APPLICATION OF MICA GLASS-CERAMICS AS GAS-SEALING MATERIALS FOR SOFC

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ABSTRACT

Adaptability of mica glass-ceramics as gas-sealing material for SOFC's has been investigated. Thermal expansion coefficient, $\alpha = 9.5-12.0 \times 10^{-6}/^\circ C$, agreed with those of SOFC's constituent materials. Solid state electrolyte (8mol% yttria-stabilized zirconia, 8YSZ) and separator ($La_{0.8}Ca_{0.22}CrO_3$) joined with mica glass-ceramics in a temperature range of about 1000 to 1300$^\circ C$. No chemical reaction was observed at the interface between mica glass-ceramics and electrolyte. An interface between mica glass-ceramics and separator was formed due to chemical reactions. A single cell unit which was made up of a single cell and separators was manufactured for testing using this mica glass-ceramics.

INTRODUCTION

We have been researching and developing a separator self-supported planar SOFC stack with an internal gas-flow manifold. In this type SOFC stack, it is necessary to join the area identified in figure 1 for gas-tight sealing. The gas-sealing material must satisfy the following points:

- Strong gas-tight sealing at operation condition (in fuel and/or air, 1000$^\circ C$)
- Matching of thermal expansion behavior such as coefficient $\alpha$ with the SOFC constituent materials ($\alpha = 9.5-11.0 \times 10^{-6}/^\circ C$)
- Thermo- and chemical-stability with the SOFC constituent materials (to electrolyte (8YSZ) and separator ($La_{0.8}Ca_{0.22}CrO_3$))

In this study, we investigated mica glass-ceramics for possible application as a gas-sealing material for SOFC.

EXPERIMENTAL

Three kinds of mica glass-ceramics having thermal expansion coefficients near that of 8YSZ were selected from commercial products as shown in table 1. Their refractoriness and thermal expansion behavior were measured using a thermal mechanical...
analyzer(TMA) in the temperature range from room temperature to softening point(T_f).

Chemical stability and joining temperature of mica grass-ceramics to electrolyte (8YSZ) and separator((La_{0.8}Ca_{0.22})CrO_3) were examined in a temperature range from 1000 to 1300°C. Each test piece was cut in the size of 25×25mm in square and 0.5–5.0mm in thickness. They were stacked up and loaded at the top (about 10g/cm² in weight). Microstructure and reactivity at the interface were observed using electron probe microanalyzer(EPMA). To clarify reactions among the elements, the powder mixtures of mica glass–ceramics and 8YSZ or mica glass–ceramics and La_{0.8}Ca_{0.22}CrO_3 were pressed and heated at 1000°C. The reaction products were identified by powder X-ray diffraction(PXD) technique. All the experiments were performed in air.

RESULTS AND DISCUSSION

Mica glass–ceramics are machinable composite materials containing numerous micro–crystalline of mica (fluoro–phlogopite, KMg_3AlSi_3O_{11}F_2) in a SiO_2–B_2O_3–Al_2O_3–K_2O–MgO–F glass matrix. Figure 2 shows microstructures of these mica glass–ceramics. These microstructures are dependent on chemical composition and processing methods. Crystallines of sample A and B prepared by melting method are finely dispersed in the glass matrix and homogeneous in shape and size. The volume fractions of crystalline component are about 40–50% as listed in table 2. However the crystallines of sample C used with hot isostatic press(HIP) treatment are 5–10μm in length. This value is smaller than those of others. The volume fraction of crystalline component is about 70%, higher than those in others.

Figure 3 shows the thermal expansion curves of these mica glass–ceramics up to T_f. It appeared that samples A and B linearly expanded up to T_f in contrast to Pyrex–glass, while a small bending behavior at the glass transformation point(T_g) was observed at about 450°C for A and 640°C for B. The linearity of sample C was superior up to 900°C, but sudden elongation was observed in a temperature range between 900 and 1000°C. This elongation may be due to the high densification treatment by HIP method. The T_g and T_f corresponded to the volume fraction of mica crystalline component as listed in table 3. It is thought that the higher crystallization of mica changes chemical composition of residual glass matrix into greater heat–resistant property which arises from lower content of alkaline and alkaline–earth metals. Figure 4 shows the average linear thermal expansion coefficient of these samples(α_A, α_B, α_C). The α of all the samples was within ±10% of α of 8YSZ (α_{8YSZ}) below T_g and the α was located within 15% of α_{8YSZ} in all temperature range. The change of α_C above and below T_g was smaller than α_A and α_B. It is suggested that the thermal expansion behavior of mica glass–ceramics can be controlled to fit to that of 8YSZ by way of preparation control.

