PREPARATION OF YSZ FILMS ON AIR ELECTRODES
BY THE THERMAL SPRAY-SINTERING PROCESS

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ABSTRACT

Yttria-stabilized zirconia (YSZ) is widely used as an electrolyte in solid oxide fuel cells (SOFCs). In SOFC applications, YSZ film requires gas-tightness to separate air and fuel gas. Plasma-sprayed YSZ film showed poor gas-tightness due to many cracks. Sintering at 1550°C improved the gas-tightness of the film, but formed a La2Zr2O7 phase at the interface, due to a reaction between the YSZ film and the air electrode. The La2Zr2O7 phase increases interfacial resistance causing decreased performance. MnO2 coating prior to YSZ spraying suppressed La2Zr2O7 forming and densified the YSZ film. A sample pre-coated with 1 mg/cm² MnO2 became gas-tight after sintering at 1400°C with no La2Zr2O7 phase.

INTRODUCTION

Yttria-stabilized zirconia is widely used as an electrolyte in fuel cells. In fuel cell applications, the electrolyte film must be gas-tight to separate air and fuel gas and as thin as possible to reduce ohmic resistance. The objective of this work is the preparation of thin and gas-tight YSZ films on air electrodes. Various attempts have been made to develop thin electrolyte film using electrochemical vapor deposition (EVD)¹ RF sputtering², spray pyrolysis³, and thermal spraying⁴,⁵.

Thermal spraying has the advantages of easy masking for patterning and low cost. However, a thermal-sprayed YSZ film shows poor gas-tightness, due to many cracks. To improve the gas-tightness of the film, sintering above 1500°C is often required. However, high-temperature sintering decreases performance due to an increase in interfacial resistance and a decrease in the porosity of the air electrodes.

A MnO2 layer between the air electrode and the sprayed YSZ film can reduce the required sintering temperature. This paper describes the preparation and properties of
YSZ films on air electrodes using the thermal spray-sintering (TSS) process with an MnO₂ pre-coating.

EXPERIMENTAL

Commercially available 8 mol% YSZ powder and MnO₂ powder were used. The MnO₂ powder was plasma sprayed at 30 kw on porous air electrode substrates of lanthanum manganite, then the YSZ powder at 40 kw. 0 to 3mg/cm² of MnO₂ and approximately 100 μm of YSZ coated the air electrode substrates. The coated substrates were sintered from 1000 to 1550°C for 3 hours in air.

The microstructure of the two-layered samples having air electrode and YSZ film was investigated using a scanning electron microscope. N₂ gas permeability was measured at room temperature to evaluate the gas-tightness of the YSZ film. The electrical resistance and open circuit voltage (OCV) of the sample were measured at 1000°C in air on the air electrode side and in humidified H₂ on the electrolyte side. Platinum (Pt) paste was used as current collectors for both sides.

RESULTS AND DISCUSSION

Conventional TSS process

Figure 1 shows backscattered electron micrographs of polished cross sections. Many cracks appeared on the sprayed YSZ film as it quickly cooled. The spray-sintered YSZ film was dense with few voids and no open pores. Sintering at 1550°C eliminated the cracks and transformed them into isolated voids. However, high-temperature sintering decreased porosity of the air electrode and formed a La₂Zr₂O₇ phase, due to the reaction between the YSZ film and the air electrode. The lighter toned area at the interface between the YSZ film and the air electrode in Fig. 1(b) corresponds to the La₂Zr₂O₇ phase which increases interfacial resistance.

Figure 2 shows N₂ gas permeability of the two-layered samples having air electrode and YSZ film. N₂ gas permeability decreased with increased sintering temperature. The sample sintered at 1550°C showed a low N₂ gas permeability of 9 × 10⁻⁹ cm³/g-sec. This value satisfies the gas-tightness level required for SOFCs' electrolytes.

High-temperature sintering of the two-layered sample causes Mn diffusion from the air electrode to the YSZ film. It has been previously reported that Mn improves the sinterability of YSZ⁶. However, the Mn diffusion causes a Mn deficiency promoting La₂Zr₂O₇ forming at the interface.
The TSS process with MnO₂ pre-coating

We applied a MnO₂ pre-coating to prepare gas-tight YSZ films on air electrodes without La₂Zr₂O₇ forming.

