Preparation of Oxygen Permeable Thin Films on YSZ Porous Substrates

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Mixed oxide-ion and electronic conductive thin films with the composition of (Ce$_{0.85}$Sm$_{0.15}$)O$_2$·15 vol%MnFe$_2$O$_4$ (CSO-MFO) were prepared on porous yttria stabilized zirconia substrates by a spin coating process, and their oxygen permeation flux densities were measured. The porous substrates were prepared from ZrO$_2$·3 mol%Y$_2$O$_3$ (3YSZ)-33 vol%carbon and NiFe$_2$O$_4$. 3YSZ porous substrates were obtained by 3YSZ-33 vol%carbon by sintering at 1350°C under Ar for 5 h and following oxidation at 800°C under air for 2 h. For 3YSZ-33 vol%NiFe$_2$O$_4$, the optimum condition was sintering at 1400°C under air for 5 h and following reduction at 800°C under H$_2$ for 2 h. A CSO-MFO film was prepared by a spin coating process on the substrate. The thickness of the CSO-MFO was approximately 150 nm. Oxygen flux density of the CSO-MFO sample was found to be $8.9 \times 10^{-8}$ mol·cm$^{-2}$·s$^{-1}$.  

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1. Introduction

The partial oxidation of methane by using oxygen permeable membrane is one of the promising techniques for hydrogen production.$^{1}$ The oxygen permeable membrane, which separates pure oxygen from air, plays an important role in this system. The characteristics required for the membrane is high oxygen flux density. (Ce$_{0.85}$Sm$_{0.15}$)O$_2$·15 vol%MnFe$_2$O$_4$ (CSO-MFO) is well-known oxygen permeable ceramics showing an oxygen flux density of $10^{-3}$ mol·cm$^{-2}$·s$^{-1}$ at 1000°C for the thickness of 200 μm.$^{2-6}$ To improve its oxygen flux at lower temperature, e.g. 700°C, preparation of thin film is expected. However mechanical properties and the oxygen flux density show trade-off relationship. To overcome this problem, porous substrates were prepared and thin films were deposited on the substrates. It has been reported that mixed conductive thin films can be produced on porous alumina.$^{7-10}$ Kakuta et al. reported a high oxygen flux density of $0.6 \times 10^{-6}$ mol·cm$^{-2}$·s$^{-1}$ at 800°C for a La-Sr-Co-Oxide (LSCF) thin film on a porous alumina substrate.$^{11}$ For the LSCF thin film, oxygen flux decreases gradually as time elapsed. This degradation was attributed to chemical reaction between the LSCF film and the alumina substrate. In addition, this asymmetric type of oxygen separation system often causes cracks between a thin film and a substrate. These cracks result from difference in thermal expansion coefficients and/or chemical reactions at the interface between thin film and substrate.$^{12,13}$

In this study, ZrO$_2$·3 mol%Y$_2$O$_3$ (3YSZ) was used to prepare porous substrates. This partial stabilized zirconia has good mechanical properties and a thermal expansion coefficient close to that of CSO-MFO. To form pores in the substrate, carbon and NiFe$_2$O$_4$ powders were adopted. After sintering, these secondary phases (carbon or NiFe$_2$O$_4$) can be removed by either oxidation or reduction process. The purpose of this study is to optimize preparation conditions of the 3YSZ porous substrate, to prepare a CSO-MFO thin film on the substrate, and to measure the oxygen flux density.

2. Experimental

3YSZ powder (TOSOH Co.) was ball-milled with carbon or NiFe$_2$O$_4$ powder. The secondary phase of NiFe$_2$O$_4$ was prepared by the Pechini method. The composition of mixture was either 3YSZ-33 vol%carbon (mean diameter 5 μm; Kojundo Chemical Laboratory Co., Ltd) or NiFe$_2$O$_4$. The powder mixture was pressed into disks with dimensions of approximately $20 \times 1\text{ mm}$, and sintered at temperature range from 1250 to 1500°C for 5 h under Ar or air. The secondly phase of carbon or NiFe$_2$O$_4$ was then removed by oxidation under air or by reduction under H$_2$, respectively.

Oxygen permeable thin film was deposited by using a spin coating process. To prepare the CSO-MFO precursor solution, Ce(NO$_3$)$_3$·6H$_2$O, Sm(NO$_3$)$_3$·6H$_2$O, Mn(NO$_3$)$_3$·6H$_2$O, Fe(NO$_3$)$_3$·9H$_2$O were dissolved into 2-methoxyethanol to be a concentration of 0.2, 1.0 and 2.5 M by using a stirrer. After Polish, the sequence of spin coating at 3000 and 6000rpm for 10 and 60 s, respectively, and pyrolysis at 400°C was conducted 2 to 10 times, and then the film was fired at 700°C for 5 min. These processes were repeated several times to increase the thickness of the film.

Microstructure was observed by using a scanning electron microscope (SEM). Oxygen permeability measurement was performed by using a quadrupole mass spectroscopy and a gas chromatograph. Gases supplied to permeation and feed sides were Ar-5% H$_2$ (200 sccm) and air (150 sccm), respectively.

