Microstructure and Electrical Conductivity of Yttria Stabilized Zirconia (8Y-CSZ) Containing Small NiO Addition

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Abstract: In this study, the effect of addition in small contents of NiO on microstructure and electrical conductivity properties of 8 mol% yttria stabilized cubic zirconia (8Y-CSZ) were investigated. Specimens were produced by colloidal processing from 1 wt% NiO and 99 wt% 8Y-CSZ powders. Specimens were pressureless sintered at 1,400 °C for 10 h. Scanning Electron Microscope (SEM) and EDS analysis results showed that an amount of 1 wt% NiO dissolved in the 8Y-CSZ and insoluble NiO in the 8Y-CSZ precipitated at the grain boundaries. Electrical conductivities of undoped and 1 wt% NiO doped 8Y-CSZ specimens were measured using a frequency response analyzer (impedance spectroscopy) in the frequency range of 100 mHz-13 MHz and at 300-800 °C. Electrical conductivity results showed that grain interior, grain boundary and total conductivity of 8Y-CSZ increased with 1 wt% NiO addition. The reason for increase of electrical conductivity in NiO doped 8Y-CSZ, due to create oxygen vacancies in the crystal lattice of dissolved NiO in 8Y-CSZ and the ion transfer of the oxygen vacancies at high temperatures.

Key words: Cubic zirconia (8Y-CSZ), NiO, electrical conductivity, impedance spectroscopy.

1. Introduction

Solid oxide fuel cell (SOFC) is a device, which is produced the electricity with the aid of an electrolyte having ionic conductivity electro-chemically and combination with a gaseous fuel, and oxidizing gas. Solid Oxide Fuel Cells operating between 700 and 1,000 °C generate the electricity between 1 kW and 10 MW at 65% efficiency [1]. The ions in a SOFC are transmitted from a porous electrode (cathode) to an electrolyte and from inside an electrolyte to a porous fuel electrode (anode). Oxygen ions in the SOFC react with the fuel (H₂, natural gas, methane, etc.) and release electrons to external circuit to generate electricity. Thus, it occurs 1 V potential between anode and cathode. Yttria-stabilized cubic zirconia

(8Y-CSZ) is generally used as an electrolyte material that is perfectly conducted oxygen ions from cathode to anode at high temperatures. NiO/Y₂O₃-ZrO₂ (Ni/YSZ) cermet is used as an anode material. Lanthanum Manganate (LaMnO₃) peroxide having electronic and ionic conductivity is used as a cathode material [2-4].

Pure zirconia has three different polymorphic transformations such as monoclinic, tetragonal and cubic. These phases can be obtained as depending on temperature and composition at equilibrium conditions. ZrO₂ has a monoclinic crystalline range from room temperature to 1,170 °C. Monoclinic ZrO₂ transforms into tetragonal crystalline at 1,170 °C with a 5% volume reduction, and tetragonal crystalline transforms into cubic crystalline at 2,370 °C. Cubic crystalline is stable up to 2,680 °C which is the melting temperature of zirconia. It must form a solid

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solution with metal oxides such as MgO, CaO, CeO₂ and Y₂O₃ in order to make the stable of cubic zirconia at room temperatures [5-7].

It has several advantages for mixed conductive composites in the selection of NiO as an electronic component. NiO is stable at a wide temperature range and partial oxygen pressures [8]. NiO is also known as excellent a catalyst for the activation of oxygen [9]. In addition to conductivity of NiO; NiO is easily compatibles with additives as Lithium when it is needed. Therefore, when the optimum composition of NiO in the 8Y-CSZ was determined, 8Y-CSZ/NiO composites may be promising as cathode material [10].

In this study, the effect of addition in a small amount of NiO on microstructure and electrical conductivity properties of the 8Y-CSZ using as SOFC were investigated.

2. Experimental Materials and Procedure

In this study, 8 mol% yttria stabilized cubic zirconia (8Y-CSZ) (Tosoh, Japan) powders and NiO powders (MTI Industrial Co. USA) up to 1 wt% were used as matrix material and additives, respectively. The average grain sizes were 0.3 μ m for 8Y-CSZ and 0.3 μ m for NiO. The chemical compositions of the powders used in the experiments are presented in Table 1.

