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Fabrication of dense $Gd_{0.1}Ce_{0.9}O_{1.95}$ sintered bodies with nano-size grain and its conducting properties

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Nano-size $Gd_{0.1}Ce_{0.9}O_{1.95}$ particles were prepared using ammonium carbonate co-precipitation method. Also the dense sintered body with the aforementioned composition was fabricated using synthesized powders. The specimens can be sintered to at least 95% of theoretical density at temperatures between 1000°–1550°C. In addition, the grain size dependence of conducting properties was observed in $Gd_{0.1}Ce_{0.9}O_{1.95}$. The conductivity decreased with decreasing grain size and reached the lowest value at an average grain size of 570nm. This tendency would be attributable to the space charge layer around the grain boundary in the sintered body. On the other hand, the conductivity increased with a decrease of grain size under 570nm. Since the change of conductivity is large when the grains are below 570nm then we suggest it is not all attributable to space charge changes. Other micro-structural features within the grain are also beginning to have an influence. Both change of the space charge layer width around grain boundary and the micro-structural features within the grain would led to improvement in the conductivity. Accordingly, it is concluded that a design of microstructure is key for improvement of conductivity in Gd doped CeO_2 system.

Key words: Gd doped CeO_2, Co-precipitation method, Oxide ionic conductivity, Grain size dependence of conductivity, micro-domain

1. INTRODUCTION

Oxide ion conductors are used in a variety of oxygen sensors,[1,2] solid oxide electrochemical cells (SOECs),[3] and solid oxide fuel cells (SOFCs).[4-6] In these applications, SOFCs are being especially developed as a clean and efficient power source for generating electricity from a variety of fuels. Gd doped CeO_2 [7-11] is now under active investigations for application as 'low' (<650°C) temperature operation of SOFCs. These electrolytes show high oxide ionic conductivity at high oxygen partial pressure. At low oxygen partial pressures associated with anodic conditions, these materials are partially reduced and develop electronic conductivity, during operation of the fuel cell. To overcome this problem and improve the conductivity for low temperature operation of SOFCs, the influence of nano-structural feature in the doped CeO_2 systems on the conducting property should be taken into account. To examine the influence of microstructure on conducting properties in Gd doped CeO_2 solid electrolytes, dense Gd doped CeO_2 sintered bodies with nano-size grain was fabricated using fine powders. The densification behavior, conducting properties in dense sintered bodies with various average grain sizes (138nm–1.78μm) and microstructure at the atomic level of dense sintered specimens prepared in this study were examined for a development of Gd doped CeO_2 solid electrolytes.

2. EXPERIMENTAL

2-1. Synthesis of nano-size Gd doped CeO_2 powders and Fabrication of sintered bodies

The starting materials used for Gd doped CeO_2 synthesis were cerium nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$; >99.99% pure, KANTO Chemical Co. Inc., Japan), gadolinium nitrate hexahydrate ($Gd(NO_3)_3 \cdot 6H_2O$; >99.95% pure, Kanto Chemical Co., Japan) and ammonium carbonate ($(NH_4)_2CO_3$; Ultrahigh purity, Wako Pure chemicals Japan). For preparation of $Gd_{0.1}Ce_{1.9}O_{1.95}$, the nitrate solution was prepared by dissolving Gd and Ce nitrates of the appropriate Gd/Ce ratio into 300ml of distilled water for a total Gd and Ce concentration of 0.15M. Dissolution was aided by stirring at 40°C for 30minutes. The precipitant solution was 300ml of 1.5M $(NH_4)_2CO_3$ which was maintained at 70°C during dissolution of the $(NH_4)_2CO_3$, as well as throughout the precipitation reaction. In the carbonate precipitation reaction, the mixed nitrate solution was added dropwise (1-2 drops/ seconds) to the precipitant solution that was kept at 70°C, with gentle stirring during the process.

When all of the mixed nitrate solution was added, the reaction mixture was left to develop for 1 hour at 70°C with gentle stirring. After this development time, this mixture was filtrated by suction filtration and the precipitate was washed four times. After repeated washing, the precipitate was dried at room temperature with flowing nitrogen gas and then calcined in flowing oxygen for 2 hours. The calcination temperatures ranged from 500° - 1000°C, depending on how fine powders was needed. The pellets were uniaxially pressed using a 16mm die at 20MPa for 30 seconds. After that, the pellets were pressed together using cold isostatic pressing for 5 minutes at 250MPs. The pellets were sintered in static air, heated at 5°C/min to the desired temperature and held isothermally for 6 hours. Sintering temperatures were in the range 1000° - 1550°C. After cooling to ambient temperature, the bulk densities of sintered bodies were determined using the Archimedes method. The relative densities of the sintered bodies were calculated from the ratio between bulk density and theoretical densities (derived from X-ray powder diffraction).

