Expansion and shrinkage in the redox process of (Mg,Ni)O solid solutions for preparation of steam reforming catalysts in SOFCs

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(Mg,Ni)O solid solutions were synthesized by calcination of MgO and NiO mixtures (MgO:NiO = 65:35 in mol) at 1500°C for 2 h in air. When the samples were firstly reduced at 1000°C in a gas mixture of 4 vol% hydrogen and nitrogen, a volume expansion was observed. The results of powder X-ray diffraction (XRD) and scanning electron microscopy/energy dispersive X-ray spectrometry (SEM/EDX) analyses suggested that the expansion after reduction was possibly caused by the creation of space between (Mg,Ni)O grains by segregation of nickel particles on (Mg,Ni)O grains. When the reduced samples were re-oxidized at 1000°C in air and then reduced again at 1000°C in a gas mixture of 4 vol% hydrogen and nitrogen, the samples revealed an accelerated expansion, which was much larger than that of the samples reduced once. The morphological characteristics of (Mg,Ni)O grains and segregated nickel particles of the samples those were reduced twice differed to those of the samples reduced once; however, the phases of the all samples were similar, as verified by XRD and SEM analyses. The accelerated expansion after re-oxidation and reduction might be related to changes in the microstructure of the (Mg,Ni)O grains with the nickel particles segregated.

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1. Introduction

Solid oxide fuel cell (SOFC) is one of the promising technologies for converting chemical energy to electrical energy with high efficiency; its power generation efficiency has been recently reported to be 49% (based on a higher heating value) using methane (CH₄) fuel in a flat tubular segmented-in-series SOFC system.¹⁾ As methane gas can not be directly used as a SOFC fuel, reforming methane to hydrogen (H₂) and carbon monoxide (CO) is required. Nickel-based catalysts are widely used in steam reforming of methane, because of their excellent catalytic performance and their ability to eliminate the need of including expensive noble metal such as platinum (Pt) or palladium (Pd).²⁾

Among the nickel-based catalysts, magnesia-supported nickel (Ni/MgO) catalyst is well known as a steam reforming catalyst of hydrocarbons not only for its higher catalytic performance but also for its resistance to coke formation due to the acidic property of the magnesia support.³⁾⁻⁵⁾ In addition, a cermet anode including the catalyst is revealed to exhibit higher reforming activity for biogas in SOFCs.⁶⁾ An active catalyst of Ni/MgO is easily obtained by reduction of a (Mg,Ni)O solid solution, in which dispersing the nickel fine particles is not necessary.⁷⁾ Therefore, the preparation of the Ni/MgO catalyst by reduction of a (Mg,Ni)O solid solution is simple and cost competitive. Future applications of the Ni/MgO catalyst in fuel cells will possibly realize the internal reforming of SOFCs.⁸⁾

Previously, it was reported that an anode material, consisting

of nickel oxide and yttria stabilized zirconia, exhibited an expansion or shrinkage behavior during a redox process,⁹⁾⁻¹¹⁾ and this volume expansion or shrinkage is responsible for the lack of material stability. Systematic investigation about the redox-induced behavior of (Mg,Ni)O solid solutions is very important for the development of Ni/MgO catalysts. To our knowledge, there is no detailed report on the volume change of a (Mg,Ni)O solid solution when it is reduced. In this study, we examine the expansion and shrinkage behavior of (Mg,Ni)O solid solutions during the redox process, and discuss volume change mechanism.

