PREPARATION OF SOLID ELECTROLYTE THIN FILMS FOR RELAXING THERMAL STRESSES

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ABSTRACT

Differences in the thermal expansion coefficients of solid electrolyte and metal materials largely affect the characteristics and durability of planar SOFC stacks. We developed a method to prepare YSZ thin films having folded structures to release the thermal stresses. Nickel foil substrates were corrugated by folding, and the YSZ thin films were deposited on the substrates by electron beam evaporation. Deposited YSZ thin films were annealed in air at 700°C for 1h. The thickness of the electrolytes is about 40μm. The tensile strength of the prepared electrolyte films on the substrates was measured. Measured strain of the sample is 1.68mm per 10cm. The strains of both YSZ and nickel at 1000°C are calculated from their thermal expansion coefficients. From the calculation, it is estimated that the thermal stresses can be released when the YSZ electrolyte is deformed over 0.7mm per 10cm.

INTRODUCTION

The research and development on planar SOFC have advanced rapidly in recent years because of its high power density and simple structure, as compared with tubular SOFC(1, 2, 3). However, many problems still remain to be solved. The difference in thermal expansion coefficients of solid oxide electrolyte and metal materials largely affects the characteristics and durability of planar SOFC stacks(4, 5). Some separator materials having the same thermal expansion coefficient of solid electrolyte have been proposed to solve this problem. In this paper, we present solid electrolyte thin films having a unique structure to release the thermal stresses. For this purpose, it is important that electrolyte thin films be elastic for in-plane directions. An example of the film structure is shown in Fig. 1. Cell is prepared in the planar area of this electrolyte film. It
is expected that the thermal stresses are relaxed at the wrinkles on the film.

In this paper, solid electrolyte thin films having a corrugated structure are fabricated. Film preparation conditions and the structure of the electrolyte films are discussed. Measurements of tensile strength and SEM observations of the electrolyte thin films are carried out.

EXPERIMENTAL

The preparation process of YSZ thin films is as follows. Thin 10μm thick nickel foil is used as substrates. The nickel foil was corrugated by folding. The substrates were placed about 10cm above the evaporation source and were heated in air at 700°C for 1h to form nickel oxide layer on the surface. Then YSZ thin films were deposited by vacuum evaporation using an electron beam heating device(6, 7). The evaporation source was prepared by sintering pellets consisting of Y₂O₃-8mol%ZrO₂ powder at 1100°C for 5h. YSZ films were deposited in a vacuum of 6 × 10⁻³ Pa at a substrate temperature of 700°C. About 40μm YSZ layer was deposited in 40 minutes. After the deposition of electrolyte film, the substrates were kept at 700°C and air was gradually introduced in the chamber so as to keep the substrate temperature constant. Through this process, the as-deposited electrolyte films were annealed and the anion defects remaining in the films were eliminated.

The tensile strengths of the prepared electrolyte films on the substrates were measured and the cross sectional views of the electrolyte films were observed by SEM. The nickel foil substrate was dissolved in 0.25M FeCl₃ aqueous solution for 30 hours and corrugated YSZ thin film was obtained.

RESULTS AND DISCUSSION

A corrugated nickel foil substrate is shown in Fig. 2. A fabrication machine with precision gears was assembled so as to produce equally spaced corrugated nickel foil during the experiment. In this fabrication machine, space of the precision gears can be adjusted closely using a micrometer.

A YSZ thin film deposited on a corrugated nickel foil substrate is shown in Fig. 3.
No cracks were observed in the tops or bottoms of the wave of the corrugated nickel foil substrate. Although the film was annealed in air at 700°C after the deposition, the surface of the YSZ thin film was smooth and uniform. This result indicates that the thermal stresses induced by the difference in thermal expansion coefficients of YSZ and nickel are reduced.

A corrugated YSZ thin film obtained by dissolving a nickel foil substrate is shown in Fig. 4. The YSZ thin film having the same form of the nickel substrate was obtained. No cracks were observed in the YSZ thin film and the surface was glossy, although nickel was dissolved. It was found that YSZ thin films were not damaged by the FeCl₃ aqueous solution (0.25M).

Figure 5 shows a cross-sectional microphotograph of a YSZ thin film and a corrugated nickel substrate. Before the experiment, it had been considered that the thickness of the deposited YSZ thin film would not be constant, that is, the thickness of the film would be thin at a top or slope and be thick at a bottom of the wave of the corrugated nickel foil substrate. However, from Fig. 5, the thickness of the film was almost constant on a whole corrugated nickel substrate.

The fine structure of the film is shown in Fig. 6. The interface of YSZ and nickel shows good contact. The figure shows the very dense structure of the YSZ film. No traces of cracks, voids or pin holes were found through the cross-sectional observation of the film.

The tensile strength of the YSZ thin film deposited on a corrugated nickel substrate was measured. Figure 7 shows the result. The sample length was 10mm, its width was 6mm, and its thickness was 40μm. A linear relationship between the tensile force and L/L₀ (L₀: initial length of the sample, L: measured length of the sample) was observed at tensions of over 5g. A crack was induced in the sample when the tension was 28g. The crack was generated at a corner of the YSZ thin film. The crack is shown in Fig. 8. The result indicates that tensile stresses are concentrated at a corner of the YSZ thin films. The thermal expansion coefficient of nickel is 17x10⁻⁶/K, and that of YSZ is 10x10⁻⁶/K. The thermal strains of both nickel and YSZ at 1000°C are calculated from these values for a planar cell with 10cm in diameter. From the calculation, the strain of nickel is 1.7mm, and that of YSZ is 1.0mm. The calculated difference between nickel and YSZ is 0.7mm. Consequently, thermal stresses can be released when the strain of YSZ is over 0.7mm at 1000°C. Fig. 7 shows that the YSZ thin film deposited on a corrugated nickel substrate can be expanded to 1.68mm per 10cm without cracking.
CONCLUSIONS

Through the preparation and measurement of corrugated solid oxide electrolyte thin films by electron beam evaporation, the following results were obtained. A corrugated YSZ thin film having the same shape as that of the substrate is obtained by evaporating electrolyte and by dissolving the nickel foil substrate. YSZ films were deposited on the whole surface of the corrugated nickel foil substrate homogeneously. When the films were stretched, stresses were concentrated at a corner of the YSZ thin films. The measured strain of the YSZ thin film deposited on a corrugated nickel substrate was enough to satisfy required value.

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Fig. 1 A scheme of a solid electrolyte thin film having a special structure to release in-plane stresses.

Fig. 2 Corrugated nickel foil substrate.
Fig. 3 A YSZ thin film deposited on a corrugated nickel foil substrate.

Fig. 4 The corrugated YSZ thin film obtained by dissolving the nickel foil substrate shown in Fig.3.
Fig. 5 Cross sectional view of a YSZ thin film deposited on the corrugated nickel foil substrate.

Fig. 6 Cross-sectional microphotograph of the electrolyte deposited on the corrugated nickel foil substrate.
Fig. 7 Tensile test of a YSZ thin film deposited on a corrugated nickel foil substrate.

Fig. 8 A crack in the YSZ thin film deposited on the corrugated nickel foil.