2-2. Particle morphology, microstructure analysis and conductivity measurements

The average grain size of the sintered bodies was observed by filed emission-scanning electron microscopy (FE-SEM, Hitachi S-5000). Prior to observation, sample pellets were polished to make a mirror finished surface. The samples were thermally etched for 1-2 hours at a temperature 100°C below sintering temperature. From SEM images, the average grain size for each sintered body was determined by the average linear intercept method from at least 250-300 grains per sample.[12] The micro-structural features in the grain were investigated using transmission electron microscopy (TEM). Ion beam thinned specimens were used for TEM observation. In order to avoid reduction of CeO_2 by ion beam milling, Ar ion beam was irradiated using cooled cold stage in liquid nitrogen. TEM observation was performed with gun voltages of 200keV. Conductivities of $Gd_{0.1}Ce_{0.9}O_{1.95}$ specimens sintered at temperatures between 1000°C and 1550°C were measured by three-terminal DC measurements in static air at 50°C intervals from 400° - 700°C. Samples were circular pellets of at least 10mm diameter and 1-2mm thickness. Pt electrodes were painted on both faces and fired in static air at 900° - 1000°C for 1 hour. Conductivity behavior was examined from Arrhenius plots of temperature/conductivity dependence in the 400°- 700°C range.

3. RESULTS AND DISCUSSION

3-1. Preparation of nano-size $Gd_{0.1}Ce_{0.9}O_{1.95}$ powders and its densification behavior

FE-SEM images showing the morphology and agglomeration of particles in the dried powders and calcined powders are shown in **Fig.1a** and **Fig.1b**, respectively.

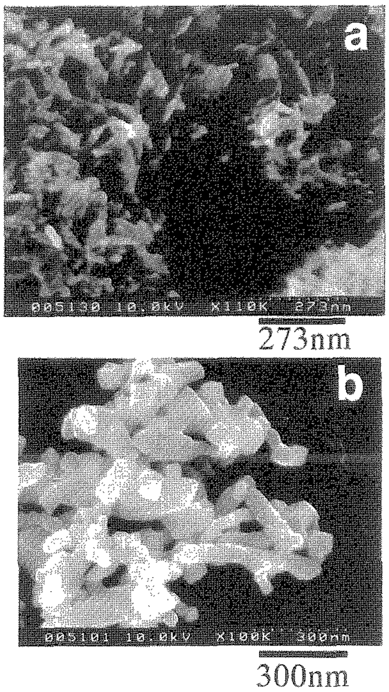

Figure 1 FE-SEM images of (a) dried Gd doped CeO_2 powders and (b) oxide powders calcined at 700°C.

As indicated in these figures, the dried powders showed particles that were mixture of nano-size round shape and rod like shape particles. On average, particle size tended to be in the range 10-100nm. Particle aggregation was open and not too strong, with the occasional regions of discrete particles that were mono-disperse or connected to only one other particle. The calcined CeO_2 powders doped with Gd^{3+} showed no appreciable morphologic changes by high temperature calcinations such as 700°C. The particle size tended to be in the range 30-300nm. The nano-sized and discrete particles are most favorable for low –temperature sintering of Gd doped CeO_2. Therefore, it is concluded that the ammonium carbonate co-precipitation method in the present study is useful for fabrication of dense sintered bodies with nano-size grain.

Figure 2 are plots of density against sintering temperatures between 1000° and 1550°C. Over a temperature range of 1000° to 1550°C, it was possible to prepare sintered bodies that were 95-100% of theoretical density (i.e. 7.248 g/cm^3). This was made possible by calcination at various temperatures (500°-1000°C). There was no calcination temperature which could provide a 'one size fits all' powder that could be sintered to high density at all temperatures of interest. The fine powders calcined at 500°-550°C were suitable for sintering at 1000°C<T<1200°C. Powders calcined at 700°C were suitable for high density sintering at temperatures between 1200° and 1400°C. Powders calcined at 850°C were suited to sintering at temperatures of 1450°C and higher. These results indicate that control of particle agglomeration in the powders is an important factor in the densification process of Gd doped CeO_2.

