Effects of Additives on Sintering Behavior of Gadolinia-Doped Ceria

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The effects of sintering additives such as Al₂O₃ and Ga₂O₃ on the sintering behavior of gadolinia-doped ceria were systematically investigated in terms of the variations in sintered density and grain size and the existing forms of Al₂O₃ and Ga₂O₃ in CeO₂. Both sintered density and grain size increased with increasing additive content up to 2 mol% for Al₂O₃ addition and up to 5 mol% for Ga₂O₃ addition. However, they decreased with further addition of the additives. At a higher additive content, grain size decreased by a pinning effect of the precipitates at grain boundaries. Lattice constant decreased with increasing additive content up to 2 mol% for Al₂O₃ addition and up to 5 mol% for Ga₂O₃ addition. This decrease will be due to the substitution of smaller Al³⁺ ions or Ga³⁺ ions for Ce³⁺ ions in the CeO₂ structure. The solubility limits of additives in Ceₓ₋₅GdₓCe₂O₇ₓ ceramics estimated using the results obtained from SEM and XRD analyses were about 2 mol% for Al₂O₃ addition and 5 mol% for Ga₂O₃ addition. The addition of Al₂O₃ or Ga₂O₃ up to the solubility limit was found to promote the sintering properties of Gd₂O₃-doped CeO₂.

[Received July 28, 2003; Accepted December 24, 2003]

Key-words : Gadolinia-doped ceria, Sintering additives, Solubility limit, Coprecipitation

1. Introduction

Oxygen ionic conductors make it suitable for a variety of applications in the electrochemical fields based on the use of solid electrolyte membranes such as oxygen sensors, fuel cells, and oxygen pumps. Among such oxygen ionic conductors, Y₂O₃-stabilized ZrO₂ (YSZ) has been the most extensively investigated and practically used. However, for special oxide fuel cell (SOFC) applications, a considerable research effort was devoted to developing alternative solid electrolytes for YSZ, which should possess higher electrical conductivity than YSZ and be operable at lower temperatures around 800°C. Thus ceria electrolytes have been given much attention as an alternative to YSZ.1 1)

However, ceria-based ceramics are difficult to densify below 1600°C.2,3 This makes them difficult for manufacturing ceria-based electrolytes which can be used for SOFC system because ceria-based electrolytes and other components such as cathode and anode have to be cofired.

In order to lower the sintering temperature, other methods such as the use of fine powders and the use of additives should be exploited. The preparation of ultrafine ceria-based ceramics powder has been studied by many investigators.2,4-5 Only limited reports, however, are available on the densification of ceria-based ceramics by using sintering additives.6-9

Yoshida et al.10 reported that sintering of samaria-doped ceria was significantly promoted by the addition of a small amount of gallia. They reported that the samples with the addition of 1% gallium sintered at 1450°C had almost the same average grain size and electrical conductivity as the samples sintered at 1600°C with no addition of Ga₂O₃ had.

It has also been reported that the transition metal oxide additives enhance densification. The effects of cobalt oxide additions on the sintering characteristics and electrical properties of Ceₓ₋₅GdₓCe₂O₇ₓ ceramics were investigated by Kleinlogel and Gauckler.11,12 They reported that the densification kinetics during sintering was strongly enhanced by the addition of a small amount of Co₂O₃ without changing the electrochemical performance. The densification was explained by a liquid-phase sintering mechanism.

Zhang et al. also investigated the effects of the transition metal oxide additives, such as Fe₂O₃13 and CoO14 on the sintering characteristics of undoped CeO₂. They reported that a small amount of Fe₂O₃ doping or CoO doping strongly enhanced the densification rate and promoted the grain boundary mobility. As a result, these additives could lower the sintering temperature of CeO₂.

It should be noted that studies on the sintering additives used for ceria-based ceramics have been limited to Ga₂O₃, CoO, Fe₂O₃ and CoO additives. For Ga₂O₃ additives, only report is available on Sm₂O₃-doped CeO₂ system among ceria-based ceramics. The starting powders used have been either commercially available powders or doped powders prepared by the conventional mixed-oxide method.

In this work, the effects of alumina and gallia additions on the sintering behavior of gadolinia-doped ceria were systematically studied. Mixtures of Gd₂O₃, CeO₂, and Al₂O₃ or Ga₂O₃ were prepared by the coprecipitation method. Emphasis is especially placed on the variations in sintered density and grain size and the existing forms of Al₂O₃ and Ga₂O₃ in CeO₂.

