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Short communication

Non-alkaline glass–MgO composites for SOFC sealant

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ABSTRACT

In this study, glass–ceramic composites as sealing materials for solid oxide fuel cells (SOFCs) were investigated. A commercially available magnesium boro-silicate glass with soften temperature of about 700 °C, and MgO powder were used for the composites in order to control and improve the thermal property as the sealing materials for low temperature SOFC. MgO was added 0–30 vol% into the glass matrix to prepare the glass–ceramic composites and the properties of each composite was investigated. An increase of the coefficient of thermal expansion (CTE) for the glass–ceramic composites and an improvement of thermal stability were observed as the amount of the MgO additive increased, while the electrical and sealing performances were degraded. As a result, the composite with 10 vol% MgO additive was shown to have high thermal stability with reasonable sealing performance.

1. Introduction

Recently, various environmental issues related to power generation systems are paid attention and the demand for the development of high performance, environmental friendly power systems with high energy efficiency gradually increased. A fuel cell generates electricity directly from chemical reactions between fuel and oxidant, and therefore it is considered to be one of candidates for such systems.

Up to today, several types of fuel cells are investigated and among them, solid oxide fuel cells (SOFCs) which typically operated at high temperature around 800–1000 °C, are considered to be most attractive fuel cell due to high fuel flexibility [1–3]. SOFCs consist of a solid oxide electrolyte with high ionic conductivity, and ceramic or cermet type electrodes, and only a few materials can be applied for SOFC components (inter-connector, sealant) due to such high operating temperatures. In order to increase the variety of choice of materials for SOFC components such as inter-connector, gas manifold and gas seal, many studies focus on lowering operating temperature of SOFCs under 650 °C [4]. Recent studies reported the improvement of SOFC performance under 600 °C [5], which opens the possibility of utilizing glass materials for gas sealant, and metals or alloy materials for gas manifold, separator, or inter-connector.

When the materials used for SOFC components were selected, it is important to grasp the coefficient of thermal expansion (CTE) for each component. For example, the CTE of typical cathode material, $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF6428) is reported about $15.3 \times 10^{-6}\,K^{-1}$ [6]. Metallic alloys, possible inter-connect materials, for examples, SUS430, Crofer 22 APU [7] and ZMG232L [8], have CTE of 10×10^{-6}, 12.2×10^{-6} and $11 \times 10^{-6}\,K^{-1}$, respectively, which recently have been investigated as SOFC components [7,8]. When a glass material, which typically has the CTE of about $10 \times 10^{-6}\,K^{-1}$, is used as sealing component between cathode and inter-connect (metallic alloy), such glass material is expected to relax the stress caused by the difference in the CTE of the cathode and the metallic alloy. Thus, the selection of the glass material needs to be well considered.

Nielsen et al. reported that the CTE of glasses could be controlled by adding MgO into glasses [9]. They used aluminum silicate type glass including sodium, and matched to the values of the CTE of some metallic alloys by adding MgO from 5 to 30 vol%. They also showed a tendency to increase pore around MgO particles in the glass as the amount of MgO increased.

Another important factor for choosing glass materials is reactivity with other components; alkaline boro-silicate glasses were conventional glass materials for SOFCs, however, Ogasawara et al. reported that sodium and typical alkaline metal were reactive with stainless metal alloy including chromium [10], which increased fragility of the metal alloy. Therefore, other types of glasses without alkaline metals have been searched for SOFC application [11–13].

In this paper, we fabricated glass–ceramic composites of non-alkaline glass materials and MgO in order to control the CTE as well as the shrinkage behavior of the composites by changing the amount the MgO additive. We selected commercially available magnesium boro-silicate (non-alkaline glass, CTE: 10×10^{-6})

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Table 1
Properties of the MBS glass used in this study

Glass name	MBS glass (AGC Co. Ltd.)
Soften temperature (°C)	~700
CTE (10^{-6} K^{-1})	~10
Main components	MgO, SiO_2, B_2O_3

and MgO powder as a matrix glass and an additive for the composites, respectively. Fabrication process, characterization of the glass–ceramic composites will be discussed by using the results of scanning electron microscope and X-ray diffraction analysis, thermal expansion, electrical resistibility and gas leak tests, to estimate the performance of the composite glasses as sealing, as well as insulating materials.