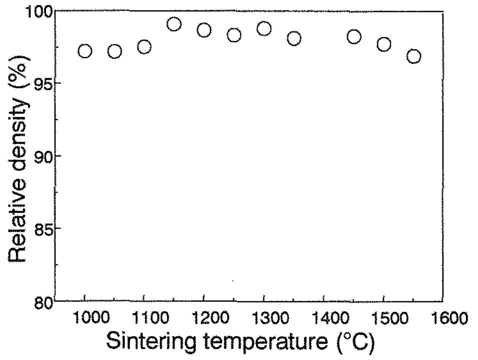

Figure 2 Plot of density vs. sintering temperature for $Gd_{0.1}Ce_{0.9}O_{1.95}$.

Over the temperature range 400°-700°C, total conductivity results showed almost linear Arrhenius plot behavior, of which an example is shown in **Fig. 3**.

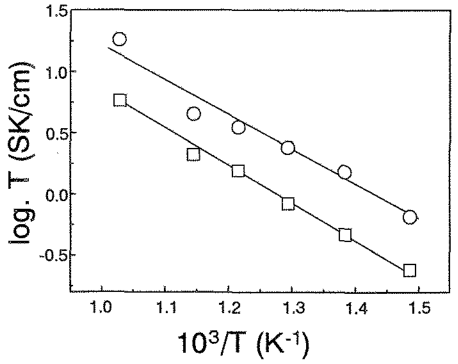

Figure 3 Arrehnius plot of oxide ionic conductivity of $Gd_{0.1}Ce_{0.9}O_{1.95}$ sintered bodies at various temperatures. (○): average grain size: 138nm, and (□): average grain size: 572nm.

The conductivity of specimens with very small grain size (138nm) was much higher than that of specimen with big grain size (572nm). This figure implies that there is some form of dependence between conductivity and average grain size. To conclude the influence of grain size on conductivity, the average grain size dependence of conducting properties was examined.

Figures 4a and 4b present the average grain size dependence of electrolytic properties of $Gd_{0.1}Ce_{0.9}O_{1.95}$ sintered bodies. The conductivity decreased with decreasing grain size and reached the lowest value at an average grain size of 570nm. Also the activation energy increased with decreasing grain size and reached maximum at aforementioned average grain size. This tendency would be attributable to the space charge layer around the grain boundary in the sintered body. On the other hand, the conductivity increased with a decrease of grain size under 570nm. The activation energy corresponded to the tendency of conductivity. In this region, it is suggested that the space charge layer with high resistivity is minimized around the grain boundary. Since the change of conductivity is large when the grains are below 570nm then we suggest it is not all attributable to space charge changes. Other micro-structural features with in the grain are also beginning to have an influence. Both change of the space charge layer width around the grain boundary and the micro-structural features within the grain would lead to improvements in the conductivity, that are observed in the sintered bodies.

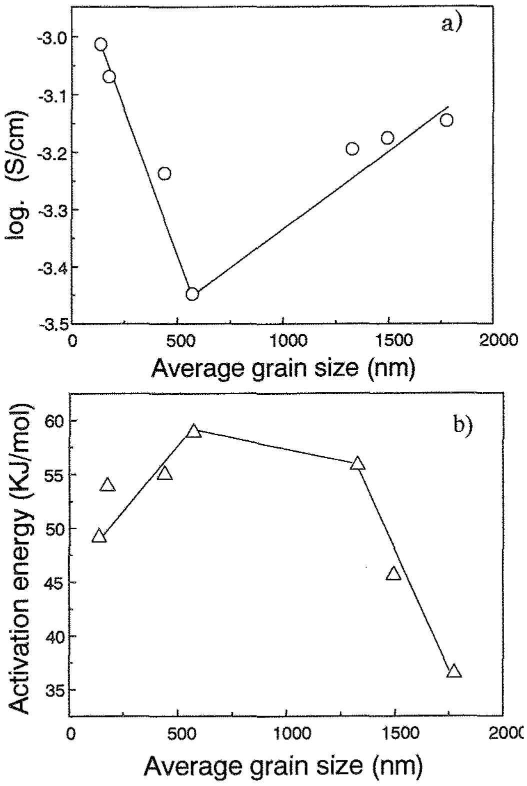

Figure 4 Electrolytic properties in $Gd_{0.1}Ce_{0.9}O_{1.95}$ sintered bodies; a): conductivity vs. average grain size, b): activation energy vs. average grain size. Measurement temperature of conductivity: 400°C.