2. Experimental procedure

Figure 1 shows a schematic flow diagram of experimental procedure. Powders of Gd₂O₃-doped CeO₂ with different concentrations of Al₂O₃ and Ga₂O₃ were prepared by the coprecipitation method. A mixed aqueous solution having a composition corresponding to (Ceₓ₋₅GdₓCe₂O₇ₓ)₋₅(Al₂O₃)ₓ (x = 0.0-0.05) and (Ceₓ₋₅GdₓCe₂O₇ₓ)₋₅(Ga₂O₃)ₓ (x = 0-0.1) was obtained by mixing different aqueous solutions prepared from Ce(NO₃)₃·6H₂O powder (Acros Organics, 99.5%), Gd(NO₃)₃·6H₂O powder (Aldrich Chemical Co., 99.9%), Al(NO₃)₃·9H₂O powder (Acros Organics, ≥ 99%), and Ga(NO₃)₃·xH₂O powder (Aldrich Chemical Co., 99.9%), respectively. The salt containing the cations was then coprecipitated by adding an aqueous solution prepared from (NH₄)₂CO₃·H₂O powder (Junsei Chemical Co., 99.5%) and NH₄OH (Junsei Chemical Co., NH₄OH 28-30%) into the mixed aqueous solution.

The precipitates were washed with distilled water three times to remove the salt anions, followed by washing with ethanol alcohol three times to lighten the agglomeration. The precipitates were cleaned and dispersed in an ultrasonic cleaner under vigorous stirring. They were then vacuum-
filtered and dried.

Drying was performed at about 120°C in a drying oven for 1 h. The dried powders were then calcined at 700°C for 1 h. To grind agglomerates produced during the calcination process, the calcined powders were ball-milled in ethanol for 24 h. For milling, a plastic jar and zirconia balls were used. After milling the calcined powders were dried again. After drying, the 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 1400°C for 5 h. The heating rate was fixed to 10°C/min.

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 of obtaining the density provided almost the same value. An average value obtained from the 5 specimens was taken.

For microstructural investigation, the cross section of the polished specimens was thermally etched. The specimens were then Au-coated and examined with a scanning electron microscope (SEM) (Model: S-2400, Hitachi). The distribution of additive elements was detected utilizing energy dispersive X-ray analysis spectroscopy (EDX) (Model: Sigma MS3, Kevex).

X-ray diffraction (XRD) technique was employed to identify the phases and to obtain the values of lattice constant. XRD was performed on the milled powders of specimens by using Rigaku D/MAX IIIA diffractometer with a Ni-filtered Cu Kα radiation.

3. Results and discussion

Figure 2 shows the sintered density as a function of Al₂O₃ content. It is shown that the sintered density increases with increasing Al₂O₃ content up to 2 mol%. The sintered density as a function of Ga₂O₃ content is shown in Figure 3. With increasing Ga₂O₃ content up to 5 mol%, the increase in sintered density is shown.

The theoretical density of Ce₀.₈Gd₀.₂O₁.₉ ceramics was calculated to be 7.279 g/cm³ by applying the measured lattice parameter of 5.415 Å into the oxygen vacancy model. The sintered density of pure Ce₀.₈Gd₀.₂O₁.₉ specimen was calculated to be 90% of the theoretical density. The sintered density of the specimen containing 2 mol% Al₂O₃ was higher than that of pure specimen. The sintered density of the specimen containing 2 mol% Al₂O₃ was 96.4% of the theoretical density. With Al₂O₃ addition over 2 mol%, the sintered density decreased as shown in Figure 2. The specimen containing 5 mol% Ga₂O₃ also had higher density of 97%. With Ga₂O₃ addition over 5 mol%, the sintered density decreased in a way similar to alumina addition.

Figure 4 shows the SEM micrographs of the polished specimens with different additive contents. The pure Ce₀.₈Gd₀.₂O₁.₉ specimen had the average grain size of 1 μm or less while 1 mol% Al₂O₃-added specimen had larger average grain size. The increase in grain size was shown with Al₂O₃ addition up to 2 mol%. The grain size decreased and the precipitates appeared in grain boundaries with the addition of Al₂O₃ content above 3 mol%.

In the case of the specimens with the addition of Ga₂O₃, the grain size also increased with increasing Ga₂O₃ content up to 5 mol% but it decreased with further addition of Ga₂O₃ in a way similar to the density. The precipitates appeared in grain boundaries and grains with the addition of Ga₂O₃ content above 6 mol%.
The precipitates were identified by the EDX analysis. Figure 5 shows a SEM micrograph and corresponding EDX spectra for the specimen containing 5 mol% Al₂O₃. The precipitates were spot-scanned for EDX analysis, and the result showed high Al concentration. The EDX analysis of the precipitates for Ga₂O₃ addition also showed high Ga concentration.

All XRD patterns for Gd₂O₃-doped CeO₂ specimens containing additives mainly showed the peaks due to the formation of the solid solution of cubic fluorite type. The XRD peaks were slightly shifted to higher angles with increasing additive content. This shift was found by the addition of Al₂O₃ to the solid solutions of Gd₂O₃-doped CeO₂ up to 2 mol% of Al₂O₃, but the peaks were not shifted by the addition above 3 mol% Al₂O₃. The peaks for Ga₂O₃ addition were shifted gradually by Ga₂O₃ additions up to 5 mol%, but the peaks were not shifted further for larger additions.

