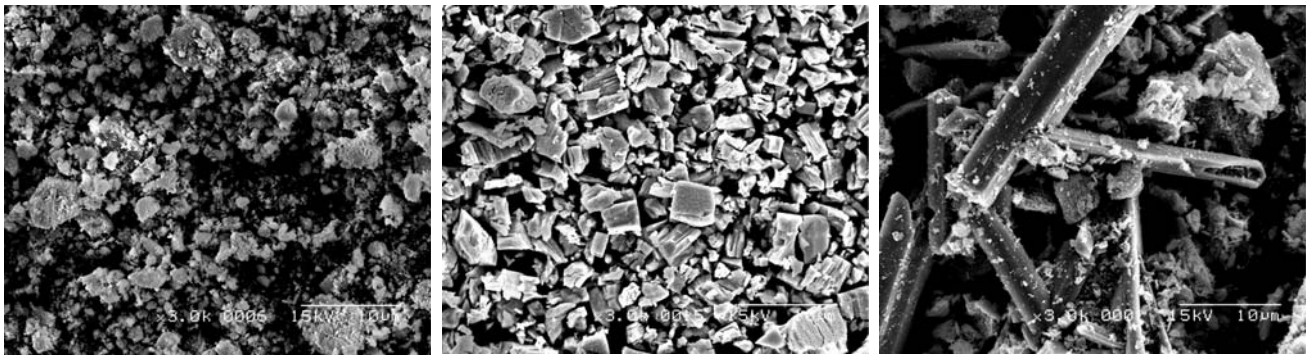

Fig. 2 SEM micrographs (×3,000) of commercial powders

X-ray diffraction (XRD) technique was employed to identify the phases. XRD was performed on the milled powders of sintered specimens by using Rigaku D/MAX IIIA diffractometer with a Ni-filtered CuKα radiation.

Results and discussion

The SEM micrographs of milled mixtures with 0.5 mol% Ga_2O_3 addition are shown in Fig. 3. The micrographs show a large difference in the particle morphologies and sizes of conventionally ball-milled and high-energy ball-milled samples. Figure 3a shows the SEM micrograph of conventionally ball-milled mixtures. It is shown that the Ga_2O_3 and/or Gd_2O_3 particles are incompletely milled.

In contrast, well-milled mixtures were obtained in high-energy planetary milling process as shown in Fig. 3b. The coarse elongated Ga_2O_3 particles used as a sintering additive were remarkably broken down by milling. The high-energy planetary-milled mixtures consisted of loose agglomerates. High-energy ball-milled mixtures had a narrower particle size distribution than conventionally ball-milled mixtures, and the particle size of about < 0.5 μm.

Figure 4 shows the sintered densities of the specimens sintered at 1,250 °C for 5 h. The specimens using high-energy planetary-milled powders exhibited higher densification than those using conventionally ball-milled powders. The better sinterability of the specimens using high-energy planetary-milled powders could be a consequence of the finer particle size with a narrow particle size distribution.

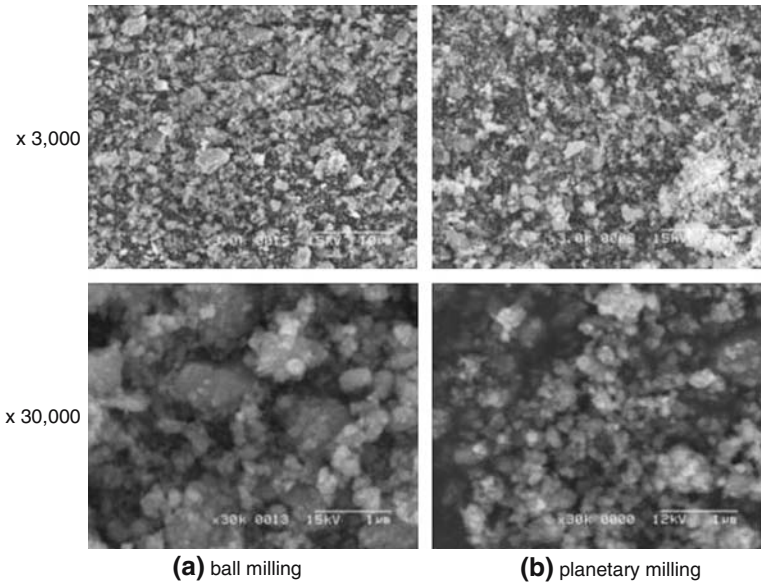

Fig. 3 SEM micrographs (×3,000 and ×30,000) of milled powders containing 0.5 mol% Ga_2O_3