2. Experimental

2.1. Preparation of glass composites

Commercially available magnesium boro-silicate glass (MBS glass: AGC Co. Ltd.) and MgO powder (purity 99.8%, Ube Material Co. Ltd.) was chosen for the fabrication of the glass–ceramic composites. Physical properties of the MBS glass was described in Table 1. Using the glass and MgO powders, the composite glasses were prepared using following manner in the pellet and sheet forms.

2.1.1. Composite pellet

The MBS glass powder and 0–25 vol% of the MgO powder were mixed in a mortar and pressed using mono-axis and cold isostatic press into green pellets (2 ton cm^{-2}), shape of 2 mm thick and 20 mm in diameter. These pellets were used for the thermal expansion analysis.

2.1.2. Composite sheet

After mixing of the MBS glass and 0–30 vol% of the MgO powder, ethanol, toluene, Poly-(vinyl butyral) resin and dispersant (amine family) were added to prepare a slurry. This slurry cast on PET film to form sheet with 0.4 mm thick. After these green sheets were cut into 20 mm × 20 mm form, these samples were annealed at 700 °C in air for 2 h at the heating rate of 4 °C min^{-1}. The thickness of annealed samples was about 0.3 mm.

2.2. Thermal expansion measurement

For the measurement of the thermal property for various glass composites, the annealed pellets were cut into rod form (Ø 3 mm × 12 mm). Thermal expansion measurement was conducted using RIGAKU TMA 8310 from 50 to 650 °C in air at the heating ratio of 4 °C min^{-1}, and then the coefficient of thermal expansion for each specimen was calculated. In addition, each specimen was kept at 650 °C for 10 min in order to observe the deformation of the sample.

2.3. Electrical measurement

Electrical resistances of the glass composite sheets were measured using a DC supplier (ADVANTEST) and a digital multi-meter (R6234 KEITHLEY 2700). Pt paste was printed on both side of each sheet (10 mm × 10 mm) to attach Ag wire and Ag mesh for current collector, and annealed at 700 °C. The resistances of these samples were measured using 2-probe method from 400 to 700 °C in air.

2.4. Gas seal test

Gas seal test of the samples were conducted using a helium leak detector M-212LD (Canon Anelva Tech. Co. Ltd.) at room temperature. Detailed information of the device can be found on the web site (http://www.canon-anelvatx.co.jp/english/products/leek/M-212LD.html.) This device measures the helium gas pressure in the chamber with a pinhole on which a specimen is placed. The leak test was conducted by applying He gas to the specimen from outside chamber. If there is a leak from the sample, helium gas can penetrate inside the chamber through the sample and can observe a change in the helium gas pressure inside the chamber. Measurement range of helium gas leak rate was from 10^{-12} to 10^{-3} Pa m^3 s^{-1}. After the pressure inside the chamber became steady, helium gas was applied to the sample about 30–40 s.

3. Result and discussion

3.1. Microstructure of the glass composites

Fig. 1 shows fracture section SEM images of various composite samples annealed at 700 °C with the MgO additive of (a) 10 vol%, (b) 10 vol% (back scattered (BS) image), (c) 20 vol%, (d) 20 vol% (BS image), (e) 30 vol% (BS image), respectively. As can been seen, dense

