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Mechanical and Electrical Properties of Rare earth-Doped Ceria Ceramics for SOFC Electrolytes

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The influences of the sintering additive content of rare-earth oxide on mechanical and electrical properties of ceria ceramics were investigated by small specimen technique and AC impedance method. A small punch testing method was employed to determine the elastic modulus and biaxial fracture stress of the ceria-based ceramics. Rare-earth oxides doped ceria powders with a composition of $(CeO_2)_{1-x}(RO_{1.5})_x$ (R = Y, Gd, Sm and x = 0, 0.10, 0.15, 0.20, 0.30, 0.40, 1.0) were prepared by a coprecipitation method. The powders were compacted by cold isostatic pressing (120MPa), and sintered at 1500°C in air for 5h. The elastic modulus and fracture stress were decreased, and total ionic conductivity was increased significantly with increasing additive content of the rare-earth oxides, possibly due to the oxygen vacancies induced by the rare-earth oxides doping.

Key words: Solid Oxide Fuel Cells, Ceria Ceramics, Rare-earth oxide, Mechanical Properties, Electrical Property

1. INTRODUCTION

Solid Oxide Fuel Cells(SOFCs) can generate high efficiency electric power using H_2 and O_2 gases without environmental pollution. Because SOFCs converts the chemical energy of the fuel directly to electrical energy without the intermediate of thermal energy, its conversion efficiency is not subject to the Carnot limitation. Because of their high temperature of operation (800~1000°C), natural gas fuel can be reformed within the cell stack eliminating the need for an expensive, external reformer system. Also, SOFCs can be successfully used as replacement for combustors in gas turbines; such hybrid SOFCs-gas turbine power systems are expected to reach efficiencies approaching 70% level. Thus, SOFCs are expected to become a major electric power source in the future [1,2]. One of the traditional electrolyte materials is yttria-stabilised zirconia ceramics that must typically be operated at high temperatures, due to the relatively high resistivity of the electrolyte at lower temperatures. Lowering temperature, however, to between 600°C and 800°C has a number of potential benefits, including, for example, cheaper materials, lower degradation problems, and closer temperature match for internal reformation possibilities. Ceria based ceramics, which have a higher oxygen ion conductivity than yttria-stabilized zirconia, is one of the possible electrolytes for SOFCs at low temperatures [3]. Many papers have been devoted to the study of rare-earth oxide additions on the electrical and the mechanical properties of ceria based ceramics [4-11]. However, in the previous studies the types and additive amount of rare-earth oxide investigated were limited and no systematic investigation has been undertaken so far. A small punch testing method and AC impedance method were employed to conduct a systematic study using small sintered specimens. This paper presents experimental results of the systematic investigation on the effects of rare-earth oxides (Y_2O_3, Gd_2O_3 and Sm_2O_3) addition on the mechanical properties and electrical property of the doped ceria ceramics.

2. EXPERIMENTAL

2.1. Sample Preparation

Rare-earth oxide doped ceria powder with a composition of $(CeO_2)_{1-x}(RO_{1.5})_x$ (R = Y, Gd, Sm, x=0, 0.10, 0.15, 0.20, 0.30, 0.40 and 1.0) were synthesized from CeO_2 (Anan Kasei Co. Ltd., Osaka, Japan, purity, 99.9%), Y_2O_3, Gd_2O_3 and Sm_2O_3(Anan Kasei Co. Ltd., Osaka, Japan, purity, 99.9%) by a co-precipitation method. The powders were then pressed into disks (ϕ12 x 1.0mm) using a die press made of a hard metal at 50MPa, followed by isostatic press at 120MPa. The disks were then sintered in atmospheric condition at 1500°C for 5h. Specimens were polished with Emery paper (#4000). After polishing, the specimens were annealed at 1000°C for 3h to remove the induced residual stresses. The specimen densities of the sintered bodies were measured by the Archimedes method. The doped ceria ceramics with Y_2O_3, Gd_2O_3 and Sm_2O_3 are designated by YDC, GDC and SDC, respectively.

2.2. Mechanical Property measurement

X-ray diffraction analysis of the sintered samples was conducted using a diffractometer (Mac science; M21Xmodel).

