

Effects of cobalt oxide additions on sintering behavior of gadolinium aluminate

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In the present study the effects of cobalt oxide additions on the densification behavior of gadolinium aluminate ceramics were investigated. It was found that the addition of cobalt oxide reduces the sintering temperature by about 150 °C, promoting simultaneously the densification process. The relative density of a pure GdAlO₃ specimen sintered at 1500 °C was 69%, whereas the specimen containing 5 mol% Co₃O₄ had a very high density of 95%. The sinterability of GdAlO₃ ceramics was significantly enhanced by the addition of Co₃O₄.

Key words: ceramics, sintering, microstructure, gadolinium aluminate, cobalt oxide.

Introduction

Oxygen ionic conductors have a wide variety of applications in the field of electrochemistry. They can be used as solid electrolyte membranes in oxygen sensors, fuel cells, and oxygen pumps. Among the oxygen ionic conductors, Y₂O₃-stabilized ZrO₂ (YSZ) with the fluorite structure has been the most extensively investigated and practically used. However, especially for solid oxide fuel cell (SOFC) applications, a considerable research effort has been devoted to developing alternative solid electrolytes for YSZ, which should possess a higher electrical conductivity than YSZ and be operable at lower temperatures around 800 °C.

Ceria-based solid electrolytes, such as gadolinia-doped and samaria-doped ceria have been widely studied as alternatives to YSZ, because of their higher electrical conductivity than YSZ [1]. The ceria-based electrolytes, however, show electronic conduction in a reducing atmosphere at a temperature as high as 800 °C [1, 2].

One class of materials that exhibits high electrical conductivity is based upon the perovskite structure. Perovskite type oxides offer two sites in doping aliovalent cations for the formation of oxygen vacancy. In contrast, doping in fluorite type oxides is limited to the one site. This structural background suggests that perovskite type oxides have the potential of exhibiting greater conductivity than fluorite type oxides. Ishihara *et al.* [3, 4] have shown that Sr and Mg-doped LaGaO₃-based oxides with the perovskite structure have extremely high electrical conductivity.

Perovskite aluminate-based oxides offer lower cost, and exhibit higher stability compared to LaGaO₃-based oxides. Recently, Sinha *et al.* [5] reported the development of

Ca-doped GdAlO₃ as a novel perovskite aluminate-based oxide ion conductor.

In this work, the sintering behavior of gadolinium aluminate is studied. Gadolinium aluminate-based ceramics are difficult to densify. 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 ultra fine gadolinium aluminate powders has been studied by several investigators [5, 6]. However, to our knowledge, there is no report on the densification of gadolinium aluminate-based ceramics using sintering additives. The present work is aimed at studying the effect of cobalt oxide additions on the sintering behavior of gadolinium aluminate ceramics prepared by the conventional mixed-oxide method.

Experimental Procedure

Mixtures having a composition corresponding to (GdAlO₃)_{1-x}(Co₃O₄)_x (x = 0 – 0.05) were prepared by the conventional mixed-oxide method. High purity commercial Gd₂O₃ (Sigma-Aldrich Co., 99.9%), Al₂O₃ (Sigma-Aldrich Co., 99.7%), and Co₃O₄ (Sigma-Aldrich Co.) were used as starting materials.

The mixtures were ball-milled in ethanol for 24 h. For milling, a plastic jar and alumina balls were used. After milling the mixtures, the powders were dried at 120 °C for 10 h. The dried powder mixtures 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 in air over the temperature range 1400 °C–1650 °C for 5 h. The heating rate was fixed at 10 °C/min.

The sintered densities were measured using the Archimedes method with water and/or calculated from the weights and the dimensions of the specimens. It was

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found that both methods used for obtaining the density provided almost the same value. An average value obtained from five specimens was taken.

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

Results and Discussion

Fig. 1 shows the relative density as a function of sintering temperature for pure GdAlO₃. It is seen that the sintered density increases as the temperature increases. The sintered density increases rapidly at 1550 °C. Pure GdAlO₃ sintered at 1650 °C has a density of 94%.

The color of the sintered specimen was changed to darkgreen from off-white after the addition of cobalt oxide.

