

## Development of composite seals derived from ceramic precursors for SOFC systems

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Novel ceramic-metal composite seals derived from ceramic precursor polymers were developed in this study. The formation, microstructure and properties of composite seals were evaluated. Polymethylsiloxane was chosen as a ceramic precursor. In addition, metal and ceramic filler were mixed and pyrolyzed at 750 °C to fabricate composites. The specimen mixed with ZrO<sub>2</sub> and Ni as filler showed a thermal expansion coefficient of  $10.5 \times 10^{-6}/^{\circ}\text{C}$  and sealing efficient of > 98%. The microstructure of seals was observed by using Scanning Electron Microscopy (SEM). And the mechanical properties of composite seals were measured and discussed.

**Key words:** Polymer derived ceramic, SOFC, Seals, Metal-ceramic composites.

### Introduction

Solid oxide fuel cells (SOFCs) based on an oxide ion-conducting electrolyte have proven to be an environmentally friendly power generation system with high efficiency and fuel flexibility [1-2]. However, SOFCs need effective, high temperature seals to prevent fuel leakage and high temperature mixing of reduction and oxidation gas for commercialization. The seal for SOFC devices must satisfy the following stringent requirements [3-5]. The seal should be too tight to allow gas leakage and be chemically stable in both oxidation and reduction atmospheres at operating temperature. In addition, the coefficient of thermal expansion of the seal must be comparable to that of other constituents of fuel cells to avoid stresses due to a thermal expansion mismatch with other constituents, such as the metal interconnector. Many glass-based materials - such as glass, glass-ceramic, and compressive seals - have been reported previously [6-7]. However the seals in such materials have not satisfied all the demands for SOFC systems.

Recently, polymer derived ceramic composites have received attention due to their potential applications to various plastic shaping technologies and their low manufacturing temperature. Tailored ceramic composites with low shrinkage and porosity can be made by varying preceramic polymers, filling materials, and synthesis conditions. It was demonstrated that a non-oxide seal material derived from polymer precursors with appropriate filler could be used to make a reliable seal for solid oxide fuel cells [8-9].

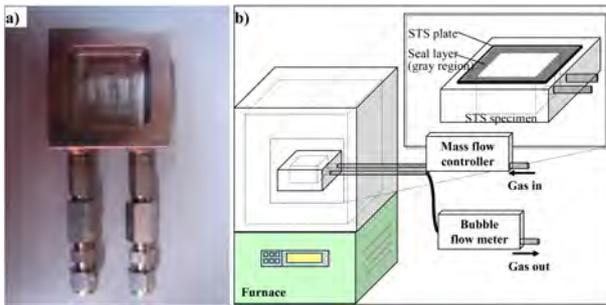
In a former work, a new method to fabricate seals had been proposed by using polymethylsiloxane and metal-ceramic composite filler to control the coefficient of thermal expansion. [10] AlCo was used as filler and showed an appropriate coefficient of thermal expansion and a stable sealing property. But AlCo reacts with Ni at a fuel cell operating temperature of 750 °C as shown in fig. 2. Ni was partially substituted to a Co site in an AlCo alloy to form (Ni,Co)<sub>3</sub>Al<sub>4</sub>. This leads to the possibility of a seal-electrode reaction, which leads to a lowered fuel cell performance.

Therefore in this work, AlCo was replaced with Ni and metal-ceramic composite filler was used to retain a chemical stability at fuel cell operating temperature. Table 1 shows the composition of a metal-ceramic composite seal. The microstructure formations, sealing characteristics, and thermal expansion behavior of the novel ceramic materials derived from the polymers, particularly the effect of the B<sub>2</sub>O<sub>3</sub> content, were investigated.

### Experimental

Polymethylsiloxane (MK, Wacker, Germany) with an average molecular weight of 9,400 g/mol was chosen as the polymeric precursor because of its high ceramic conversion rate and low ceramic conversion temperature. Furthermore, metals that have high coefficients of thermal expansion, like AlCo, and Ni, and ceramic that was chemically stable both in oxidation and reduction atmospheres, like ZrO<sub>2</sub>, were used together as a metal-ceramic composite filler; and B<sub>2</sub>O<sub>3</sub> was added as a supplement to form the liquid phase that contributed to bonding and densification. Table 1 shows the composition. The polymer/composite filler mixture was prepared by ball milling for 12 hours with methyl alcohol and dried. The versatility of various plastic shaping technologies

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**Fig. 1.** (a) Sealing test specimen and (b) schematic diagram of sealing efficiency test.