The mechanical properties of the sintered bodies, the Young's modulus and fracture stress were measured by a small punch (SP) testing method [12,13] using miniaturized disk specimens. The punch and specimen holder, designed for SP tests, are shown in Figure 1. The SP tests were performed on a universal testing machine (Instron 1185 type) in atmospheric condition at room temperature. The diameter and thickness of specimens were ϕ10mm, and 0.7mm, respectively. The specimen holder consists of an upper and lower die. The load application was performed through the puncher until a final failure occurred at a crosshead speed of 0.1mm/min. The deflections of the specimens were measured by monitoring the movement of an Al_2O_3 rod using a linear variable differential transducer (LVDT) fixed on to the Instron machine.

Deformation and stress analysis for SP tests have been performed using a finite element method (FEM), assuming linear elastic response of the specimen [12]. In this study, the numerical data were used to compute the Young's modulus and fracture stress. The Young's modulus and biaxial tensile stress of SP specimens can be expressed by the following equations [14]

$$E_{SP} = f(t/a)\frac{3a^2P(1-\nu)(3+\nu)}{4\delta\pi t^3} \quad (1)$$

$$\sigma_{SP} = \frac{P}{t^2}(1+\nu)\left[0.485\ln\frac{a}{t}+0.52+\frac{3}{2\pi(1+\nu)}\right] \quad (2)$$

where P is the load, d the deflection at the specimen center, v the Poisson's ratio, t the specimen thickness (=0.7mm), a the bore diameter of the lower die (=2.38mm) and f(a/t) the correction factor for specimen thickness (=1.13). The value of Poisson's ratio was assumed to be 0.33, following the reported data for doped ceria ceramics[8]. The Young's modulus was calculated from the initial linear slope of the load-deflection curve using Eq.1. The fracture stress was calculated from the maximum load using Eq.2. The Young's modulus and fracture stress were determined from the SP method is referred to as E_{SP} and σ_{SP}, respectively. Four or five specimens were tested for each dopant content. In order to observe the fracture mode, the specimens were examined using indentation method. Indentation was performed on the polished dry-surface of the sample, using an Akashi MVK-E type Hardness Tester with a standard Vickers indentor. The indentor load was kept at 9.8N for 15 sec. Crack path was observed by scanning electron microscopy (SEM)..

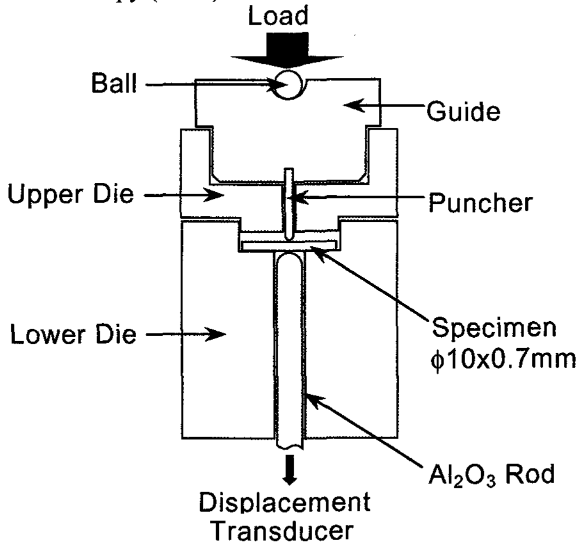

Fig.1 Schematic illustration of Small Punch testing method.

2.2. Electrical Property measurement

Ionic conductivity in air at temperatures between 600 and 800°C was measured by an AC impedance spectroscopy in a tubular oven. Platinum electrodes of 7 mm diameter were applied by a screen-printing method symmetrically on opposite sides of the specimen. During measurement the temperature was closely monitored by three thermocouples kept in the vicinity of the specimen. The frequency range 13MHz down to 1Hz (Solatron SI1260, Schlumberger Electronics) was covered.