Figure 3 shows N₂ gas permeability of the two-layered samples pre-coated with MnO₂ as a function of the sintering temperature. MnO₂ pre-coating densified the YSZ films. Thus, MnO₂ pre-coating can reduce the sintering temperature.

Figure 4 shows N₂ gas permeability of the two-layered samples as a function of MnO₂ weight. To achieve a N₂ gas permeability of under 1 × 10⁻⁸ cm³/g·sec., 1 and 3 mg/cm² MnO₂ pre-coating were needed at 1400 and 1370°C, respectively.

Figure 5 shows backscattered electron micrographs of polished cross sections of two-layered samples. There is no La₂Zr₂O₇ phase at the interface. MnO₂ pre-coating suppressed La₂Zr₂O₇ forming. The 1 mg/cm² MnO₂ pre-coated YSZ film densified at about 40 μm from the interface. However, excess MnO₂ remained at the interface as Mn₃O₄ phase for the 3 mg/cm² MnO₂ pre-coated sample. The darker toned area at the interface in Fig.5(b) was the Mn₃O₄ phase. The Mn₃O₄ phase decreases the three-phase boundaries where the electrode, electrolyte and gas contact. Electrochemical reactions mainly occur at the boundaries. Therefore, excess MnO₂ coating decreases performance of the two-layered sample. In our experiment, the optimum weight of the MnO₂ pre-coating was 1 mg/cm², sintered at 1400°C.

Table I shows the electrical resistance and OCV of the 1 mg/cm² MnO₂ pre-coated sample (φ 14mm) under SOFC operating conditions. The resistance was 130 mΩ·cm², which included the resistances of the YSZ film, the air electrode, the Pt current collectors, and their interfaces. This resistance value indicates that the adhesion of the YSZ film to the air electrode is good, and there is no secondary phase which increases interfacial resistance. The OCV was the same as the theoretical voltage calculated from the PO₂ difference between the air electrode side and the electrolyte side. This means that the YSZ film has sufficient gas-tightness to separate air and fuel gas, and the transference number of the YSZ film is close to one.

| MnO₂ pre-coating | Sintering temperature | YSZ thickness | Electrical resistance | OCV      | Theoretical voltage |
|------------------|-----------------------|---------------|-----------------------|----------|---------------------|
| 1 mg/cm²         | 1400°C × 3h           | 100 μm        | 130 mΩ·cm²            | 1050 mV  | 1060 mV             |

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CONCLUSIONS

We applied a MnO\textsubscript{2} coating prior to YSZ spraying to suppress La\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} forming. For a 1 mg/cm\textsuperscript{2} MnO\textsubscript{2} pre-coated sample, sintering at 1400°C sufficiently prepared the gas-tight YSZ film. The YSZ film densified at about 40 \(\mu\)m from the interface with no La\textsubscript{2}Zr\textsubscript{2}O\textsubscript{7} phase at the interface. This indicates that MnO\textsubscript{2} pre-coating compensates for the Mn deficit induced by Mn diffusion which improved the sinterability of the YSZ film.

The electrical resistance of the two-layered sample was 130 m\(\Omega\)·cm\textsuperscript{2}, which meant that the adhesion of the YSZ film to the air electrode is good with no high-resistance phase at the interface. The OCV of the two-layered sample under SOFC operating conditions was the same as the theoretical voltage calculated from the \(P_02\) difference between the air electrode side and the electrolyte side. This indicates that the YSZ film has sufficient gas-tightness to separate air and fuel gas, and the transference number of the YSZ film is close to one.

In conclusion, the two-layered sample prepared by the TSS process with an MnO\textsubscript{2} pre-coating has high performance which can be applied to the SOFC.

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Fig 1. Backscattered electron micrographs of polished cross sections of (a) sprayed (b) spray-sintered (1550°C × 3h) YSZ films on air electrode substrates.

Fig 5. Backscattered electron micrographs of polished cross sections of two-layered samples ((a)1mg/cm², (b)3mg/cm²) MnO₂ pre-sprayed (sintered at 1400°C × 3h)
Fig 2. \(N_2\) gas permeability of the two-layered samples as a function of sintering temperature.

Fig 3. \(N_2\) gas permeability of the two-layered samples pre-coated with MnO\(_2\) as a function of sintering temperature.
Fig 4. $N_2$ gas permeability of the two-layered samples as a function of $\text{MnO}_2$ weight.