Table 4 shows the joining test results of these mica grass–ceramics with electrolyte(8YSZ) or separator(La_{0.8}Ca_{0.22}CrO_3) in a temperature range from 1000 to 1300°C.
Sample $A$ and $B$ with the higher residual glass matrix could join electrolyte and separator above 1000°C. Sample $C$ with the lowest residual glass matrix did not join with the electrolyte and separator up to 1200°C and severely reacted with separator above 1250°C. However, a trace of melting was found on the surface of sample $C$ even at 1000°C. These results suggest that the joining characteristic of mica glass–ceramics depends on the residual glass matrix.

Figure 5 shows microstructures of the joining interface between electrolyte (8YSZ) and mica glass–ceramics $A$ or $B$ which were joined at 1050°C for $A$ and 1150°C for $B$. At these temperatures, a small deformation was observed in appearance of each mica glass–ceramics. It showed that sample $A$ completely joined with electrolyte without cracks and any reaction products at the interface. A few traces of cohesive and elution of mica crystalline were observed at the sample $A$ side of interface about 10μm in thickness by EPMA method. It showed that sample $B$ also joined with electrolyte without crack, but formation of a glassy layer and two types of precipitates were observed at the sample $B$ side of interface. One type of precipitate with about 10μm in size condensed on surface of electrolyte and the other with 40–60μm in length was distributed in the glassy layer about 80μm in thickness. It was identified that both types of the precipitates were forsterite (Mg$_2$SiO$_4$) crystalline and fluorine content of the glassy layer was lower than that of sample $B$ by EPMA and PXD methods. It was thought that these differences of microstructure mainly depend on the difference of joining temperature because no mutual chemical diffusion was observed between 8YSZ and mica glass–ceramics (sample $A$ or $B$).

Figure 6 shows microstructures of joining interface between separator (La$_{0.8}$Ca$_{0.2}$CrO$_3$) and mica glass–ceramics $A$ and $B$ which were joined at 1050°C and 1150°C, respectively. Both samples completely joined with separator without cracks. In both cases, it was observed that a glassy layer was formed at mica glass–ceramics side of interface and a reaction product layer was formed at separator side of interface. The thickness of these reaction layer depended on the joining temperature. These thickness of glassy layer were respectively 20–45μm for sample $A$ and 40–80μm for sample $B$ and these of reaction product layer of sample $A$ and $B$ were 5–25μm and 20–40μm, respectively. In the glassy layer of sample $A$, there were small suspended bubbles and there were cohesive large bubbles and branch-like precipitates in the case of sample $B$. These bubbles and branch-like precipitates were almost the same chemical composition as that of mica crystalline. Figure 7 shows EPMA results for a cross section of interface between sample $B$ and separator. EPMA results of sample $A$ were similar to those of sample $B$. It was observed that La and Ca elements from the separator diffused into the glassy layer and Cr element condensed at the separator side of interface. It was also observed that Mg, Al and Si elements in the mica glass–ceramics diffused into the reaction product layer of the separator side of interface. This layer was chemically analyzed as a mixture of Mg(Cr,Al)$_2$O$_4$ and Ca$_2$La$_{0.8}$(SiO$_4$)$_2$O$_2$ by EPMA and PXD. These results suggested that the joining between mica glass–ceramics and separator was caused by the melting of residual glass matrix and chemical reactions between this silicate glass component and separator. The diffusion of La and Ca into the glass.
matrix is caused by the elution of mica crystalline and the formation of La and Ca rich glassy layer. A permeation of the glass matrix which may consist MgO–Al₂O₃–SiO₂ would form reaction product layers such as Mg(Cr,Al)₂O₄ and Ca₂La₈(SiO₄)₆O₂. It has been reported that chemical composition of grain boundaries is complex in non-stoichiometric lanthanum chromites used for separator. It is expected that this permeation of silicate glass might be accelerated through Ca rich grain boundaries.

Figure 8 shows construction of a single cell unit manufactured for testing using mica glass–ceramics. Its dimension is 16×16cm and 100cm² (10×10cm) in effective generation area. The single cell unit consists of two separators (La₀.₈Ca₀.₂₂CrO₃) and a single cell which is made up of an electrolyte (8YSZ), an air electrode (La₀.₈Sr₀.₂MnO₃) and a fuel electrode (Ni/8YSZ cermet). These components are joined with sample B at 1150°C for 3 hours. Figure 9 shows an external view of single cell unit. There was no cracks and no leakage of fuel gas. The open circuit voltage (OCV) of this single cell unit was 0.95V at 1000°C.

