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Journal of Alloys and Compounds 408–412 (2006) 632–636

Journal of ALLOYS AND COMPOUNDS

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Effects of additives on the sintering properties of samaria-doped ceria

Hiroyuki Yoshida*, Toru Inagaki

Energy Use R&D Center, The Kansai Electric Power Co. Inc., 11-20 Nakoji 3-Chome, Amagasaki, Hyogo 661-0974, Japan

Received 30 July 2004; received in revised form 27 October 2004; accepted 15 December 2004
Available online 14 July 2005

Abstract

In this study, Mn_2O_3 and Co_3O_4 were found to be alternative additives of Ga_2O_3 reported previously, to promote grain growth of SDC (samaria-doped ceria) effectively. Sintering at 1500 °C with additives gave sufficient density and grain growth, while those of SDC sintered without additives were low at the same temperature. The enhancement of grain boundary mobility was observed by adding Mn_2O_3, and Co_3O_4 to SDC. It was found that Mn_2O_3 and Co_3O_4 promoted grain growth of SDC even at initial stage of sintering, while Ga_2O_3 promoted rearrangement of particles first. The electrochemical property of SDC with Co_3O_4 sintered at 1400 °C was comparable to SDC without additives sintered at 1600 °C.

Keywords: Samaria-doped ceria; Grain growth; Scanning electron microscope; Ionic conduction

1. Introduction

Ceria-based electrolytes doped with rare earth elements are worth noticing as a candidate for electrolyte materials of intermediate temperature operative (600–800 °C) solid oxide fuel cells (SOFCs) [1,2]. On preparing ceria-based oxides, however, a sintering temperature higher than 1600 °C is necessary to obtain ceramics from oxide powder with densities high enough for use as electrolytes of SOFCs [1,3]. If dense ceria-based oxides can be prepared at lower temperatures on common solid-state reaction methods, they can be co-sintered with electrode materials without chemical reactions between electrolyte and electrode, which makes the preparation process steps easier and the preparation costs lower.

In order to sinter doped ceria compounds at lower temperatures, some methods have been used, which are mainly classified into two categories; (i) preparing ultrafine powders by synthesis in aqueous solution, such as oxalate coprecipitation methods [4,5] or by milling raw materials with special equipment [6], and (ii) adding a sintering promoter for doped ceria compounds. In the coprecipitation methods, however, many parameters (e.g., metal ion concentration, organic acid concentration and pH of the solution) should be controlled carefully [4,5]. In the case of grinding methods for preparing fine powder, secondary cohesion of fine particles and contamination with the components of balls and wall should be minimized [6].

Use of sintering promoter is easier to prepare electrolyte, but there are few reports concerning the densification of ceria powders by using sintering promoters [7]. The author searched sintering promoters for samaria-doped ceria (SDC) and found that Ga_2O_3 (gallia) was a promising candidate [8]. In our study, Mn_2O_3 and Co_3O_4 were also found to be alternative additives to promote grain growth of SDC effectively. In this paper, the variations of the microstructure and electrical conductivity of SDC containing additives with sintering temperatures and period have been investigated and the effects of additives on sintering behavior of SDC are discussed.

2. Experimental

Doped ceria compounds with and without additives were prepared by a common solid-state reaction method from each oxide having a purity of more than 99.9%. CeO_2

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* Corresponding author. Tel.: +81 6 6494 9715; fax: +81 6 6494 9709.
E-mail address: yoshida.hiroyuki@c2.kepco.co.jp (H. Yoshida).

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doi:10.1016/j.jallcom.2004.12.155

(Shin-Etsu Chemicals Co.), Sm_2O_3 (Shin-Etsu Chemicals Co.), Ga_2O_3 (Kojyundo Chemicals Co.), Mn_2O_3 and Co_3O_4 (Rare Metallic Co.) were weighed at an atomic ratio of Ce:Sm:M = 80:20:0 (without additive) or 80:19:1 (with additive). The average particle sizes of the starting powders were in the range between 0.5 and 1.5 μm. Mixing, pressing and sintering procedures were carried out as described elsewhere [8]. The sintering period at 1500 °C was varied from 10 min to 24 h to investigate sintering behavior of doped ceria compounds without and with additives.