**Table 1.** Composition of metal-ceramic composite seal.

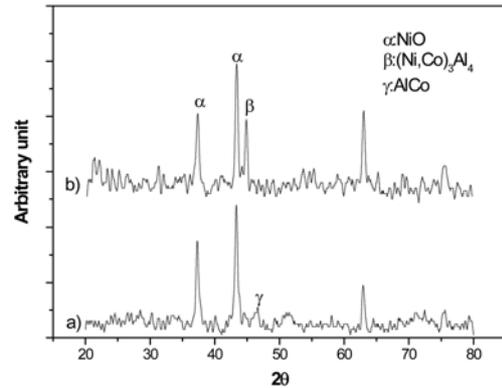
name	composition	B <sub>2</sub> O <sub>3</sub> (Vol %)
MNZ342	MK 33.3 vol% + Ni 44.4 vol% + ZrO <sub>2</sub> 22.2 vol%	16
MNZ111	MK 33.3 vol% + Ni 33.3 vol% + ZrO <sub>2</sub> 33.3 vol%	16
MNZ326	MK 27.3 vol% + Ni 18.2 vol% + ZrO <sub>2</sub> 54.5 vol%	16

for polymers can be used for shaping. The polymer-filler mixture powder was molded with an axial pressure of 30 MPa at 200 °C for 60 minutes in a metal die with a diameter of 20 mm. Pyrolysis was carried out at 750 °C in N<sub>2</sub> and air atmospheres. The density and open porosity of the specimens were measured using the Archimedes method. The level of thermal expansion of the specimen was examined using a thermomechanical analyzer (Rigaku Model Tas 100, Japan). The microstructure was observed by using Scanning Electron Microscopy.

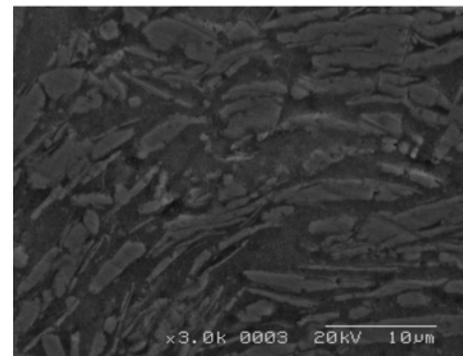
For the sealing test, specimens were made of STS (stainless steel), and then polymer/filler paste that was molted in isopropyl alcohol was pasted on the specimen and dried at room temperature for 24 hours. The specimen was heated at 750 °C. Then, the heat treated specimen was placed in a box furnace and heated at 750 °C. N<sub>2</sub> gas, which was controlled by a MFC (Mass Flow Controller), was flowed into the specimen and the gas that flowed out of the specimen was measured by a digital bubble flowmeter. The sealing efficiency was calculated by the ratio of the gas that flowed in to the gas that flowed out. Fig. 1 shows the specimen for the sealing test and the schematic diagram of the system for the sealing test.

## Result and Discussion

Fig. 3 shows the microstructure of a MNZ342 specimen observed by using SEM. The bright region is Ni and the dark region is a ceramic phase composed of ZrO<sub>2</sub> and a SiO<sub>2</sub> glass phase derived from polymer. Dense microstructures composed of metal and metal surrounding ceramic could be obtained because polymers melt and infiltrate through pore channels of filler during heat treatment; then, the polymers convert to ceramic by



**Fig. 2.** XRD result of a) before heat-treatment and b) after heat-treatment of NiO-AlCo mixture powder.



**Fig. 3.** Micro image of MNZ342 specimen.

**Table 2.** Properties of MNZ series specimens sintered in air atmosphere.

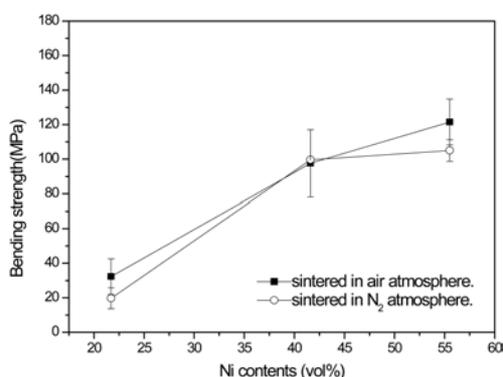
	Density (g/cm <sup>3</sup> )	Absorption coeff. (%)	Shrinkage (%)	Bending strength (MPa)
MNZ342	5.09	3.77	1.30	121.5
MNZ111	4.72	4.42	0.24	97.6
MNZ326	3.67	9.35	-0.48	32.3

