ADHESIVE CHARACTERISTICS BETWEEN ELECTROLYTE/ELECTRODE MEMBRANE AND SEPARATOR

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ABSTRACT

Adhesive characteristics between electrolyte/electrode membrane and separator were investigated. Residual stress caused by thermal expansion mismatch between electrolyte and separator is calculated by using finite element method. We obtained a good bonding cell with the combination of YSZ and separator which has the smallest calculated value of residual stress calculated by computer simulation. With the other combinations, residual stress caused the cracking of tri-layer membrane, or delamination between tri-layer membrane and separator. We also studied a method to detect the delamination using the acoustic microscopy technique. By using this technique, the cell with an insufficient bonding could be distinguished without destructive evaluation.

INTRODUCTION

Murata Mfg. Co. and Osaka Gas Co. have jointly developed Osaka Gas (OG) type SOFC. OG type SOFC is a new type of planar SOFC which has a structure suitable for stacking. The structure of OG type SOFC is shown in Figure 1. Each single cell is made by bonding two components, an anode/electrolyte/cathode membrane and a separator with ditched air flow channels on one side. The anode/electrolyte/cathode layer is made of sintered electrolyte layer on which the anode and the cathode are postfired using the screen-printing technique and the subsequent firing. Each cell is made independently so that the quality of each cell can be easily controlled. These single cells are sandwiched between nickel felts, which form fuel flow channels, and piled up. The nickel felts can release the thermal stress between cells. Each single cell is supported by ceramic materials acting as gas manifolds, so that each cell is supported against loading of the upper cells. As described above, the new Osaka Gas type planar SOFC is characterized
by easily stacking, good quality control capability, and good thermal cyclic characteristics. This new structure was established by Osaka Gas, and the development of single cell was cooperated with Murata. The materials used for the electrolyte and separator are YSZ (8 mol% Y$_2$O$_3$ stabilized ZrO$_2$) and Sr doped LaCrO$_3$. The surface area of each cell is 144 cm$^2$. The electrodes used are Ni/YSZ for the anode and (LaSr)MnO$_3$ for the cathode. The performance was evaluated by a 65–cell stack at 1000 °C. Figure 2 shows the I–V characteristics of this stack. The maximum power was 870 W using H$_2$ humidified by water at 30 °C and air. The stack was operated for 1000 h. A thermal cyclic characteristics were estimated using a 5–cell stack. The change of performance after a thermal cycle was scarcely observed (1).

On the development of single cells for the OG type SOFC, good bonding characteristics between electrolyte and separator are required. A mismatch of thermal expansion profiles between them causes stresses in the cell body during the cell stacking process with any sealing material, resulting in cell cracking and performance deterioration. The delamination between them is occurred when the stress at their interface exceeds their bonding strength.

In the case of stack construction using many single cells, the reliability of each cell is very important because the reliability of the stack is proportional to the products of reliability of individual cells. For quality control, the undestructive detection of cracking and delamination of each cell are essential.

The aim of the present study is to characterize the adherence of the membranes and the separators experimentally, by computer simulation as well as by an acoustic microscopy technique.

**EXPERIMENTAL**

Bonding between electrolyte/electrode membrane and separator

For electrolyte, 8 mol% Y$_2$O$_3$-doped ZrO$_2$ (YSZ) and 3 mol% Y$_2$O$_3$-doped ZrO$_2$ (TZP) were employed. Their thermal expansion coefficients (α) were 10.4 and 10.9, respectively. These membranes were 12 cm×12 cm and 300 μm thickness. For anode, NiO/YSZ mixed powder was prepared in the paste form, and screen-printed onto the electrolyte, followed by firing at 1400 °C. (LaSr)MnO$_3$ in the paste form was screen-printed onto it, and then fired at 1200 °C.

Two types of separators, A and B, were prepared. The thermal expansion coefficients are 10.1 and 10.5 respectively. They were ditched air channel on one side.

We tried to bond separators and electrolyte/electrode membranes with various combinations of them. The bonding temperature was 1100 °C. As adhesive agents, conductive ceramics was used at the air channel, and grassy material was used at edge of both sides.
Estimation of bonding strength

The bonding strength under shear or tensile stress is estimated. The shear strength was evaluated by JIS K6850 at room temperature. The tensile strengths at room temperature and an elevated temperature are evaluated by the methods illustrated in Figure 3.

Detection of cracking and delamination

The principle of the measurement is illustrated in Figure 4. The acoustic wave (20–25 MHz) transmitted from any piezoelectric crystal is reflected at the mismatched part of acoustic impedance such as ceramics/air interface mean there is no connection, i.e. delamination, so that a strong echo is introduced to a receiving piezoelectric crystal. As shown in Figure 4, echo from the bonding layer without connection (indicated A) is more intensive than that with sufficient connection (indicated B). The echo intensity is determined from the peak height shown on the CRT display.

Scanning of the cell is performed by moving the probe on x–y plane (C–mode Scanning Acoustic Microscope, C–SAM). Thus, delamination beneath tri–layered membrane can be detected.