Densities of a few sintered samples for each composition were calculated from their weights and volumes derived from scaled length and thickness, because reasonable density was not observed on some samples by the Archimedes method due to the presence of many open pores. The crystal structures of the samples were confirmed by X-ray diffraction (XRD, Shimadzu XRD-6000) measurement. The microstructures were observed with a scanning electron microscope (SEM, Hitachi S-2380N). The surfaces of the samples were polished and thermally etched at temperatures by 100 °C lower than the sintering temperatures prior to SEM observation. Porosity and average grain sizes were estimated from SEM images using the intercept method. The electrical conductivity of the samples of 3 mm × 3 mm × 20 mm was measured at 800 °C in oxidative and reductive atmospheres using the conventional dc four-probe method.

SDC samples with additives were abbreviated as CSGa, CSMn and CSCo, where Ga, Mn and Co in abbreviation meant each metallic element of additives, respectively.

3. Results and discussion

The crystal structures of samaria-doped ceria compounds with and without additives were measured. The XRD pattern of SDC showed that the sample was comprised of a single phase of the fluorite-type structure. The pattern of a garnet phase ($Ga_5Sm_3O_{12}$, JCPDS File Card No. 12-0764) was observed for CSGa. In the case of CSMn and CSCo, any other phases except fluorite were not observed, which is considered due to the solution of Mn and Co into ceria and/or smaller amounts of other phases below the detection limit of XRD.

The microstructures of SDC with and without additives changed dramatically with sintering period at 1500 °C. Fig. 1 shows SEM images of SDC without additives prepared at 1500 °C for various sintering period. It was confirmed that grains of SDC grew with sintering time at 1500 °C. Even after sintering for 24 h, however, small grains having almost equal sizes as calcined powder, and some large pores were observed. Dense SDC was difficult to be obtained by sintering at 1500 °C from calcined powder synthesized by common solid-state reaction method, as was reported previously [8].

Fig. 2 shows SEM images of SDC with additives sintered at 1500 °C for 10 min and for 24 h. Even with sintering at

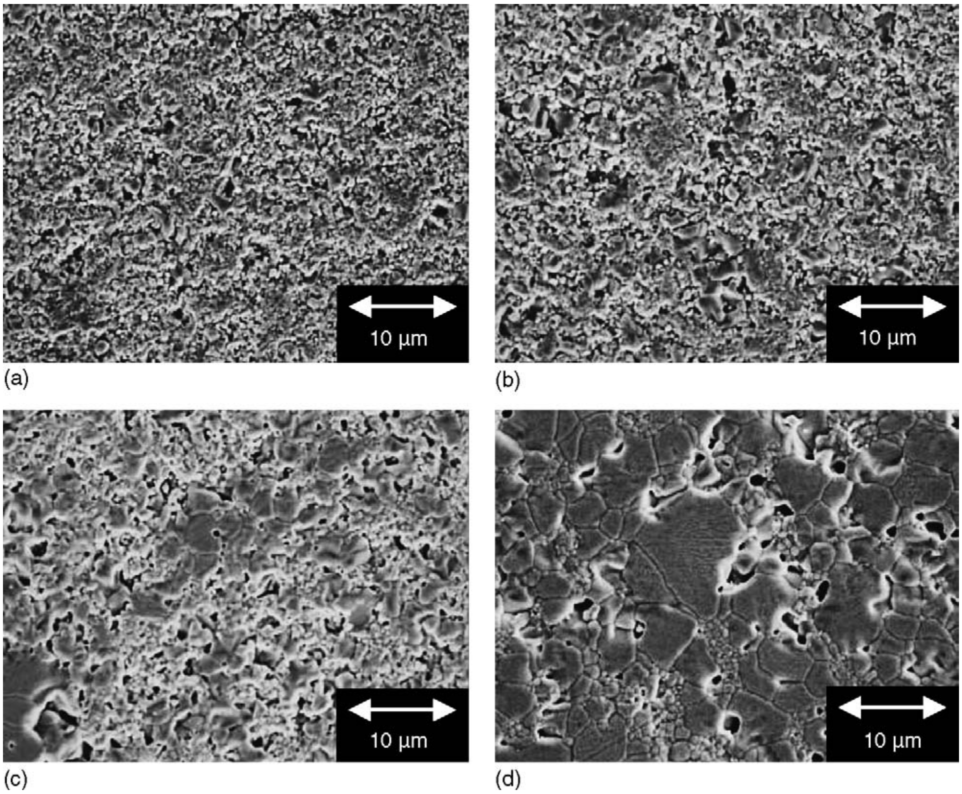

Fig. 1. SEM images of SDC sintered at 1500 °C for various period: (a) 10 min, (b) 1 h, (c) 5 h and (d) 24 h.