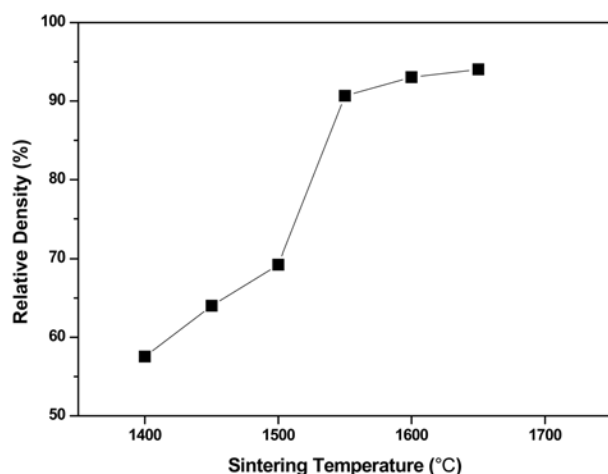


Fig. 1. Relative density as a function of sintering temperature for pure GdAlO₃.

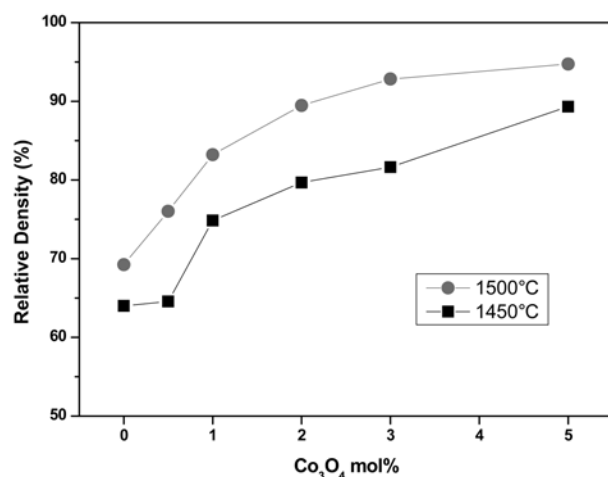


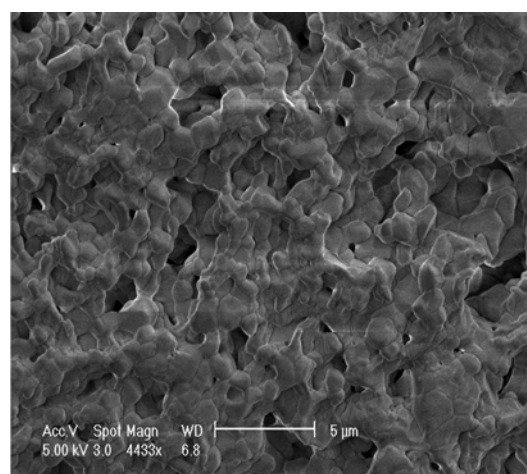
Fig. 2. Relative density as a function of Co₃O₄ content for the specimens sintered at 1450 °C and 1500 °C.

Fig. 2 shows the relative density as a function of Co₃O₄ content for the specimens sintered at 1450 °C and 1500 °C. The sintered density increases gradually with increasing Co₃O₄ content. The relative density of a pure GdAlO₃ specimen sintered at 1500 °C is 69%, whereas the specimen containing 5 mol% Co₃O₄ has a very high density of 95%. Upon adding Co₃O₄, the sintering behavior changes greatly.

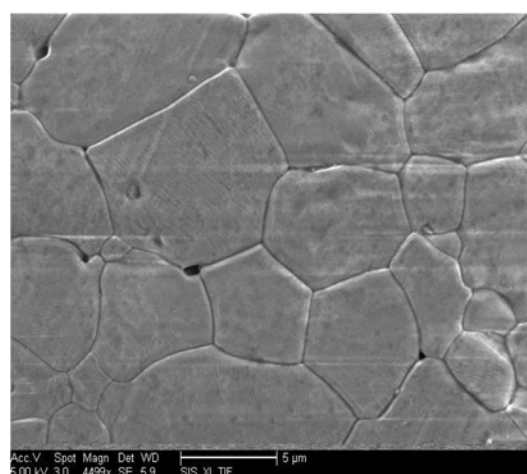
In the case of pure GdAlO₃, a relative density of 95% is attained at a sintering temperature of above 1650 °C as shown in Fig. 1. This result suggests that the addition of Co₃O₄ can reduce the sintering temperature by about 150 °C.