Calculation of residual stress

We tried to calculate the residual stress by the finite element method. The result were calculated using their Young's modulus, Poisson's ratios, and thermal expansion coefficients. These values were evaluated using the ultrasonic pulse method (sing–around method, JIS R1602) and the dilatometer. In order to simplify the calculation, the Young's modulus and the Poisson' ratios at room temperature, and the average value of linear thermal expansion coefficients between room temperature and 1000 °C were used. The bonding is assumed to be completed at 1000 °C. The surface area of an electrolyte and a separator are 144 cm², and the thickness of them are 300 μm and 3 mm, respectively.

RESULTS AND DISCUSSION

Bonding between electrolyte/electrode membranes and separators

The results of bonding with various combinations were summarized in Table 1. When TZP is joined with separator A or B, no crack was formed in the membranes, but delamination occurred in the air channel with both combinations. With the combination of separator A and YSZ, YSZ could not withstand the stress. Only the cell with the combination of YSZ and the separator B had a good bonding without cracking and delamination.

Estimation of bonding strength

The typical results of bonding strength are shown in Table 2. Using the conductive ceramics at the air channel, the bonding shear strength was 1.18 MPa.
Using the glassy material at the edge of both sides, bonding shear strength was more than 20 MPa.

Simulation of residual stress

The result of computer simulation of stress distribution in electrolyte/separator interface is shown in Figure 5. In this figure, the deformation of single cell body is illustrated. The stress was calculated to be the largest at the edge of the membrane/separator interface. With the combination of YSZ and separator B, one can find that the residual stress is the smallest. The stress with the other combinations are more than twice as large as the stress with the combination YSZ and separator B.

If the tensile strength of electrolyte is smaller than the residual stress, it might be cracked before occurring delamination. On the otherhand, the bonding strength is smaller than the residual stress, delamination might occur between them.

With only the combination of YSZ and separator B, which residual stress is the smallest, good bonding between them was achieved. Since the calculation value of the residual stress occurring the interface between YSZ and separator B is smaller than the tensile strength of YSZ, the crack didn't occur. The bending strength of the YSZ membrane which we used is 267 MPa. As tensile strength is experientially about from 50 % to 70 % of bending strength, the tensile strength of YSZ is estimated about 133 MPa. With the combination of YSZ and separator B, the calculation residual stress value is about one-third as the tensile strength value, so that no cracks occurred. Furthermore, the stress with the other combination is compressive while the stress with the other combinations are tensile. For almost all ceramics, the compressive strength is larger than the tensile strength. That was another reason why YSZ membrane didn't crack. These results indicate that $\alpha$ of electrolyte should be the same as that of separator, or lightly smaller, for the optimal combination of the electrolyte and the separator.

The calculated value with the glassy material support is much higher than 1.18MPa, but the adherense between YSZ and separator B was very good, and no delamination was found. Thus, the bonding at the edge of both sides might prevent from delamination between them. At the air channel, the formation of microcrack in the bonding layer might reduce the stress caused by the thermal expansion mismatch between the electrolyte and the separator.

As shown here, the computer simulation of stress distribution using some thermomechanical properties is useful to estimate the bonding characteristics.

Detection of cracks and delamination

As shown in Figure 6, cracking and delamination were detected visually on x–y plane by C mode scanning (C–SAM) in the cell. Using this method, we can evaluate the bonding quality of cells easily without destruction.

We can eliminate the cells with insufficient adherence before stack them without destructive evaluation. It is very useful to control quality of SOFCs.
SUMMARY

In developing the OG type single cell, the following conclusions were obtained.

1) Two kinds of separators having different thermal expansion coefficients were applied to TZP and YSZ membranes. The experimental results were consistent with the computer simulation. When the residual stress calculated by the computer simulation was compressive, with the least stress among the combination mentioned above, good bonding was obtained.

2) The comparison of bonding strength at the edge and at the air channel position indicates that the bonding at the edge using glassy material prevents from the delamination between electrolytes and separators.

3) We applied the acoustic microscopy technique to detect cracks and delamination. This nondestructive technique is very useful for SOFC quality control.

REFERENCE

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Table. 1 The results of bonding between electrolyte/electrode membranes and separators

|        | separator A                     | separator B     |
|--------|---------------------------------|-----------------|
| TZP    | delamination                    | delamination    |
| YSZ    | delamination and crack formation| good bonding    |

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Table 2. Typical bonding strength between electrolytes and separators.

| Strength using the conductive ceramics bond / MPa |          |          |          |
|-------------------------------------------------|----------|----------|----------|
| Shear strength (25 °C) | Tensile strength (25 °C) | Tensile strength (1050 °C) |
| 1.2 | 0.3 | 0.5 |

| Strength using the glassy material / MPa |          |
|----------------------------------------|----------|
| Shear strength (25 °C)                 | > 20 |

OG type SOFC stack

Figure 1. Structure of OG type stack and single cell.
Figure 2. I–V/P characteristics of the 65-cell stack

Figure 3. Evaluation of bonding strength under tensile load;
(A) in measurement at 25°C, (B) measurement at 1050°C.
Figure 4. Principle of acoustic microscopy measurement.
Figure 5. Computer simulation of stress at electrolyte/separator interface.

Figure 6. Visual expression of intensity of acoustic echo from defects.