3. Results and Discussion

The preparation conditions of porous substrates were firstly optimized for 3YSZ-33 vol%carbon and 3YSZ-33 vol%NiFe$_2$O$_4$. Figure 1 shows the weight change of 3YSZ-33 vol%carbon after sintering as a function of the sintering temperature, in which a broken line corresponds to a weight fraction of carbon in 3YSZ-33 vol%carbon. The sample weight decreased during sintering due to oxidation of carbon, even though samples were sintered in Ar atmosphere. The weight loss appeared to be significant at 1400°C or higher. The weight loss exceeding total weight of carbon at
1400 °C or higher suggests partial reduction of 3YSZ. Carbon removal during sintering has to be avoided for obtaining the high porosity substrate; the sample was sintered at 1350 °C for 5 h. To optimize oxidation temperature of carbon removal, then thermogravimetric analysis was performed. Figure 2 shows a thermogravimetry curve of 3YSZ-33 vol% carbon sintered at 1350 °C for 2 h. A broken line corresponds to a weight fraction of carbon in 3YSZ-33 vol% carbon sintered at 1350 °C. The oxidation appears to start at around 500 °C and finish at 700 °C; therefore, the carbon removal condition was set to 800 °C for 2 h. Figures 3 show SEM images of 3YSZ-33 vol% carbon (a) after sintering at 1350 °C under Ar for 5 h, and (b) after oxidation at 800 °C under air for 2 h.

For 3YSZ-33 vol% NiFe₂O₄, samples were firstly sintered at 1400 °C under air for 5 h. Thermogravimetric analysis was also performed for 3YSZ-33 vol% NiFe₂O₄ under H₂ as shown in Fig. 4. A broken line corresponds to a weight fraction of oxygen in 33 vol% NiFe₂O₄. As temperature increases, weight loss starts at around 600 °C. By holding the sample at 800 °C for 1 h or longer, NiFe₂O₄ was completely reduced. The weight loss of 8.19 mass% agrees well with the expected value of oxygen loss of 8.31 mass%. Therefore, the reduction condition was set to 800 °C under H₂ for 2 h. Figures 5 show SEM images of 3YSZ-33 vol% NiFe₂O₄ sample (a) after sintering at 1400 °C under air for 5 h and (b) after reduction at 800 °C under H₂ for 2 h. The well-sintered 3YSZ porous substrate was developed after reduction.

A CSO-MFO thin film was tried to prepare on the 3YSZ porous substrates. For the 3YSZ porous substrates prepared from 3YSZ-33 vol% carbon, to prevent the precursor solutions from soaking into the substrate, viscous 2.5 M solution was firstly coated 2 times at 6000 rpm for 60 s. Then 1.0 M solution was spin-coated on the substrate for 16 times, and finally 0.2 M solution was done for 38 times to homogenize the surface of the film. Regardless of these treatments, many clacks were observed for the thin film, presumably due to use of the first thick solution (2.5 M). As a result of these clacks, electrochemical oxygen permeation is hindered by mechanical leakage.
Because of the presence of many pores, it is difficult to prepare the thin film on the substrates by spin coating process. Therefore, for 3YSZ-33 vol%NiFe$_2$O$_4$ system, the thin film was firstly deposited on a dense sintered body before reduction. After preparation of the thin film, to make pores, the substrate side is exposed to reduction atmosphere during oxygen permeation test. The CSO-MFO thin film was deposited on 3YSZ-33 vol%NiFe$_2$O$_4$ disk sintered at 1400°C by repeating the coating process for 35 times using 0.2 M solution. The homogeneous thin film with a thickness of 150 nm was prepared on the surface as shown in Fig. 6(a). The oxygen flux density was measured at oxygen partial pressures difference between air with flow rate of 150 sccm (thin film side) and Ar-5% H$_2$ with flow rate of 200 sccm (substrate side). However, the oxygen flux density was limited to $8.9 \times 10^{-8}$ mol cm$^{-2}$ s$^{-1}$, which is approximately 100 times smaller than expected value. Figure 6(b) shows SEM micrograph of a cross section view of the thin film and substrate after an oxygen permeation test. Dense 3YSZ-NiFe$_2$O$_4$ layer with a thickness of approximately 10 μm remained. Even though this dense layer seems to be oxygen permeable, it presumably limits the oxygen flux. To increase the oxygen flux density, appropriate reduction conditions need to be determined.

4. Conclusions

(Ce$_{0.85}$Sm$_{0.15}$)O$_2$-15 vol%MnFe$_2$O$_4$ thin film was deposited on ZrO$_2$-3 mol%Y$_2$O$_3$ porous substrate by spin coating process and the oxygen flux density of this film was measured. 3YSZ porous substrates obtained from 3YSZ-33 vol%carbon showed a high porosity of 58% and sufficient gas permeability. 3YSZ porous substrates obtained from 3YSZ-33 vol%NiFe$_2$O$_4$ showed well-sintered microstructure. For porous substrates prepared from 3YSZ-33

Fig. 4 Thermogravimetric analysis of reduction of 3YSZ-33 vol%NiFe$_2$O$_4$ under H$_2$.

Fig. 5 SEM images for 3YSZ-33 vol%NiFe$_2$O$_4$ sintered at 1400°C under air for 5 h (a) before and (b) after reduction at 800°C under H$_2$ for 2 h.

Fig. 6 SEM images for (a) (Ce$_{0.85}$Sm$_{0.15}$)O$_2$-15 vol%MnFe$_2$O$_4$ oxygen permeable thin film on a 3YSZ-NFO substrate and (b) thin film side after reduction during oxygen permeation test.
vol%NiFe$_2$O$_4$, homogeneous thin film with a thickness of 150 nm was successfully fabricated. However, the oxygen flux density was limited to $8.9 \times 10^{-8}$ mol·cm$^{-2}$·s$^{-1}$. To improve oxygen permeation flux, optimization of reduction condition of the substrate is required.

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