3.RESULTS AND DISCUSSION

3.1 Mechanical Properties

The test specimens used in this study had a relative density of 99±0.2% and an average grain size of 1.2~2.5mm for YDC, GDC, and SDC (Pure ceria 4.1mm). The Young's modulus E_{SP} of the doped ceria ceramics is plotted as a function of the dopant content in Fig. 2. All the doped ceria ceramics gives lower Young's modulus values than that of the pure ceria within the range of the dopant content used in this study. In the case of the YDC, E_{SP} appears to decrease as the dopant content is increased and give a minimum value at the dopant content of 15mol%. The GDC and SDC show a similar trend and give a minimum E_{SP} value at the dopant content of 20mol%. It is well accepted that a half-value width obtainable from XRD analyses provides a good measure of crystallinity of the body. Figure 3 shows the half-value width for the doped ceria ceramics as a function of the dopant content. The half-value width has been determined using the diffraction pattern with a maximum peak intensity. It has been reported that the addition of elements in ceria increases oxygen vacancies in the doped ceria ceramics when the valence of the dopant differs from that of the ceria [3]. Thus, the half-value width is expected to give a measure of the concentration of oxygen vacancies in the doped ceria ceramics. The crystallinity of the body generally increases when the half-value width decreases. It can be noted in Fig. 3 that the YDC gives a maximum half-value width at the dopant content of 15mol%, and the GDC and SDC appear to yield a maximum at 20mol%. There is a general correspondence between the results of the Young's modulus and half-value width. Thus, the reduction of the Young's modulus in the doped ceria ceramics may be possibly due to the Nonuniformity. Figure 4 summarizes the fracture strength of the doped ceria ceramics determined using the SP method. It is seen that the variation of the fracture strength with the dopant content is approximately similar to that of the Young's modulus. Thus, the strength reduction induced by the doping may be due to the increased concentration of oxygen vacancies. Fracture strength usually increases with the decreasing grain size. However, the fracture strength shows a minimum value approximately for the range of the smallest grain size (10~20mol% dopant). It appears that the influence of the increased oxgen vacancies override strengthening effect due to the finer grain size. Figure 5 shows the ratio of transgranular fracture determined from the indentation tests. It can be seen that the transgranular fracture ratio in the doped ceria ceramics increases with the increasing dopant content, reflecting probably the reduced grain strength due to the increased concentration of oxygen vacancies.

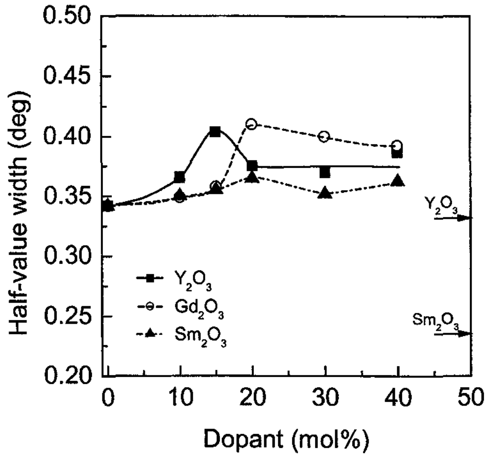

Fig.3 Half-value width of $(CeO_2)_{1-x}(RO_{1.5})_x$ as a function of rare-earth oxide dopant.

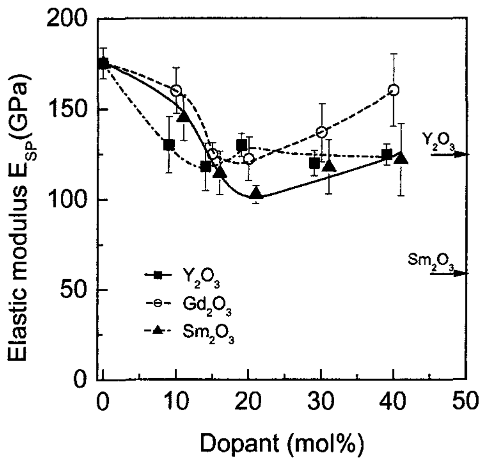

Fig.2 Elastic modulus E_{SP} of $(CeO_2)_{1-x}(RO_{1.5})_x$ as a function of rare-earth oxide dopant.