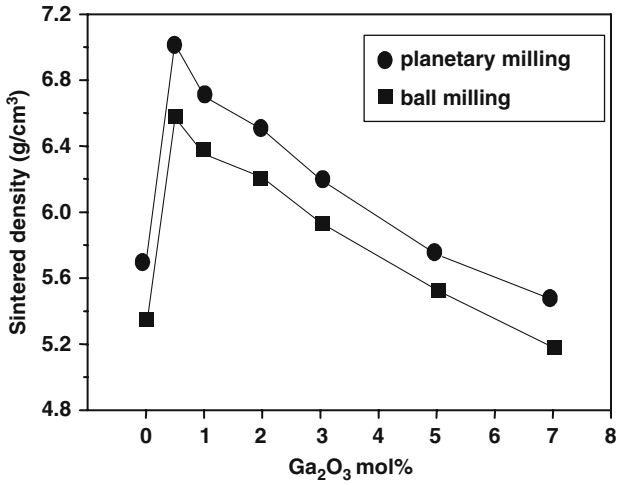

Fig. 4 Sintered density as a function of Ga_2O_3 content

Further increase in sintered density could be achieved by the addition of Ga_2O_3. The sintered density increased rapidly at 0.5 mol% Ga_2O_3 addition and then it decreased with further addition of Ga_2O_3. It is noted that a very high sintered density is obtained in 0.5 mol% Ga_2O_3-added specimen using high-energy planetary-milled powders. Dense $Ce_{0.8}Gd_{0.2}O_{1.9}$ ceramics with 97% of the theoretical density was obtained at 1,250 °C. This high value obtained at 1,250 °C is analogous to a value obtained in 0.5 mol% Ga_2O_3-added specimen sintered at 1,400 °C using conventionally ball-milled powders [12]. This result indicates that the introduction of high-energy ball milling process can reduce the sintering temperature by about 150 °C.

A decrease in density was shown with Ga_2O_3 addition over 0.5 mol%. The sintered density of the specimen containing 3 mol% Ga_2O_3, however, was higher than that of pure specimen. Thus, a small addition of Ga_2O_3 is believed to usefully improve the sinterability of Gd_2O_3-doped CeO_2.

The enhanced sinterability of the high-energy planetary-milled powder was also verified by microstructural observations of the sintered specimens derived from the high-energy planetary-milled and conventionally ball-milled powders.

Figure 5 shows the SEM micrographs of the fracture surfaces of Ga_2O_3-added $Ce_{0.8}Gd_{0.2}O_{1.9}$ ceramics produced by the different milling processes. There is an obvious difference in the microstructures of specimens derived from the high-energy planetary-milled and conventionally ball-milled powders. Higher densification is shown in the specimens using high-energy planetary-milled powders. The specimen containing 0.5 mol% Ga_2O_3 exhibits the morphology of a higher densification also. All the SEM micrographs show microstructures that correspond to the variation in density.

Figure 6 shows the XRD patterns of sintered specimens with different Ga_2O_3 contents. The sintered specimens were made by using high-energy planetary-milled powders. All patterns show the peaks of cubic fluorite type. A series of peaks related with a new phase, however, appear in the addition of Ga_2O_3 content above 2 mol%. These peaks are marked as ♦ in figure. The new phase was identified as $Gd_3Ga_5O_{12}$. With increasing Ga_2O_3 content the peaks of the $Gd_3Ga_5O_{12}$ phase became more distinct. Similar XRD