The enhanced sinterability of Co₃O₄-added specimens was also verified by microstructural observations of the sintered specimens. Fig. 3 shows SEM micrographs of pure GdAlO₃ and 5 mol% Co₃O₄-added GdAlO₃ sintered at 1500 °C. There is an obvious difference in the microstructures of the specimens. Higher densification and distinct grain growth are observed in the Co₃O₄-added specimens. The specimen containing 5 mol% Co₃O₄ exhibits a morphology corresponding to a high value of 95% in relative density.

The XRD patterns of the specimens sintered at 1500 °C



(a)



(b)

Fig. 3. SEM micrographs of (a) pure GdAlO₃ and (b) 5 mol% Co₃O₄-added GdAlO₃ sintered at 1500 °C.

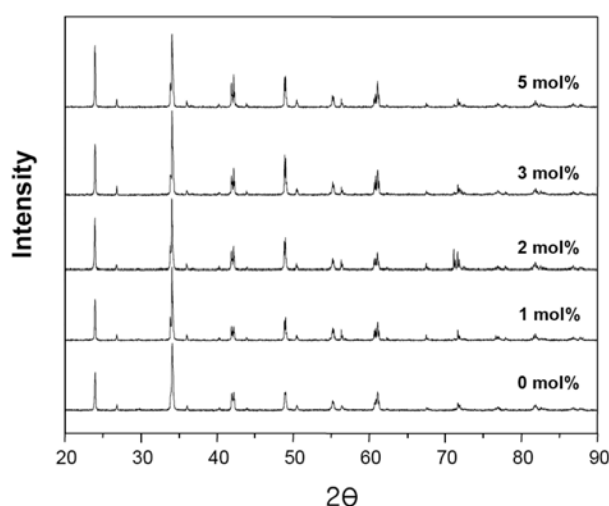


Fig. 4. X-ray diffraction patterns of the specimens sintered at 1500 °C with different Co_3O_4 contents.

with different Co_3O_4 contents are shown in Fig. 4. All the patterns show the peaks of GdAlO_3 . No peaks corresponding to a new phase appeared.

The above results show that the addition of cobalt oxide has a profound effect on densification and microstructure. In the last few years, cobalt oxide has been used as sintering aid to densify doped ceria-based ceramics [7-10]. Kleinlogel and Gauckler [7] reported the sintering of $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ at temperatures as low as 900 °C using cobalt oxide additive. Transmission electron microscopy (TEM) analysis of the grain boundary of 1 mol% Co_3O_4 -doped $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}$ samples revealed an amorphous cobalt oxide grain boundary film of 2-4 nm for the material sintered at 900 °C for 10 min. The authors suggested that this grain boundary layer melts at sintering temperature as low as 900 °C and facilitates densification via liquid phase sintering.

However, Zhang *et al.* [10] attributed the effect to viscous flow sintering. Due to the high volatility of cobalt oxide, cobalt oxide can easily diffuse onto the surface of matrix particles to form a thin amorphous film between the particles at a low temperature. This thin amorphous layer reduces the friction of inter-particles, leading to the occurrence of a viscous flow mechanism [10].

Cobalt oxide has been also used as sintering aid to densify alumina and yttrium aluminum garnet [11, 12]. Satapathy [11] reported that alumina undergoes liquid phase sintering in the presence of 0.5 wt% cobalt oxide as a sintering aid based on a microstructural investigation. It was also reported that the predominant densification mechanism is the formation of a cobalt oxide liquid phase for yttrium

aluminum garnet [12].

We consider that the densification observed for the present system may be associated with liquid phase sintering. The densification rate is proportional to the amount of cobalt oxide.

We believe that this study is the first report for the densification of GdAlO_3 with cobalt oxide as a sintering aid. It was observed that cobalt oxide is an effective additive in densifying GdAlO_3 .

Conclusion

The effects of cobalt oxide additions on the densification behavior of gadolinium aluminate ceramics were investigated. It was found that the addition of cobalt oxide reduces the sintering temperature by about 150 °C, promoting simultaneously the densification process. The relative density of a pure GdAlO_3 specimen sintered at 1500 °C was 69%, whereas the specimen containing 5 mol% Co_3O_4 had a very high density of 95%. The addition of cobalt oxide was found to promote the sintering properties of GdAlO_3 ceramics.

Acknowledgements

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