The specimens for the microstructural and electrical conductivity investigations were produced by means of colloidal processing. The doping process was carried out in a plastic container by mechanical mixing of NiO up to 1 wt% and 8Y-CSZ powders with zirconia balls and ethanol. The mechanical mixing was done in a "speks" type mixer at 200 rpm for 12 h. The prepared slurries were left to dry for 24 h by leaving the lid open. After the drying process,

the agglomerated powders with medium hardness were ball milled for 10 min to obtain a good dispersion and to break up the agglomerates. The powders obtained were sieved through a 60 μ m sift and pressed under 200 MPa of pressure in a single axis die with a radius of 10 mm and a height of 4 mm. The inner surface of the steel die was cleaned after each dry pressing process, and stearic acid was applied to the side walls of the die.

Sintering was carried out in a box type furnace under normal atmospheric conditions. The pressed pellets were sintered at 1,400 °C for 10 h at heating and cooling rates of 5 °C/min. The surfaces of the specimens were ground and polished using normal metallographic methods after the sintering process, and the specimens were thermally etched by keeping them in a furnace at 50 °C below the sintering temperature for 1 h. Microstructural investigation of the sintered specimens was performed using a scanning electron microscope (SEM Jeol Lv 6060). Grain sizes were measured using the mean linear intercept method.

The electrical conductivity measurements were carried out with pellet specimens with a 10 mm diameter and about 3 mm thickness. The two surfaces of each sintered pellet were slightly polished with abrasive paper, and platinum paste was applied to both sides of the specimens. The specimens were then dried in an oven at 100 °C to eliminate the solvent and annealed at 800 °C for 30 min to avoid an excessive shrinkage of the platinum electrodes. The temperature dependence of electrical conductivity was measured using a frequency response analyzer (Solartron Model 1260) in the frequency range of 100 mHz-13 MHz. Measurements were made in the air and in the temperature range of 300-800 °C at an interval of

Table 1 The chemical composition of powders used in the experimental works.

Powders	wt%									
	ZrO ₂	Y ₂ O ₃	MgO	NiO	TiO ₂	FeO ₂	Na ₂ O ₃	CaO	Al ₂ O ₃	SiO ₂
8Y-CSZ	85.9	13.6	-	-	0.1	0.003	0.01	0.02	0.25	0.1
NiO	-	-	< 0.01	99.8	-	< 0.012	< 0.01	< 0.01	-	-

100 °C. The Ac impedance diagrams were analyzed using Zview software.

3. Results and Discussion

The microstructures of the undoped and 1 wt% NiO doped 8Y-CSZ specimens sintered at 1,400 °C for 10 h are presented in Fig. 1. The microstructure of the undoped 8Y-CSZ showed that it was composed of coarse-grained and coaxial polygonal grains (Fig. 1a) and the microstructure of 1 wt% NiO doped 8Y-CSZ specimen formed a smaller and more fine-grained structure (Fig. 1b). Due to the fact that 1 wt% NiO doped 8Y-CSZ specimen has a lower grain boundary diffusion, it slowed down the movement of grain boundaries and occurred the less grain growth in the 1 wt% NiO doped 8Y-CSZ. The main differences in microstructure of the sintered specimens are change in the grain size and amount of porosity. Batista et al. reported that the addition of small amount of NiO into 8Y-CSZ slightly slowed down the grain growth and increased densification of 8Y-CSZ [11].

The changes in the grain size of the undoped and 1 wt% NiO doped 8Y-CSZ specimens are presented in Fig. 2. The addition of 1 wt% NiO brought about a slight decrease in the grain size of 8Y-CSZ. The grain sizes of undoped and 1 wt% NiO doped 8Y-CSZ specimens were calculated as 4.15 and 3.61 μm , respectively. Due to precipitation in low amount of

Y_2O_3 at the grain boundaries of 8Y-CSZ and high-energy at grain boundaries, the grain size of the undoped 8Y-CSZ is larger than NiO doped 8Y-CSZ [12].