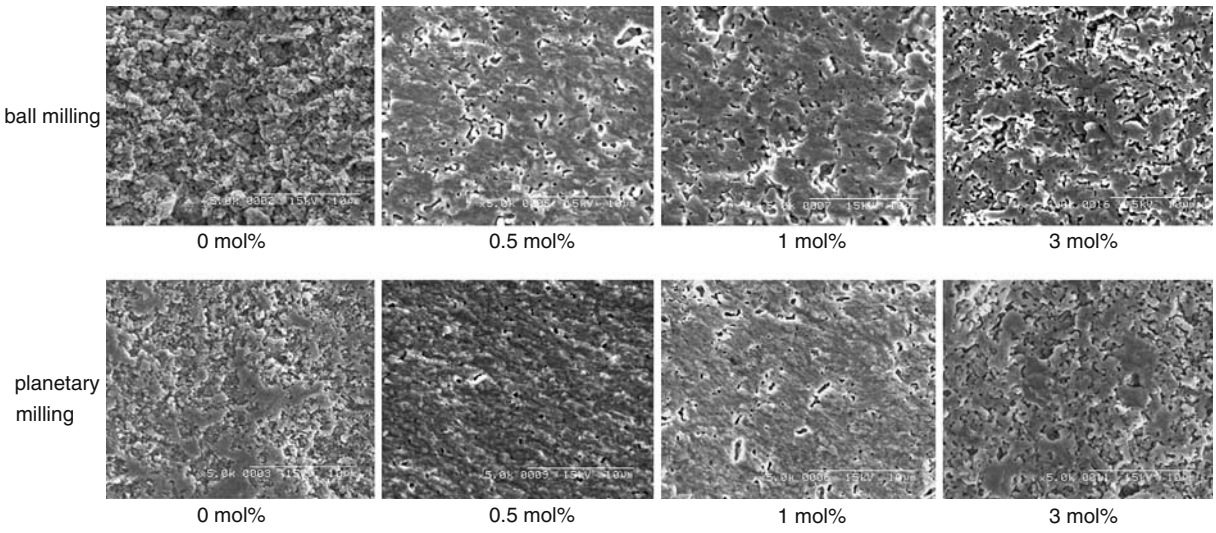

Fig. 5 SEM micrographs (×5,000) of the fracture surfaces of sintered specimens with different Ga_2O_3 contents

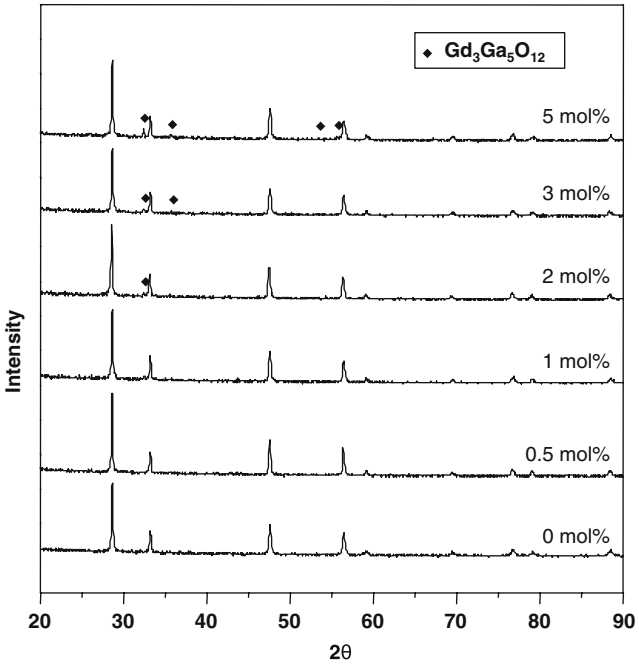

Fig. 6 X-ray diffraction patterns of sintered specimens with different Ga_2O_3 contents—planetary milling

patterns were obtained for specimens using conventionally ball-milled powders.

Figure 7 shows a SEM micrograph and the corresponding EDX spectra for a specimen containing 3 mol% Ga_2O_3. The grains having a grain shape different from ceria grain appear as it is shown on SEM micrograph. The different grain indicated by arrow ⓐ was spot-scanned for EDX analysis, and the result showed high Ga concentration. For arrow ⓑ, high Ce concentration was shown, and it was assigned to be ceria grain.

The results of EDX and XRD analyses indicate that the different grains could be assigned to have the $Gd_3Ga_5O_{12}$ phase. Yoshida et al. [10] reported that the gallium samarium garnet ($Ga_5Sm_3O_{12}$) phase was detected as a second phase in the case of samaria-doped ceria with ≥5% gallium addition. They reported the XRD peaks of the second phase and a SEM image showing grains having a grain shape different from that of ceria in the case of 5% gallium-added specimen.

Contary to the results of the present study, peaks due to the $Gd_3Ga_5O_{12}$ phase were not observed during another study using coprecipitated powders [11]. The secondary phases of garnet type have only been observed in studies using commercial powders i.e., this study of Gd_2O_3-doped CeO_2 system and Yoshida et al.'s study of Sm_2O_3-doped CeO_2 system.

A high-energy ball milling process provided a considerable particle size reduction and a narrow particle size distribution. The reduction in particle size results in an increase in specific surface area and an enhancement of chemical reactivity. The narrow size distribution results in the homogeneous packing of powders. The enhanced chemical reactivity and homogeneous packing can reduce the sintering temperature and promote densification of ceria-based ceramics.

As reported in a previous study [11, 12], it is possible that Ga_2O_3 additions result in the substitution of Ga^{3+} ions for Ce^{4+} ions within its solubility limit. The addition of Ga_2O_3 in a CeO_2 system would lead to the formation of oxygen vacancies because of charge compensation. It is expected that these oxygen vacancies enhance the densification rate and promote grain boundary mobility. Moreover, the addition of Ga_2O_3 may induce a large distortion of the surrounding lattice because the Ga^{3+} ion is substantially smaller than the Ce^{4+} ion. It is also expected that this lattice distortion promotes grain boundary mobility due to the effect of severely undersized dopant [18].