Figure 5(a) displays the selected area electron diffraction pattern recorded from the sintered body with the average grain size of 1.78μm (1,780nm). The diffuse scattering exists in the background of electron diffraction pattern. This indicates that micro-domain with coherent interface is present in the grain. In addition, small extra spots which are indicated by dashed arrow lines coexisted with main fluorite type spots in the electron diffraction pattern. These extra spots, which can be indexed on a distorted b-type rare earth structure (ex. Gd_2O_3) by a comparison between observed and calculated patterns, suggest that coherent domains of this structural arrangement exist in this material. In general the Gd^{3+} is known to replace Ce^{4+} and create oxygen vacancies. However, it is known that segregation of dopant cations to the grain boundary region occurs. The lattice distortion would be introduced into fluorite lattice by this segregation. To minimize the lattice distortion in CeO_2 lattice, micro-domain with ordered structure would be formed in the lattice. The micro-domain would be developed in the grain to minimize this lattice distortion. It is expects that the further careful observation of lattice image will clarify the micro-domain structure in detail.

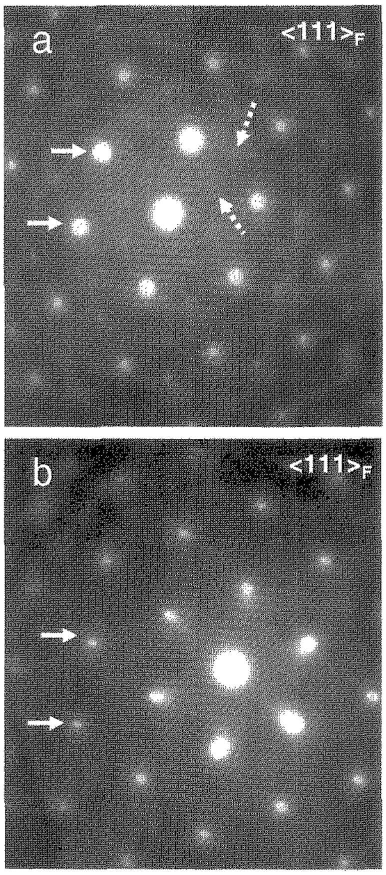

Figure 5 Selected area electron diffraction patterns recorded from (a) the sintered bodies with big grain size (1.78μm) and (b) the sintered bodies with small grain size (138nm). The dashed arrow line indicates extra reflection. Solid arrow line indicates fluorite spot.

On the other hand, the specimen with small grain size has different micro-structural features as compared with aforementioned specimen with large grain size. **Figure 5(b)** displays the selected area electron diffraction pattern recorded from the sintered body with the average grain size of 138nm. The diffuse scattering was observed in the background of electron diffraction pattern, but the intensity of the extra reflection is very weak. Also it is hard to see extra reflection in the electron diffraction pattern. This suggests that the heterogeneity in the grain was lowered by low temperature sintering. Also it is concluded that low temperature sintering minimizes the micro-domain size in the grain and improves the conducting property in the specimen. While this micro-structural change is subtle, the nano-hetero structure with micro-domain in the grain has a significant influence on the electrolytic properties. We believe that the design of this hetero structure with micro-domain is a key for improvement of conducting property in Gd doped ceria electrolytes.

4. SUMMARY

Dense $Gd_{0.1}Ce_{0.9}O_{1.95}$ sintered bodies with nano-size grain (over 95% of theoretical density) was fabricated using nano-size Gd doped CeO_2 powders. And the influence of grain size of sintered bodies on conducting properties was examined for development of low temperature operation of fuel cells. Nano-sized round shape Dy doped CeO_2 powders were prepared using carbonate co-precipitation method. The fine powder was required for the fabrication of dense sintered body with nano-size grain. The obtained specimens with large grain size had micro-domain with distorted b-type rare earth structure or its related structure. On the other hand, the aforementioned micro-structural feature was not so clear in the specimens with nano-size grain. The size of micro-domain would be small in the aforementioned specimens with small grain size. Therefore, it is concluded that a design of microstructure with micro-domain is a key for improvement of conductivity in Gd doped CeO_2 system.

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