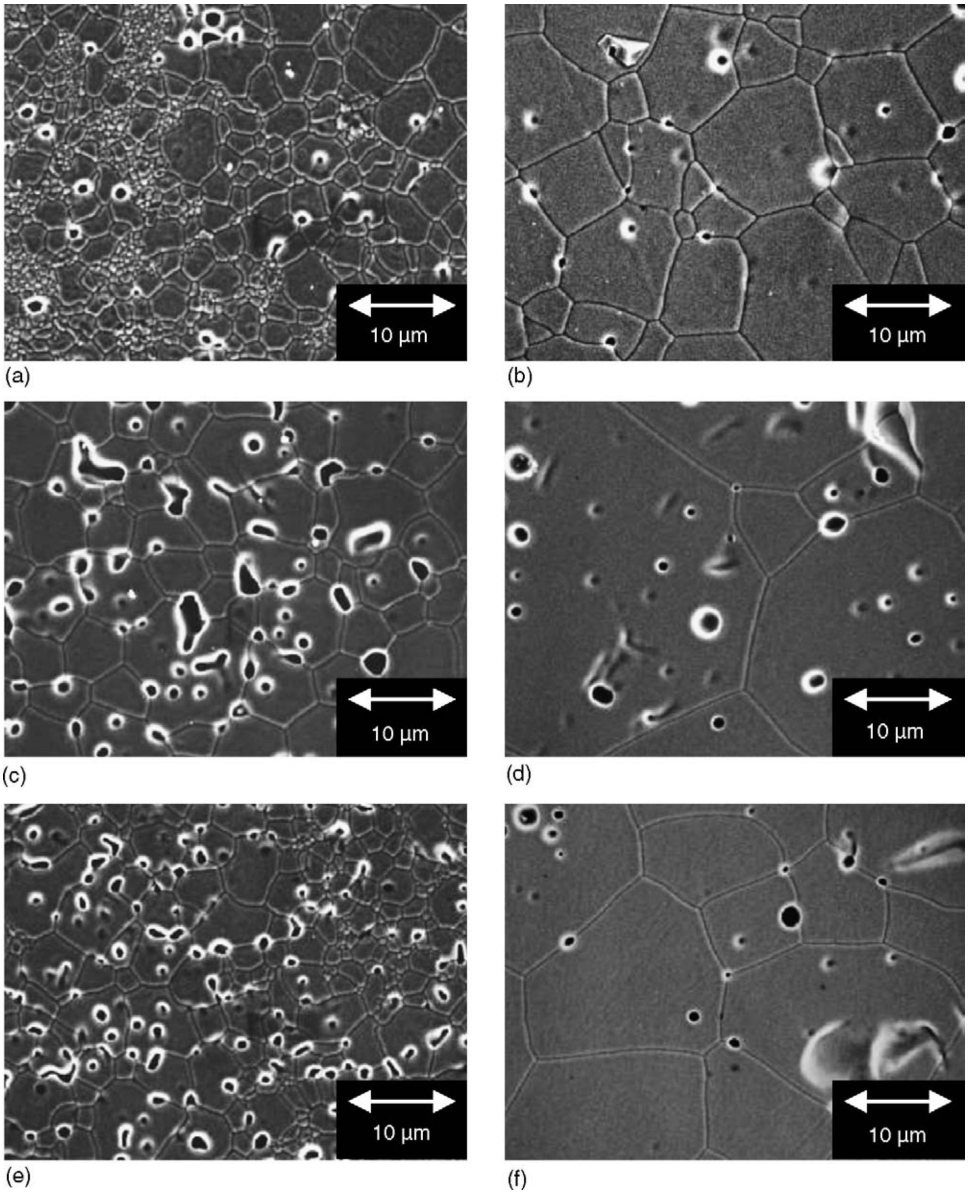

Fig. 2. SEM images of SDC with additives sintered at 1500 °C for 10 min and 24 h, (a) CSGa for 10 min, (b) CSGa for 24 h, (c) CSCo for 10 min, (d) CSCo for 24 h, (e) CSMn for 10 min and (f) CSMn for 24 h.