NiO, which precipitated at the grain boundaries of 8Y-CSZ restricted the movement of grain boundaries with solid solution drag mechanism. The necessary condition for solid solution drag is precipitation at the grain boundaries of one of the components of solid solution.

EDS analysis results of 1 wt% NiO doped 8Y-CSZ sintered at 1,400 °C for 10 h are presented in Fig. 3. 1 wt% NiO completely didn't dissolve in the 8Y-CSZ. EDS results showed that NiO insoluble in the 8Y-CSZ segregated at the grain boundaries.

The measurement of electrical conductivity is one of the important requirements for an electrolyte in Solid Oxide Fuel Cells. As reported earlier, generally, the Ac impedance of an ionic conductor contains contributions from grain, the grain boundary and electrode-electrolyte interface at high, intermediate and low frequencies, respectively, which can be reflected in a complex plane by three successive arcs [13, 14]. A schematic plot of the complex impedance for zirconia and its equivalent electrical circuit was originally proposed by Bauerle [15]. The Ac impedance spectroscopies of 1 wt% NiO doped 8Y-CSZ specimen at different temperatures are shown in Fig. 4.

Fig. 1 The microstructures of the undoped and 1 wt% NiO doped 8Y-CSZ specimens sintered at 1,400 °C for 10 h. (a) Undoped 8Y-CSZ and (b) 1 wt% NiO doped 8Y-CSZ.

Fig. 2 The average grain sizes of the undoped and 1 wt% NiO doped 8Y-CSZ specimens.

EDS analysis points	wt %			
	Zr	Ni	Y	O
A	62.967	0.270	13.312	19.188
B	61.710	0.507	12.573	20.763

Fig. 3 EDS results of 1 wt% NiO doped 8Y-CSZ specimen sintered at 1,400 °C for 10 h.

When ac impedance curves of the 1 wt% NiO doped 8Y-CSZ specimen examined in Fig. 4, grain interior resistance (R_{gi}) is lower than grain boundary resistance (R_{gb}). It was obtained three semicircles at 300, 400 and 500 °C in the 1 wt% NiO doped 8Y-CSZ (Figs. 4a-4c). But it wasn't obtained three semicircles at temperatures above 500 °C (Figs. 4d-4f) and, it was seen that the electrical circuit model changed as depending on each temperature.

The grain interior (σ_{gi}) and grain boundary conductivity (σ_{gb}) were calculated using the following Eq. (1):

$$\sigma_{gi} = \frac{1}{R_{gi}} \cdot \frac{L}{A}$$

$$\sigma_{gb} = \frac{1}{R_{gb}} \cdot \frac{L}{A} \quad (1)$$

where, R_{gi} is the grain interior resistance, R_{gb} is the grain boundary resistance, and L and A are the thickness of the specimen and cross-sectional area of the specimen, respectively.

The effect of NiO content on the grain interior, the grain boundary and total conductivity of 8Y-CSZ at 400 °C was presented in Fig. 5. The electrical conductivity results showed that the addition in a small amount of NiO into 8Y-CSZ brought about an increase in the grain interior, grain boundary and total conductivities. NiO, which dissolved in the 8Y-CSZ crystal structure and precipitated at the grain boundaries, disrupted charge neutrality of crystalline of the 8Y-CSZ and led to the formation of oxygen vacancies. This oxygen vacancies provide ion transfer and cause the electrical conductivity. Song et al. reported that NiO could be dissolved up to 0.5 mol% in the 8Y-CSZ [16].

The grain interior and grain boundary activation energies for undoped and 1 wt% NiO doped 8Y-CSZ specimens were calculated using the following Arrhenius equation. The grain interior and grain boundary data were plotted as conductivity as shown in Figs. 6 and 7, by analyzing the temperature (T) dependence of the ionic conductivity (σ) and the activation energies for the grain interior and the grain boundary were calculated from the slope of the line obtained from the plot of $\ln\sigma$ - T .

$$\sigma = \sigma_0 \exp(-E_a/RT) \quad (2)$$

where, T is absolute temperature, σ_0 is pre-exponential factor and E_a and R are activation energy and gas constant, respectively.