**Table 3.** Properties of MNZ series specimens sintered in N<sub>2</sub> atmosphere.

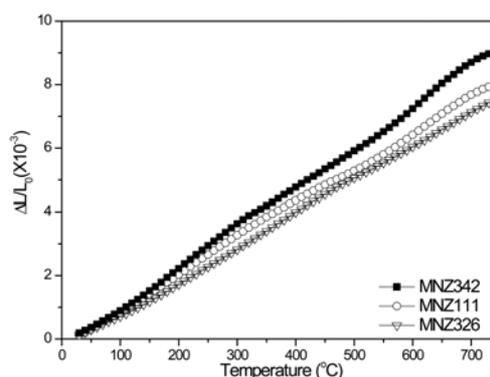
	Density (g/cm <sup>3</sup> )	Absorption coeff. (%)	Shrinkage (%)	Bending strength (MPa)
MNZ342	4.93	2.40	1.06	105.0
MNZ111	4.61	2.21	0.72	99.6
MNZ326	3.62	10.67	0.43	19.7

polymer pyrolysis.

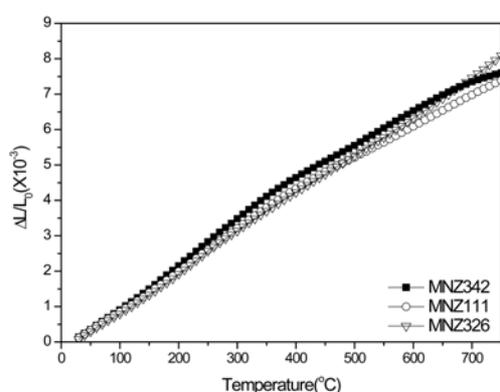
Tables 2 and 3 show the properties of an MNZ specimen sintered in air and N<sub>2</sub> atmospheres. In general, the specimens sintered in the N<sub>2</sub> atmosphere show low absorption coefficients. Because the gas generation velocity of the polymer pyrolyzed in the air atmosphere was faster than that of polymers pyrolyzed in the N<sub>2</sub> atmosphere, the specimen sintered in air atmosphere became porous as a result of the polymer pyrolysis gas. All specimens show a low shrinkage of < 2%, which



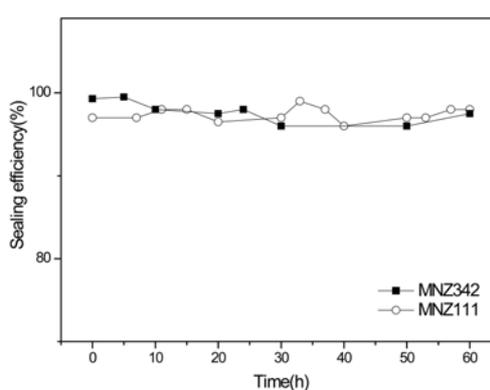
**Fig. 4.** Bending strength of MNZ series specimen as a function of Ni contents.



**Fig. 6.** Thermal expansion behavior of MNZ series specimen sintered in  $N_2$  atmosphere.



**Fig. 5.** Thermal expansion behavior of MNZ series specimen sintered in air atmosphere.



**Fig. 7.** Sealing properties of MNZ342 and MNZ111.

makes it possible to avoid thermal stress between seals and other components of fuel cells during fabrication and show low absorption coefficients; therefore, good sealing property was expected.

Fig. 4 shows the bending strength of an MNZ series specimen sintered in air and  $N_2$  atmospheres, respectively. As Ni content increased, the bending strength of the specimen increased and the specimen sintered in the air atmosphere showed a higher bending strength than the specimen sintered in the  $N_2$  atmosphere. Even the specimen sintered in the  $N_2$  atmosphere showed a lower absorption coefficient than the specimen sintered in the air atmosphere. It is assumed that the specimen sintered in the  $N_2$  atmosphere has a larger glass phase because the  $B_2O_3$  evaporates a little in the air atmosphere. Bending strengths of MNZ342, MNZ111, and MNZ326 sintered in the air atmosphere were 121.5, 97.6, and 32.3 MPa and those sintered in the  $N_2$  atmosphere were 105.0, 99.6, and 19.7 MPa, respectively.