1500 °C for 10 min, SDC with additives showed initiation of grain growth, and pores were concentrated at grain boundaries. The ratio of small grains left after sintering at 1500 °C for 10 min depended on what kind of additive was used. Many of small grains were left for CSGa, a few percent of small grains were left for CSMn, and all grains grew in the case of CSCo. From Fig. 2, it was considered that Ga_2O_3, promoted rearrangement of particles and that Mn_2O_3 and Co_3O_4 promoted grain growth at initial stage of sintering. After sintering at 1500 °C for 24 h, all samples were densely sintered though some pores were left in the grains, which indicated that the mobility of grain boundaries were much faster than that of pores [9].

Fig. 3 shows porosities and densities of SDC with and without additives varied with sintering period at 1500 °C. It was confirmed that the density increased as the porosity decreased. After sintering at 1500 °C for 24 h, all samples gave high density and low porosity. The tendency was different in the case of shorter sintering period. SDC samples sintered at 1500 °C for 1 h or shorter period gave large porosity of higher than 20% and lower densities, which showed that sintering did not proceed under the same conditions. As was seen in Fig. 1, sintering of large grains were observed only after long sintering period (c and d), which was in agreement with the results of porosity and density. CSGa gave low porosity and high density, which indicated that the rearrangement of particles was extremely promoted. The acceleration of grain growth in CSGa was considered to be the effect of the liquid phase partly formed during sintering, as was reported previously [8]. CSCo and CSMn had almost equal porosity

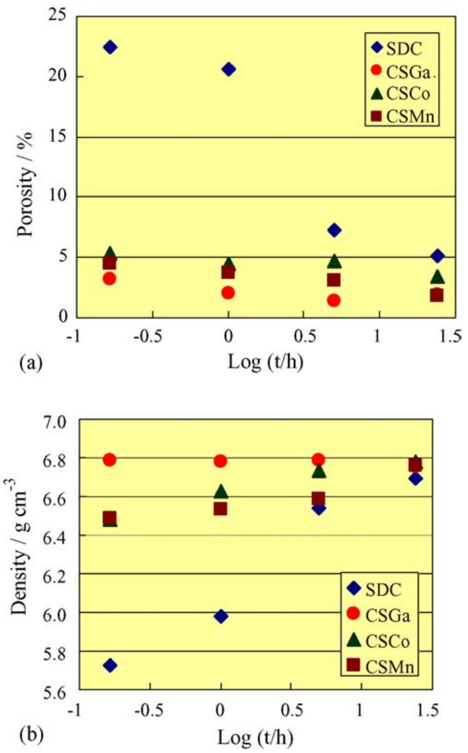

Fig. 3. Porosities and densities of SDC with and without additives varied with sintering period at 1500 °C.

and density with each other. It was suggested that the mechanism of grain-growth promotion on sintering of CSCo and CSMn was similar to each other. Evidence of the presence of any liquid phases on sintering could not be found in CSCo and CSMn. As Co^{2+} and Mn^{2+} are much smaller than Ce^{4+}, they can enhance grain boundary mobility due to the large distortion of the surrounding lattice that facilitates defect migration of ceria [10].

Fig. 4 shows average grain sizes of SDC with and without additives sintered at various temperatures for various sintering period. Higher temperature and longer sintering period gave larger average grain size for all compounds. All of the additives used in this study promoted grain growth of SDC at each temperature and sintering period. The average grain size of CSGa sintered at 1450 °C was almost the same as that of SDC sintered at 1600 °C, as was reported previously [8]. The average grain size of CSCo sintered at 1400 °C was larger than that of SDC sintered at 1600 °C. This leads to the possibility of the decreasing of sintering temperature more than 200 °C without deterioration of electrochemical performance by adding small amount of Co_3O_4 into SDC, as reported on CSGa [8]. The sinterability of CSCo was almost the same as that of SDC prepared by the oxalate coprecipitation method [5].