The grain interior activation energies for undoped and NiO doped 8Y-CSZ specimens are shown in Fig. 6. As can be seen from this figure, all data coincided on a straight line. The grain interior activation energy (E_a) values of the undoped and 1 wt% NiO doped 8Y-CSZ

Fig. 4 The ac impedance spectroscopies of 1 wt% NiO doped 8Y-CSZ at different temperatures.

Fig. 5 The change of the electrical conductivities with addition of NiO at 400 °C test temperature.

Fig. 6 The grain interior activation energies of the undoped and 1 wt% NiO doped 8Y-CSZ specimens.

specimens were calculated as 1.15 and 1.06 eV, respectively. The activation energy results showed that the grain interior ion transport in the 1 wt% NiO doped 8Y-CSZ would be easier than in undoped 8Y-CSZ. 1 wt% NiO addition into 8Y-CSZ brought about oxygen vacancies in the 8Y-CSZ matrix and these oxygen vacancies helped in the ionic transport. Therefore, the grain interior activation energy decreased in the 1 wt% NiO doped 8Y-CSZ.

The grain boundary activation energies (E_a) for undoped and 1 wt% NiO doped 8Y-CSZ specimens are shown in Fig. 7. The grain boundary activation energy (E_a) values of the undoped and 1 wt% NiO doped 8Y-CSZ specimens were calculated as 1.50 and 1.06 eV, respectively. Due to Y_2O_3 segregation at the grain boundaries in the 8Y-CSZ, the activation energy value of the undoped 8Y-CSZ was higher than NiO doped 8Y-CSZ.

It is known as the blocking effect of grain boundaries that increased resistance to ion transfer of grain boundaries (according to grain interior resistance). Impurities which existed in the grain boundaries caused blocking of grain boundaries. Specific conductivity of the grain boundary at 8 mol %

Fig. 7 The grain boundary activation energies of the undoped and 1 wt% NiO doped 8Y-CSZ specimens.

yttria-stabilized cubic zirconia (8Y-CSZ) is lower than grain interior [13, 17].

If a specimen has more total grain boundary area, it means that this specimen has a lower total conductivity. Guo and Maier pointed out that this internal grain boundary resistance seen in materials at high temperatures might occur as a result of a disappearance of the space charge-oxygen vacancy [13]. As a result of decreased oxygen vacancy in the space charge layer of the grain boundary, a blocking effect of the grain boundary and grain boundary core may occur and can be considered as divided into two space charge layers. Yttria segregation at the grain boundaries of 8Y-CSZ are twice as high as at the grain interior. Oxygen vacancy decreases when these defects interact with defects or a mechanism with vanished oxygen vacancy is revealed. Y_2O_3 segregation existing at the grain boundaries of 8Y-CSZ brings about a blocking effect of the grain boundary and causes to vanish of oxygen vacancies. Thus, the activation energy of the grain boundary was expected to be higher for the undoped 8Y-CSZ. The addition of a small amount of NiO into 8Y-CSZ reduced the negative effects of Y_2O_3 segregation and led to the new transmission paths for ion conduction. Therefore, the grain boundary activation energy of 1 wt% NiO doped 8Y-CSZ is lower than undoped 8Y-CSZ.

4. Conclusions

The addition of 1 wt% NiO into 8Y-CSZ gave rise to a decrease in the grain size. NiO could be dissolved in the 8Y-CSZ up to 0.5 mol%. Insoluble NiO in the 8Y-CSZ precipitated at the grain boundaries. The presence of the NiO precipitation at the grain boundaries of 8Y-CSZ restricted the movement of grain boundaries. Therefore, the grain size of NiO doped 8Y-CSZ was smaller than undoped 8Y-CSZ.

The Ac impedance spectroscopy results showed that the grain interior and grain boundary resistances with addition in a small amount of NiO decreased increasing temperature. The grain interior resistance of 1 wt% NiO doped 8Y-CSZ was lower than grain boundary resistance. The grain interior, grain boundary and total conductivities of the 8Y-CSZ increased with addition of a small amount of NiO.

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