CONCLUSION

Application of mica glass–ceramics as a gas–sealing material for SOFC has been investigated. Thermal expansion behavior and refractoriness were roughly suitable for SOFC constituent materials and these properties are expected to be controllable within a limited range. The mica glass–ceramics joined electrolyte with separator above operation temperature of SOFC. The mica glass–ceramics are chemically stable to electrolyte. However the mica glass–ceramics reacted with separator. Further improvement is necessary in order to adopt mica glass–ceramics as the gas–sealing material for SOFC.

REFERENCE

1. N. Sakai, T. Kawada, H. Yokokawa, M. Dokiya and I. Kojima, J. Am. Ceram. Soc., 76[3], 609(1993).
Table 1. Mica glass–ceramics selected in this experiment

|                  | sample A            | sample B           | sample C            |
|------------------|---------------------|--------------------|---------------------|
| Production       | Macor\(^1\)         | Photoveel\(^2\)    | Macerite\(^3\)      |
| Density (g/cm\(^3\) at 4°C) | 2.52                | 2.59               | 2.67                |
| Thermal Expansion Coefficient (×10\(^{-6}\)/°C) | 9.4(400°C)           | 8.5(400°C)         | 9.6(400°C)          |
|                  | 12.3(800°C)         | 10.5(800°C)        | 9.4(600°C)          |
| Refractoriness (°C) | 1000                | 1000               | 700                 |
| Preparation      | melting method      | melting method     | melting method      |
|                  | 8YSZ addition       | HIP treatment      |                     |

1) Corning Glass Work Co., Ltd.
2) Sumitomo Photon Ceramics Co., Ltd.
3) Mitsui Mining Material Co., Ltd.

Table 2. Feature of mica crystalline in mica glass–ceramics

|                  | Volume fraction of mica crystalline (%) | Shape   | a  | Size(μm) | b  | c  |
|------------------|----------------------------------------|---------|----|----------|----|----|
|                  |                                        |         |    |          |    |    |
| sample A         | 40.3                                   | needle–like | 14.6–20.0 | 1.7–2.3 | 0.5–0.9 |
|                  |                                        |         | (16.9) | (1.9)   | (0.7) |
| sample B         | 47.0                                   | rod–like | 7.4–13.7 | 1.4–3.7 | 0.5–1.0 |
|                  |                                        |         | (10.0) | (2.4)   | (0.6) |
| sample C         | 70.0                                   | rod–like | 4.9–10.9 | 1.0–2.3 | 0.5–0.9 |
|                  |                                        |         | (7.6)  | (1.8)   | (0.6) |

* The average value shown in parentheses.
Figure 2  Microstructures of mica glass–ceramics (SEM)

Figure 3  Temperature dependence of thermal expansion curves of mica glass–ceramics
Figure 4  Average linear thermal expansion coefficient of mica glass–ceramics

Table 3. Thermal expansion behavior of mica glass–ceramics

|                      | sample A | sample B | sample C |
|----------------------|----------|----------|----------|
| Grass transformation | 450      | 643      | 650      |
| temperature (°C)     |          |          |          |
| Softening temperature| 979      | 1048     | 1212     |
| Average linear thermal expansion coefficient/°C |          |          |          |
| 400°C                | 8.36     | 8.29     | 10.13    |
| 600°C                | 11.20    | 8.28     | 10.14    |
| 800°C                | 12.60    | 11.41    | 11.15    |
| 1000°C               | 11.76    | 11.96    | 17.50    |

Table 4. Results of joining test of mica glass–ceramics

| Temperature (°C) | 1000 | 1050 | 1100 | 1150 | 1200 | 1250 | 1300 |
|------------------|------|------|------|------|------|------|------|
| sample A         |      |      |      |      |      |      |      |
| Electrolyte      | J    | D    | D    | RM   |      |      |      |
| Separator        | J    | D    | D    | RM   |      |      |      |
| sample B         |      |      |      |      |      |      |      |
| Electrolyte      | J    | J    | J    | D    | RM   |      |      |
| Separator        | J    | J    | J    | D    | RM   |      |      |
| sample C         |      |      |      |      |      |      |      |
| Electrolyte      | N    | N    | N    | N    | N    | J    | D    |
| Separator        | N    | N    | N    | J    | J    | J    | RM   |

J : joined with no deformation in appearance
D : joined with deformation in appearance
RM : observed serious reaction or melting
N : not joined
Figure 5  Microstructures at the interface between electrolyte(8YSZ) and mica glass–ceramics

Figure 6  Microstructures at the interface between mica glass–ceramics and separator($La_{0.6}Ca_{0.22}CrO_3$)
Figure 7 Results of EPMA method of the interface between sample B and separator (La$_{0.8}$Ca$_{0.22}$CrO$_3$)
Figure 8  Schematic representation of the single cell unit using sample B as gas-sealing material

Figure 9  External view of single cell unit manufactured for testing in this investigation