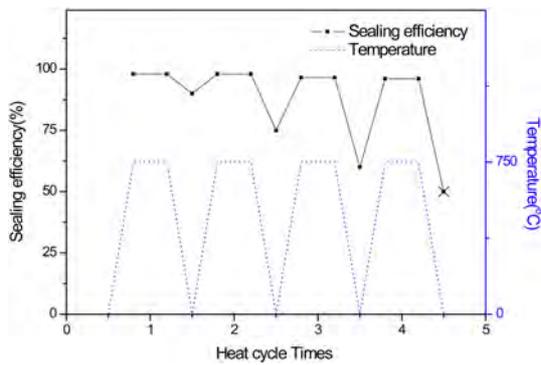
Fig. 5 and Fig. 6 show the thermal expansion behavior of the specimen sintered in air and  $N_2$  atmospheres, respectively. As shown in Fig. 5 and Fig. 6, all composition specimens show stable linear thermal expansion behavior. If other conditions are similar, the specimen sintered in the  $N_2$  atmosphere showed a higher coefficient of thermal expansion than the specimen

sintered in the air atmosphere. If the polymer was pyrolyzed in the  $N_2$  atmosphere, free carbon remained and because the silicon oxide phase derived from polymer pyrolysis showed a low coefficient of thermal expansion of  $3.14 \times 10^{-6}/^{\circ}C$  [11], residual free carbon remained in the specimen sintered in the  $N_2$  atmosphere was a reason for a relatively high coefficient of thermal expansion. The coefficients of thermal expansion of MNZ342, MNZ111, and MNZ326 sintered in air atmosphere were  $10.5$ ,  $10.1$ , and  $11.1 \times 10^{-6}/^{\circ}C$ ; and those sintered in  $N_2$  atmosphere were  $12.3$ ,  $11.0$ , and  $10.4 \times 10^{-6}/^{\circ}C$ , respectively.

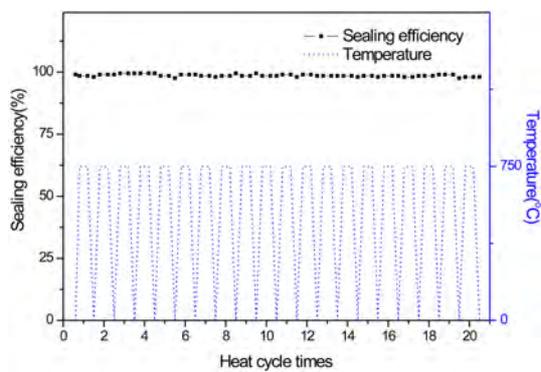
As a result, the MNZ series specimen showed an appropriate coefficient for thermal expansion and excellent linear thermal expansion. Therefore, long-time reliability was expected under a long operation time and heat cycle.

Because MNZ342 and MNZ111 compositions show low absorption, shrinkage, high strength, and an appropriate coefficient of thermal expansion, sealing properties were measured for 60 hr at  $750^{\circ}C$ . As shown in Fig. 7, both specimens show good sealing properties.

Considering the real operating conditions, the seal needs to endure a heat cycle. So a heat cycle was induced for the seal. Fig. 8 shows the result of the heat cycle induced sealing test that the MNZ111 seal applied. As shown in Fig. 8, the MNZ111 seal applied



**Fig. 8.** Heat cycle induced sealing properties of MNZ111 specimen.



**Fig. 9.** Heat cycle induced sealing properties of MNZ342 specimen.

specimen shows a high sealing efficiency of 750 °C at first, but during cooling a leakage occurred and sealing efficiency dropped. The crack generated during cooling was filled by a  $B_2O_3$  liquid phase during re-heating and the sealing efficiency was recovered; but as the heat cycle was repeated, the sealing efficiency gradually dropped and after four heat cycles, the seal failed. Fig. 9 shows the result of the heat cycle induced sealing test that the MNZ342 seal applied. It shows stable sealing efficiency for 20 heat cycles. It is believed that the MNZ342 seal shows a stable sealing property under repeated heating-cooling cycles because the MNZ342 seal has a more comparable coefficient of thermal expansion with the STS specimen. Furthermore, the bending strength of the MNZ342 seal was higher than that of the MNZ111 seal.

## Conclusion

A novel metal-ceramic composite seal for an SOFC device was fabricated by using a ceramic precursor. A metal-ceramic composite with tailored properties was easily obtained by controlling filler material and synthesis conditions. A dense microstructure composed of filler and ceramic derived from polymers was observed by using scanning electron microscopy.

MNZ series specimens sintered in  $N_2$  and air atmospheres showed a low absorption coefficient, shrinkage, a high bending strength, and an appropriate coefficient of thermal expansion. Especially, MNZ342 and MNZ111 specimens sintered in  $N_2$  and air atmospheres showed an absorption coefficient of  $< 5\%$ , shrinkage of  $< 2\%$ , and a coefficient of thermal expansion of  $10\text{--}12 \times 10^{-6} \text{ } ^\circ\text{C}$ .

Sealing properties of MNZ342 and MNZ111 were measured, and both specimens showed high sealing efficiency at 750 °C for 60 hrs. Then, heat cycles were induced: the MNZ111 seal was fragile to heat cycles, but MNZ342 showed stable sealing efficiency for 20 heat cycles.

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