2. Experimental procedure

A (Mg,Ni)O solid solution was prepared by calcination of a mixture of MgO powder, which was provided by calcination of Mg(OH)₂ powder (> 99%, Ube Material Industries) at 1000°C for 10 h, and NiO powder (> 99%, Seido Chemical Industry Co.). As starting material of MgO powder (approximately 3 μm in size) and NiO powder (approximately 0.7 μm in size) was mixed in a ratio of 65:35 (Mg:Ni in mol). Since higher porosity leads to higher catalytic activity, a pore forming agent (microcrystalline cellulose type, Asahi Kasei Chemicals Corp.) of 20 mass% was added to the mixture. A solution of poly-vinyl butyral (BM-1, Sekisui Chemical Co.) (10 mass% of the mixture) in ethanol was added to the mixture to prepare pellets without cracks. The resultant paste was mixed well at room temperature until the ethanol solvent evaporated sufficiently. Then, the mixed powder was pressed uniaxially into the pellets (20 mm in diameter) at a pressure of 320 kg/cm². The pellets were calcined at 1500°C for 2 h in air to synthesize the (Mg,Ni)O solid solution.

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The reduction of the (Mg,Ni)O solid solution was carried out at 1000°C in a gas mixture of 4 vol% hydrogen and nitrogen (500 ml/min in total), while the oxidation of the samples was carried out at 1000°C in air. The expansion or shrinkage behavior of the samples was examined by measuring the change in the diameter of the sample pellet. The redox treatments were repeated until the expansion or shrinkage became negligible. The porosity was estimated by measuring the volume and weight of the sample pellet. Scanning electron microscopy (SEM) (JSM-5510LV, JEOL Ltd.) equipped with energy dispersive X-ray spectrometry (EDX) (EX-23000BU, JEOL Ltd.) was used for observing the morphological microstructures of the samples and analyzing the element distribution. The crystal structure of the samples was examined by Cu K α X-ray diffraction (XRD) using a RINT-TTR II X-ray diffractometer (Rigaku Corp.).

3. Results and discussion

The phase of synthesized (Mg,Ni)O solid solutions was analyzed by XRD. As shown in **Fig. 1(a)**, only a single phase of (Mg,Ni)O solid solution existed in the sample. The SEM microstructure of the sample is shown in **Fig. 2(a)**. The figure revealed that it consisted of (Mg,Ni)O grains, approximately 2–5 μm in size. The SEM photograph of cut and polished surface of (Mg,Ni)O grains, as shown in **Fig. 3(a)**, revealed that no space nor pore existed inside the grains. Therefore, addition of the pore forming agent was considered not to work as pore forming inside the grains but to work as pore forming between the grains.

After the (Mg,Ni)O solid solutions were firstly reduced for 30 h, the reduced samples were characterized. XRD profile of the

reduced sample, shown in **Fig. 1(b)**, indicated that the sample consisted of (Mg,Ni)O solid solution and nickel metal. The segregation of nickel metal from the (Mg,Ni)O solid solution after reduction corresponded well with previously reported results.¹²⁾ Estimation of equilibrium oxygen partial pressure of Ni/NiO in (Mg,Ni)O solid solution at 1000°C was carried out using the ideal solution model and shown in **Fig. 4**. The figure obviously indicated that the (Mg,Ni)O solid solution ($\text{Ni}/(\text{Mg} + \text{Ni}) = 0.35$) would be reduced at 1000°C and under 1×10^{-16} atm which is an upper limit of measured oxygen partial pressures in the reduction condition. Thus, the nickel segregation in this experiment

Fig. 1. X-ray diffraction (XRD) patterns of (Mg,Ni)O solid solutions using Cu K α radiation. Solid line (a) represents an as-synthesized sample and dotted line (b) represents a sample reduced once.

Fig. 2. Scanning electron micrographs (SEM) of the fracture surfaces of (Mg,Ni)O solid solutions. Image (a) shows an as-synthesized sample, and image (b) shows a sample reduced once.

Fig. 3. Scanning electron micrographs (SEM) of the cut and polished surfaces of (Mg,Ni)O grains. Image (a) shows an as-synthesized sample, and image (b) shows a sample reduced once.

was confirmed to be reasonable. It was also shown that almost all nickel could be segregated from (Mg,Ni)O solid solution in the reduction condition.