The sintered density increased rapidly at 0.5 mol% Ga_2O_3 addition. This indicates that Ga_2O_3 additions within the solubility limit accelerate the densification rate remarkably and promote grain boundary mobility.

However, at a higher Ga_2O_3 content above 2 mol%, $Gd_3Ga_5O_{12}$ is precipitated. These precipitates inhibit grain growth and lead to the decrease in grain size by a pinning effect. The precipitates cause the decline in density probably because the strain is produced due to the difference in both the elastic modulus and the thermal expansion coefficient between the precipitates and CeO_2.

Introduction of high-energy ball milling process and Ga_2O_3 doping had a good effect on the sinterability of gadolinia-doped ceria.

Conclusion

We applied high-energy ball milling process to the gadolinia-doped ceria system. The sinterability of gadolinia-doped ceria was found to be significantly enhanced by the high-energy ball milling process. We also compared the sintering behavior of milled powders after gallia doping, and found that a significant increase in density was obtained after adding 0.5 mol% Ga_2O_3. Dense $Ce_{0.8}Gd_{0.2}O_{1.9}$ ceramics with 97% of the theoretical density could be obtained by sintering the milled mixture with 0.5 mol% Ga_2O_3 addition at 1,250 °C for 5 h.

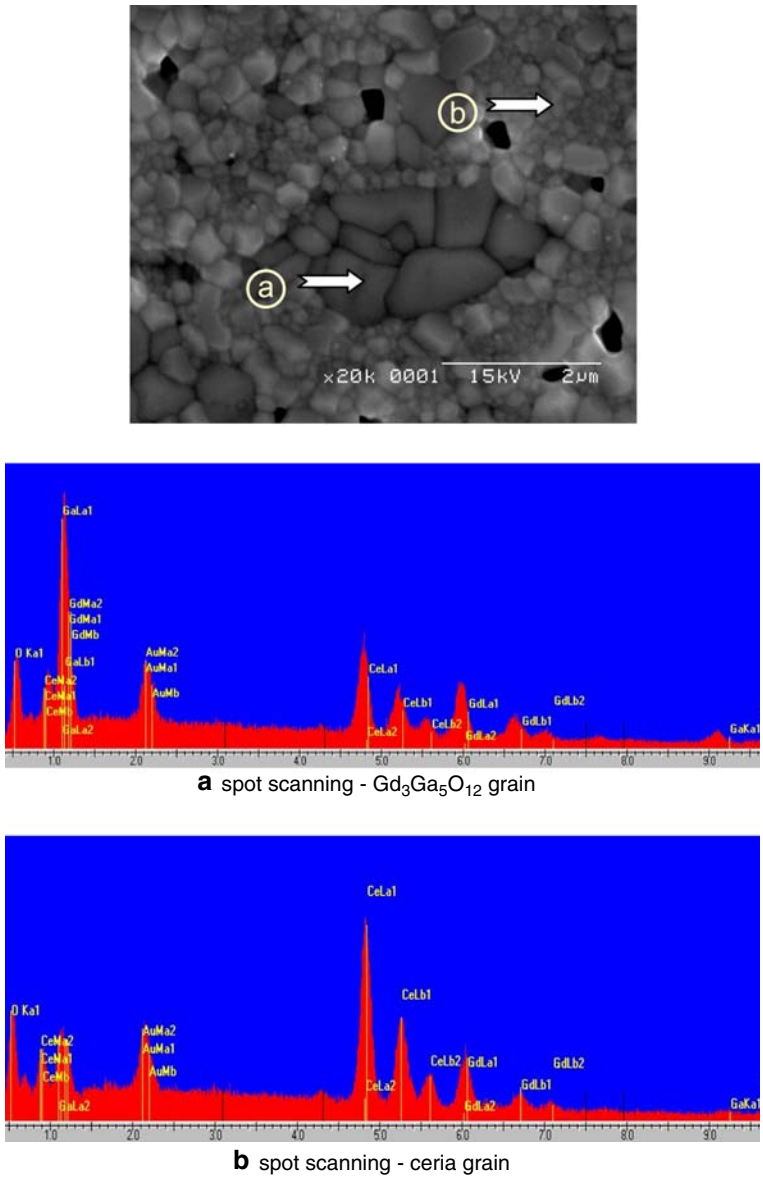

Fig. 7 SEM micrograph (×2,000) and corresponding EDX spectra for Gd_2O_3-doped CeO_2 containing 3 mol% Ga_2O_3—planetary milling

a spot scanning - $Gd_3Ga_5O_{12}$ grain

b spot scanning - ceria grain

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