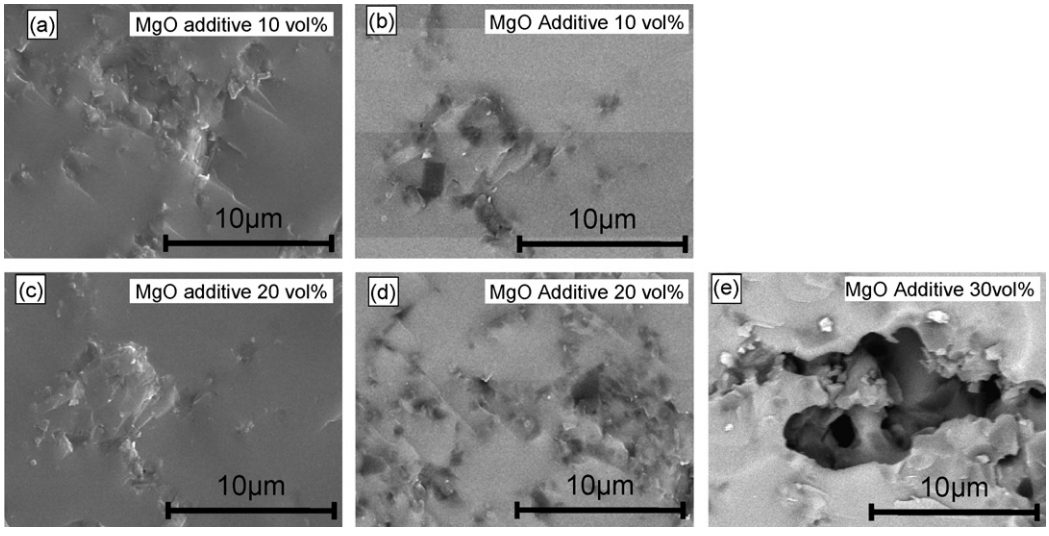

Fig. 1. Microstructures of cross-section of the MgO and MBS glass composites heat treated at 700 °C; the MgO additive of (a) 10 vol%, (b) 10 vol% (back scattered (BS) image), (c) 20 vol%, (d) 20 vol% (BS), (e) 30 vol% (BS).

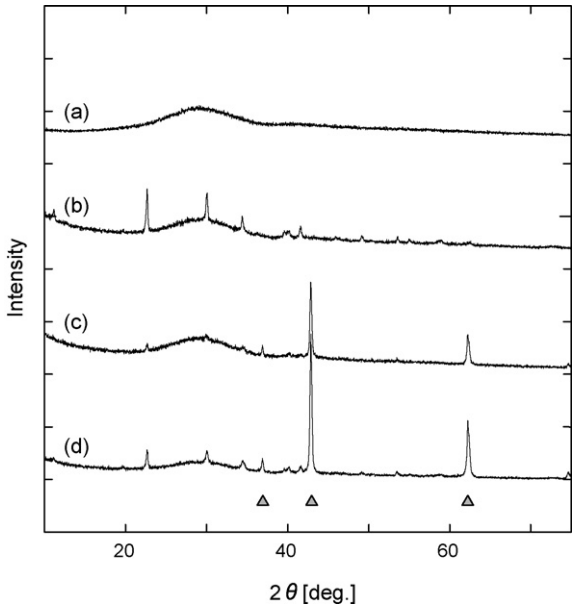

Fig. 2. XRD patterns of the MBS glass, and the glass–ceramic composites with various amount of the MgO additive (a) MBS glass (no heat treatment), (b) MBS glass (700 °C for 2 h), (c) composite with 10 vol% MgO additive (700 °C for 2 h) and (d) composite with 25 vol% MgO additive (heat treated at 700 °C for 2 h). (▲) MgO corresponding to periclase-type MgO.

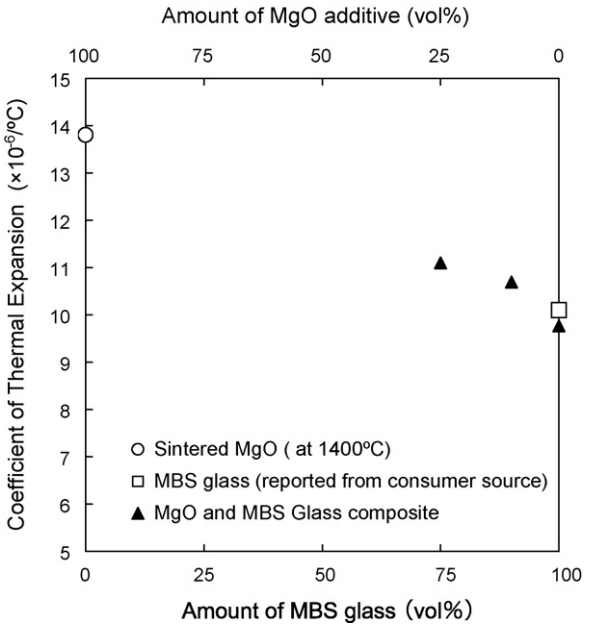

Fig. 3. Variation of thermal expansion behavior as a function of amount of the MgO additive in the composites.