According to the composition dependence of the lattice parameter in (Mg,Ni)O solid solutions, as reported previously,¹³⁾ the estimated nickel content of the (Mg,Ni)O solid solution was approximately 34 mol% for the as-synthesized sample. After the reduction, the nickel content in the (Mg,Ni)O solid solution decreased to approximately 2 mol% with the remainder segregating to the surface as nickel metal. The weight loss of the sample by the reduction process was measured to be approximately 10.2%, which is close to the calculated weight loss of 10% when assuming the de-oxygenation shown in **Table 1**. This suggests

Fig. 4. Estimated equilibrium oxygen partial pressure of Ni/NiO in (Mg,Ni)O solid solution at 1000°C. The calculation was performed using the ideal solution model.

that some nickel and oxygen elements are eliminated from (Mg,Ni)O solid solution during the reduction process, and nickel metal segregates.

The SEM microstructure of the reduced sample is shown in Fig. 2(b). Small round particles, approximately 0.3–1.0 μm in size, were deposited on the surface of the (Mg,Ni)O solid solution grains. Because the XRD result of the reduced sample showed the existence of nickel metal as shown in Fig. 1(b) and EDX mapping images of nickel and magnesium elements indicated that the small particles on the grains had a high concentration of nickel as shown in **Fig. 5**, the small particles were considered to be mainly nickel metal. The initial reduction of the (Mg,Ni)O solid solution segregated small particles of nickel metal from the (Mg,Ni)O grains.

Figure 6 shows the expansion and shrinkage profiles characterized by the average size of three samples prepared in the same condition during the reduction and oxidation treatments. Point (a) in Fig. 6 reveals that the apparent volume of the (Mg,Ni)O solid solution expanded up to approximately 3% (the cube of 0.9% in linear expansion) when reduced once, although the estimated volume without void of the sample decreased by approximately 13%, as shown in **Table 1**. As the volume without void of the (Mg,Ni)O grains was estimated to decrease with segregation of nickel from the grains during reduction, the apparent expansion of the reduced sample shown at point (a) in Fig. 6 has to accompany creation of space inside or outside the grains. This estimation was supported by the result that measured porosity (approximately 57%) of sample reduced once was higher than that (approximately 50%) of as-synthesized sample. Because the SEM photograph of cut and polished surface of the (Mg,Ni)O grains of sample reduced once, as shown in Fig. 3(b), revealed that no space nor pore existed inside the grains, the space was

Table 1. Relative Weight and Relative Volumes without Void were Estimated from Magnesium to Nickel Ratios for an as-Synthesized (Mg,Ni)O Solid Solution and a Firstly Reduced Sample Assuming the de-Oxygenation. Magnesium to Nickel Ratios in (Mg,Ni)O Solid Solutions were Calculated Using Lattice Constants Measured by XRD

Samples	Materials	Measured lattice constant (nm)	Estimated Mg:Ni ratio (mol)	Estimated density without void (g/cm^3)	Molar fraction (%)	Relative weight (%)	Relative volume without void (%)
As-synthesized sample	(Mg,Ni)O	0.41981	66:34	4.67	100	100	100
Firstly reduced sample	(Mg,Ni)O	0.42108	98:2	3.65	67	53	68
	Ni metal	0.35253	-----	8.90	33	37	19
	Total	-----	-----	4.81	100	90	87

Fig. 5. (a) SEM image and energy dispersive X-ray spectrometry (EDX) mapping images of (b) nickel and (c) magnesium K-line for the fracture surface of the (Mg,Ni)O solid solution after the first reduction.

Fig. 6. Expansion and shrinkage behavior of the (Mg,Ni)O solid solution by redox treatment. The dotted line shows that the sample was reduced, and the solid line shows that it was oxidized. Point (a) shows that the sample was reduced for 30 h, point (b) shows that it was re-oxidized for 20 h, and point (c) shows it was reduced again for 220 h. The error bars show the standard deviation of three samples prepared in the same condition.