The lattice constants were calculated from high-angle XRD patterns as a function of additive content. The lattice constant decreased linearly with increasing additive content up to 2 mol% for Al₂O₃ addition and up to 5 mol% for Ga₂O₃ addition. However, the value became almost constant for larger additions. The lattice constant calculated as a function of Ga₂O₃ content is shown in Fig. 6.

The decrease in lattice constant will be due to the substitution of smaller Al³⁺ ions (0.53 Å) ¹⁶ or Ga³⁺ ions (0.61 Å) ¹⁵ for Ce⁴⁺ ions (0.97 Å) ¹⁶ in the CeO₂ structure. Thus the solid solubility limits of additives in Gd₂O₃-doped CeO₂ are considered to be 2 mol% for Al₂O₃ addition and 5 mol% for Ga₂O₃ addition.
In general, dopants in alkaline earth oxide-doped ceria systems or rare earth oxide-doped ceria systems have large cation solubilities. However, it is expected that a dissolution of Al_2O_3 or Ga_2O_3 in a CeO_2 system will be limited because the ionic radius of Al^{3+} or Ga^{3+} is much smaller than that of Ce^{4+}.

Only limited reports are available on solid solubility limits of sintering additives in solid electrolyte. Reports for the solubility limit have been mainly performed on the dissolution of Al_2O_3 in ZrO_2 electrolyte. In the case of Al_2O_3 addition in Y_2O_3-stabilized ZrO_2, it has been reported that the estimated solubility limits of Al_2O_3 were 0.5 mol% at 1700°C and 0.1 mol% at 1300°C. It has also been reported that the equilibrium solubility of Al_2O_3 in CaO-stabilized ZrO_2 increased up to 1 mol% at 1400°C by employing the coprecipitated powders.

In this study, the CeO_2 system is easy to accommodate the additives because of larger host lattice than ZrO_2 system, and each constituent in starting powders is homogeneously dispersed at atomic level because the powders were prepared by the coprecipitation method. Therefore, it is estimated that the solid solubility limit of Al_2O_3 can be increased up to 2 mol%.

It is also estimated that the solubility limit of Ga_2O_3 can be increased up to 5 mol%, because the ionic radius of Ga^{3+} (0.61 Å) is close to the ionic radius of Ce^{4+} (0.97 Å) than that of Al^{3+} (0.53 Å).

As noted previously, it is possible that the addition of additives resulted in the substitution of Al^{3+} ions or Ga^{3+} ions for Ce^{4+} ions within the solubility limit. Such substitution reaction 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 the grain boundary mobility. Moreover, the addition of additives may induce the large distortion of the surrounding lattice because Al^{3+} ion and Ga^{3+} ion has much smaller size compared with that of Ce^{4+} ion. It is also expected that the lattice distortion promotes the grain boundary mobility due to the effect of severely undersized dopant.

Both sintered density and grain size increased with increasing additive content up to 2 mol% for Al_2O_3 addition and up to 5 mol% for Ga_2O_3 addition. However, they decreased with further addition of the additives. These results indicate that the additions of additives within the solubility limit accelerates the densification rate remarkably and promote the grain boundary mobility.

However, at a higher additive content over the solubility limit, excess additives are precipitated. The precipitates inhibit the 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.

The addition of Al_2O_3 or Ga_2O_3 up to the solid solubility limit promoted the grain growth, and it brought the decrease in grain boundary density. It is suggested that soluble Al_2O_3 or Ga_2O_3 has an affirmative effect on the sintering behavior of Gd_2O_3-doped CeO_2.

4. Conclusion

The effects of sintering additives such as Al_2O_3 and Ga_2O_3 on the sintering behavior of gadolinia-doped ceria were systematically investigated in terms of the variations in sintered density and grain size and the existing forms of Al_2O_3 and Ga_2O_3 in CeO_2.

Both sintered density and grain size increased with increasing additive content up to 2 mol% for Al_2O_3 addition and up to 5 mol% for Ga_2O_3 addition. However, they decreased with further addition of the additives. At a higher additive content, grain size decreased by a pinning effect of the precipitates at grain boundaries. The solubility limits of additives in Ce_0.95Gd_0.05O_1.99 ceramics estimated using the results obtained from SEM and XRD analyses were about 2 mol% for Al_2O_3 addition and 5 mol% for Ga_2O_3 addition. The addition of Al_2O_3 or Ga_2O_3 up to the solubility limit caused the promotion of grain growth and an increase in density. It is suggested that soluble Al_2O_3 or Ga_2O_3 gives an affirmative effect on the sintering behavior of Gd_2O_3-doped CeO_2.

Acknowledgment

This work was supported by ECC (Electronic Ceramics Center) at Dong-Eui University as RRC-TIC program which is financially supported by KOSEF (Korea Science and Engineering Foundation) under MOST (Ministry of Science and Technology), ITEP (Korea Institute of Industrial Technology Evaluation and Planning) under MOICE (Ministry of Commerce, Industry and Energy), and Busan Metropolitan City.