Grain growth depends on sintering time and temperatures by grain growth kinetic equation [7],

$$G^n - G_0^n = Kt \qquad (1)$$

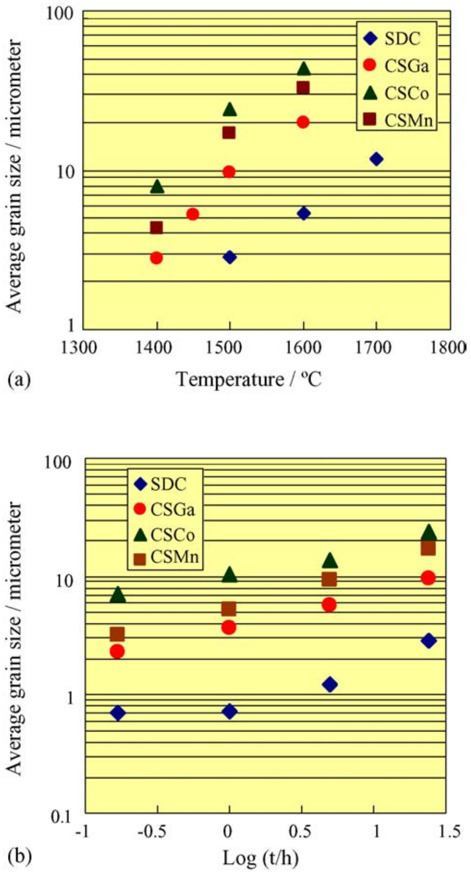

Fig. 4. Average grain sizes of SDC with and without additives: (a) sintered at various temperatures for 24 h and (b) sintered at 1500 °C for various period.

G is the average grain size at time t, G_0 the average grain size at $t = 0$ (measured value was 0.7 μm), K the rate constant and is a function of temperature and n is the growth exponent, which is considered to represent the mechanism of grain growth [7]. n can be estimated from a slope of $\log G - \log t$ plot (Fig. 4b) when G^n is much larger than G_0^n. From Fig. 4b, G^n values of CSCo and CSMn were much larger than G_0^n. G^n value of CSGa sintered for 10 min was about 30 times larger than G_0^n, which did not affect the n value of CSGa. Average grain sizes of SDC sintered for 1 h or less were almost the same as G_0, thus n value of SDC was not calculated. When grain growth is related to mobility of grain boundary, n is equal to 2 [11]. However, n values of SDC with additives were between 3 and 4, which was due to promoted high mobility of grain boundaries and/or impurities at grain boundaries.

The conductivities of SDC with and without additives were measured at 800 °C. The conductivity of CSCo sintered at 1400 °C was 8.7×10^{-2} S/cm, which was almost equal to that of SDC sintered at 1600 °C (8.9×10^{-2} S/cm). Therefore, SDC-based electrolyte can be prepared at 1400 °C by adding small amount of Co_3O_4. The conductivity variation with sintering time of each sample showed the same tendency of porosity and density. The conductivity of CSCo was constant in the oxygen partial pressure (p_{O_2}) range between 3.7×10^{-11} and 1 atm; therefore, ionic transport number of CSCo in air was almost equal to unity. Conductivity of CSCo (sintered at 1600 °C) at the reductive atmosphere ($p_{O_2} = 3.3 \times 10^{-15}$ atm) was 2.1×10^{-1} S/cm, which was almost equal to that of SDC sintered at 1600 °C (2.2×10^{-1} S/cm).

4. Conclusions

Mn_2O_3 and Co_3O_4 were found to be sintering promoters of samaria-doped ceria (SDC). Sintering at 1500 °C with additives gave sufficient density and grain growth, while those of SDC sintered without additives were poor at the same temperature. The enhancement of grain boundary mobility was observed by adding Mn_2O_3 and Co_3O_4 to SDC. It was found that Mn_2O_3 and Co_3O_4 promoted grain growth of SDC even at initial stage of sintering, while Ga_2O_3 promoted rearrangement of particle first. As Co^{2+} and Mn^{2+} are much smaller than Ce^{4+}, they can enhance grain boundary mobility due to the large distortion of the surrounding lattice that facilitates defect migration of ceria. The electrochemical property of SDC with Co_3O_4 sintered at 1400 °C was comparable to SDC without additives sintered at 1600 °C.

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