Fig. 7. X-ray diffraction (XRD) patterns of (Mg,Ni)O solid solutions using Cu K α radiation. Solid line (a) represents the re-oxidized sample, and dotted line (b) represents the sample reduced twice.

Fig. 8. Scanning electron micrographs (SEM) of fracture surfaces of (Mg,Ni)O solid solutions. Image (a) shows the re-oxidized sample, and image (b) shows the twice reduced sample.

estimated to be created outside the grains. Considering the segregation of nickel particles on the (Mg,Ni)O grains, it possibly cause the expansion by creating the space between the (Mg,Ni)O grains.

Next, the reduced (Mg,Ni)O solid solution was re-oxidized. The XRD profile shown in Fig. 7(a) for the sample after re-oxidation indicates that the sample consisted of a single phase of (Mg,Ni)O solid solution, and the phase of the re-oxidized sample was similar to that of the as-synthesized sample (Fig. 1(a)). The SEM microstructure of the sample shown in Fig. 8(a) reveals that the (Mg,Ni)O grains have a rough surface, and that the microstructure of the re-oxidized sample is different from that of the as-synthesized sample, as shown in Fig. 2(a). Point (b) in Fig. 6 indicates that the sample exhibited shrinkage up to approximately 1% (0.4% in linear) during re-oxidation. It is noted that the size at point (b) did not shrink up to the size of the as-synthesized sample before reduction and re-oxidation treatments. The shrinkage during re-oxidation of the reduced sample is considered to be caused by partial dissolution of the nickel particles into the (Mg,Ni)O grains or sintering of the (Mg,Ni)O grains. The apparent volume of the sample might not shrink to the as-synthesized sample size partly because of the rough surface of the re-oxidized grains. Further studies are necessary to elucidate the detailed mechanism.

To examine the influence of the second reduction on the structure of the re-oxidized (Mg,Ni)O solid solution, XRD and SEM measurements were performed for the treated sample. The XRD profile of the sample reduced twice, as shown in Fig. 7(b), indicates that the sample consisted of (Mg,Ni)O solid solution and nickel metal, and that the XRD peak profile in terms of both position and intensity was similar to that of the sample reduced only once, as shown in Fig. 1(b). It reveals no change in the phase between the sample reduced once and the one reduced twice. Although the XRD results were similar, the microstructures of the sample reduced twice, as shown in Fig. 8(b), differed from that of the sample reduced once (Fig. 2(b)). The sample reduced twice had more rough surface than that of the re-oxidized (Mg,Ni)O grains produced in the first reduction. The expansion of the sample reduced twice was measured to be approximately 9% (2.9% in linear), corresponding to an expansion of 11% (3.4% in linear) from the original size, as plotted at point (c) in Fig. 6. The degree of expansion of the sample reduced twice is much larger than that of the sample reduced once, as found by comparing points (a) and (c) in Fig. 6. This accelerated expansion for the sample reduced twice was assumed to result from the large change in the morphological microstructure of the sample. The change of microstructure is considered to cause an enlargement in the size of (Mg,Ni)O grains with an

apparent rough surface, resulting in an increase of the porosity in the sample.

4. Summary

(Mg,Ni)O solid solutions for steam reforming catalysts of SOFCs were prepared from calcinations of MgO and NiO mixtures (65:35 in mol) at 1500°C for 2 h in air, and the redox behaviors, including phase and volume change, were investigated. When (Mg,Ni)O solid solutions were reduced at 1000°C in a gas mixture of 4 vol% hydrogen and nitrogen, a volume expansion was observed. XRD and SEM/EDX results indicated that the expansion mechanism in the reduction process results from creation of space between (Mg,Ni)O grains possibly caused by segregation of nickel particles on (Mg,Ni)O grains. When the reduced (Mg,Ni)O solid solution was re-oxidized and then reduced again, it showed an accelerated volume expansion. The accelerated expansion for this sample was assumed to result from the increase of porosity in the microstructure of the sample.

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