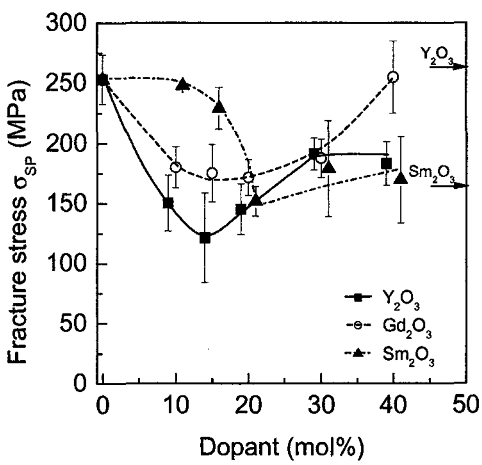

Fig.4 Fracture strength σ_{SP} of $(CeO_2)_{1-x}(RO_{1.5})_x$ as a function of rare-earth oxide dopant.

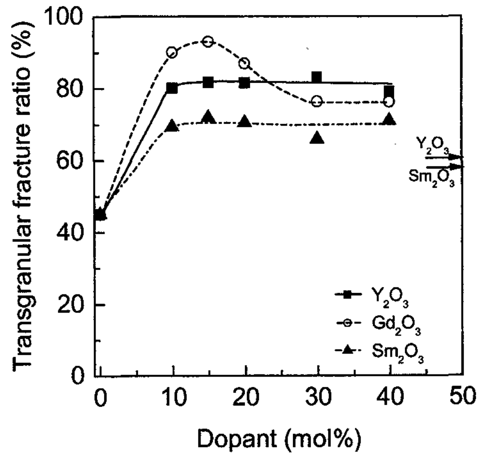

Fig.5 Transgranular fracture ratio of $(CeO_2)_{1-x}(RO_{1.5})_x$ as a function of rare-earth oxide dopant.

3.2 Electrical Property

Figure 6 shows the total conductivity σ of the YDC as a function of the dopant content specimens determined from the AC impedance method. The σ appears to increase as the dopant content is increased and give a maximum value at the 15~20mol% for the three temperatures tested in this study. The conductivity increases rapidly especially at the dopant content of 30mol% and 40mol%, as the temperature increases. The strength property has an inverse relationship with the electrical property. In other words, the optimal dopant content for the electrical property may not yield suitable material for SOFC systems from the view point of mechanical properties.

The above-mentioned experimental results suggest that the change in the mechanical properties should be taken into account in the use of the ceria-based ceramics for solid oxide fuel cells, in addition to the improvement of oxygen ionic conductivity.

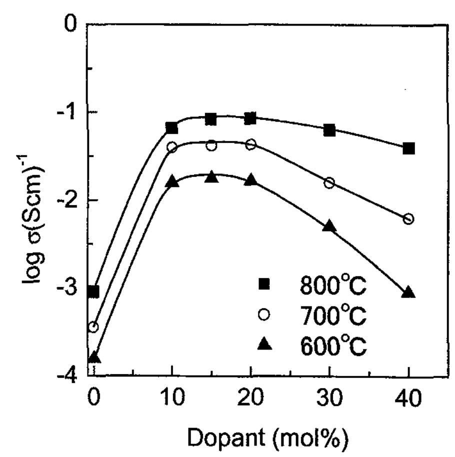

Fig.6 Ionic conductivity of YDC in air as a function of temperature and rare-earth oxide dopant content.

4.CONCLUSIONS

The influences of the sintering additive content of rare-earth oxide (Y_2O_3, Gd_2O_3, Sm_2O_3) on the mechanical properties and electrical property of ceria ceramics were investigated by employing a small punch testing method and AC impedance method. The main results obtained from this study can be summarized as follows:

(1) The Young's modulus and fracture stress of the doped ceria ceramics determined by a small punch testing method were lower than that of a pure ceria within the range of the dopant content used in this study. Especially, the mechanical properties gave a minimum value at the dopant content of 15~20mol%.

(2) The transgranular fracture ratio in the doped ceria ceramics increased with the increasing dopant content, reflecting probably the reduced grain strength due to the increased concentration of oxygen vacancies.

(3) The ionic conductivities determined by AC impedance method were higher than that of the pure ceria within the range of the dopant content used in this study. Especialy, the ionic conductivity gave a maximum value at the dopant content of 15~20mol%. In other words, the optimal dopant content for the electrical property may not yield suitable material for SOFC systems from the view point of mechanical properties.

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