structure was observed for the composites with 10 and 20 vol% MgO additive, without any obvious pores. On the other hand, a lot of open pores were observed for the composite with 30 vol% MgO additive, which simply showed the limitation of MgO addition in the glass.

Results of XRD measurement for various MBS glass and MgO composites were shown in Fig. 2. Unknown peaks were observed for the annealed MBS glass in Fig. 2(b), which was considered to be derived from partial crystallization of glass components. It is, however, almost all of the peaks were weak and broad, and the structure showed similar to amorphous from the SEM observation. For the composite samples as shown in Fig. 2(c) and (d), some peaks derived from the MgO and MBS glass were observed, but no peaks were resulted from reactions between MgO and MBS glass. Thus, MgO can be used as an additive in the MBS glass without undesirable reactions.

3.2. Thermal expansion analysis

Fig. 3 shows the coefficient of thermal expansion as a function of amount of the MgO additive. As can be seen, the CTE increased almost linearly as the amount of the MgO additive increased, and indicated that the CTE could be controlled by changing the composition of the glass and MgO. Only the addition of the MgO additive is limited to 20 vol% for the use of the glass–ceramic composites as sealing components.

Fig. 4 shows the thermal expansion behavior of various specimens obtained at the heating ratio of 4 °C min^{-1} up to 650 °C and held for 10 min. During in the constant temperature of 650 °C, only the 100% glass specimen showed a change as shown in Fig. 4, which is correlated to the deformation of the specimen. On the other hand, the glass–ceramic composites showed almost no changes in the expansion, which shows high structural stability with the change of the time. The thermal behavior of 100% glass specimen is due to its fluidity, typical for glass materials. Composite specimens included the MgO additive showed almost no changes and thus, it was thought that MgO particles in glass matrix acted as obstacles to prevent the deformation of the specimens. This property seems more attractive for the SOFC application, when it comes to the long term stability of the sealing materials.

3.3. Electrical resistance

Fig. 5 shows the specific resistance of various composite samples with the MgO additive of 10–30 vol% as a function of temperature. All samples showed the resistively above 1 MΩ cm at the temperature range between 400 and 700 °C. The glass composite with 10 vol% MgO additive showed that constant specific resistance over 100 MΩ cm, independent of the temperature. As the amount of the MgO additive increased, it showed that the specific resistance decreased at higher temperature range. Although the specific resistance of some glass composites decreased at the temperature range between 500 and 700 °C, the values were still attractive to use these composites for SOFC application [14].

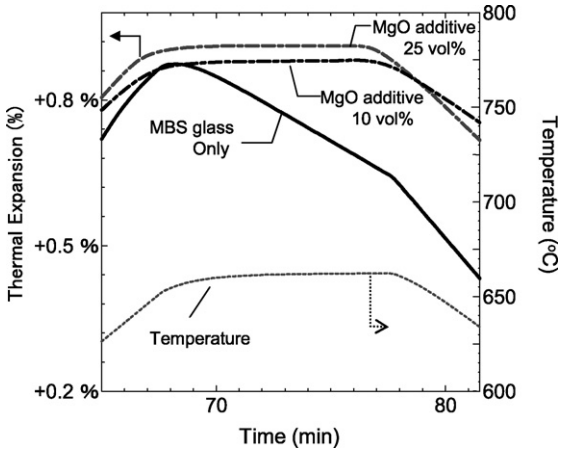

Fig. 4. Thermal expansion behavior of the MgO and MBS glass composites at about 650 °C. Solid line, MBS glass only (no MgO); dot-2-dashed line, composite with 10 vol% MgO additive; dot-dashed line, composite with 25 vol% MgO additive; doted line, transition of the temperature (right axis).

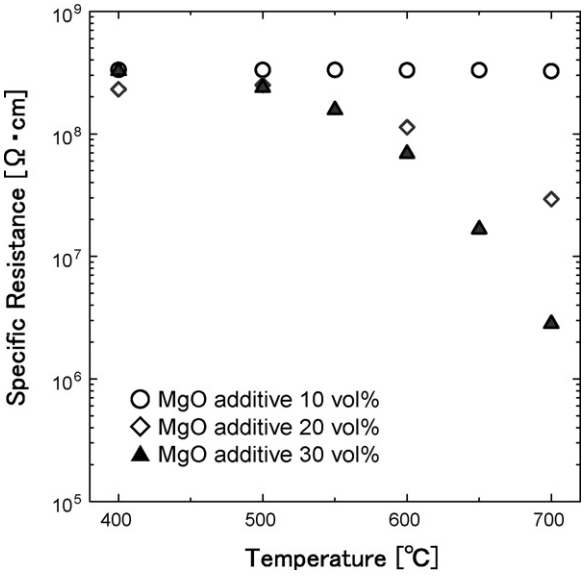

Fig. 5. Temperature dependence of the specific resistance of various composites in air from 400 to 700 °C.

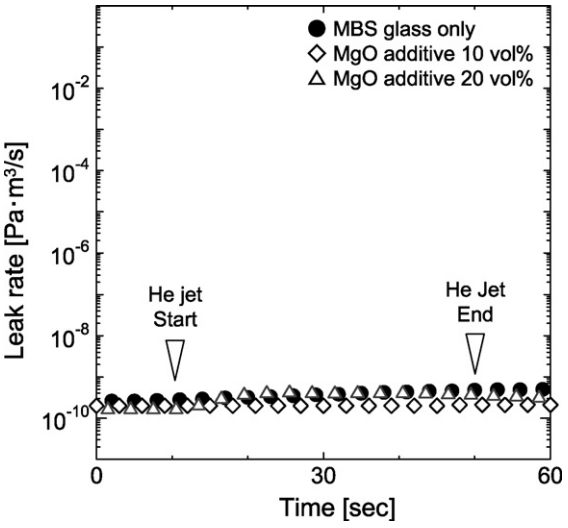

Fig. 6. Results of the helium leak test for various glass–ceramic composites.

3.4. Investigation of sealing property

Fig. 6 shows the result of helium gas leakage test for the glass–ceramic composites with different amount of the MgO additive. As can be seen, the leak rates of all samples were in the range of 10^{-9} to 10^{-10} Pa m s^{-1}, which can be considered almost no gas leakage. Also, slight improvement of the sealing property for the composite with 10 vol% MgO additive was observed. Therefore, the glass–ceramic composites can be used as sealing components for low temperature SOFC application less than 650 °C. Currently, the examination of sealing property of these composites were undergoing at the actual SOFC conditions.

4. Conclusion

This study showed that the MgO additive in the glass matrix could improve physical properties of the composites and the summary of this study were following:

1. Microstructures of these composites were influenced by the amount of the MgO additive. In the case of the composites with 10–20 vol% MgO additive, dense structure was observed, however, a lot of large pores were observed in the composite with 30 vol% MgO additive. According to X-ray diffraction analysis, no obvious reactions between MgO and the glass matrix were observed, which suggested that the glass–ceramic composites may have reasonable chemical stability for practical application.
2. Thermal expansion test showed that the MgO additive improved the thermal stability of the composites. And the CTE of the glass composites increased from 10 to 11 ($\times 10^{-6}$ K^{-1}) as the amount of the MgO additive increased from 0 to 25 vol%.
3. While an increase of the CTE and an improvement of the thermal stability for the composites were confirmed as the amount of the MgO additive increased, the electrical property and sealing performance were degraded. As a result, the composite with 10 vol% MgO additive was shown to have high thermal stability with reasonable sealing and electrical performances.

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