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Evaluation of $CaO–Al_2O_3$ adhesive bonding properties for β''-Al_2O_3 solid electrolyte sealing for alkali metal thermal electric converter

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Abstract

The β''-Al_2O_3 solid electrolyte (BASE) tube is an essential component of the alkali metal thermal electric converter (AMTEC) system for inducing the conduction of Na ions and generating electricity. Maintaining gas-tightness to produce Na vapor pressure deference and providing insulation to prevent the loss of generated current from BASE are important factors for the AMTEC system. The Na–sulfur (NAS) battery has a similar driving system and uses glass adhesives, which are not adequate for operation temperatures higher than 800 °C or in a Na atmosphere. In this study, $CaO–Al_2O_3$ was used as the adhesive to resolve such bonding issues. The bonding strength changes were evaluated as the adhesive bonding process temperature varied and also the results showed that $CaO–Al_2O_3$ maintained bonding shear strength of 400 MPa for more than 1000 h in a molten Na environment. This study also proposes an experimental technique based on tube-type impedance measurement to assess the bonding between the BASE and the α-Al_2O_3 insulator and to detect Na leakage. After conducting the experiment for 500 h, $CaO–Al_2O_3$ adhesive can offer higher reliability than glass adhesives.

Keywords: D. Al_2O_3; Sealing; Bonding strength; AMTEC

1. Introduction

The alkali metal thermal electric converter (AMTEC) system is a static generator without any moving parts that uses liquid Na to generate electricity. Because an AMTEC system does not produce noise, vibration, or pollutants and has high efficiency, it is attracting attention from the viewpoint of aerospace, hybrid vehicle, military, and home applications.

An AMTEC system uses the β''-Al_2O_3 solid electrolyte (BASE), which was first introduced by Rankin and Merwin in 1916. Since then, BASE has undergone continuous evolution, marked by Ford's engine development in 1968 and studies conducted for space power generation in the 1980s [1].

BASE passes Na cations while blocking neutral or negatively charged particles and this phenomenon generates electricity [2]. Tube-type BASE is primarily used in an AMTEC system because it is easy to increase generation capacity by connecting several tubes [3,4]. In a tube-type AMTEC system, Na heated inside a high-temperature, high-pressure BASE tube (600–1000 °C) is ionized on the BASE surface, and then, it is transferred to the low-temperature, low-pressure exterior of the tube (100–500 °C) where it accepts electrons to generate electricity. For the construction of an AMTEC system, the heating unit—a metal conductor—needs to be attached to the BASE tube. However, if the heating unit is directly bonded to the BASE, loss of current occurs. To prevent this, α-Al_2O_3 ceramic insulator is inserted between the BASE and the metal heating unit as a barrier. For bonding with α-Al_2O_3, an adhesive that has resistance against high temperature (600–1000 °C) and the Na gas environment and that minimizes cracks caused by thermal expansion and residual stress is required. Recently, bonding methods such as brazing or thermo-compression bonding (TCB) have been used; however,

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these caused cracks in BASE tube due to localized heating and difficulties in the pressurizing process, posing major problems in implementation of the AMTEC system. Glass adhesives used in the Na–sulfur (NAS) battery system, which is similar to the AMTEC system, are also limited in their application because of degradation caused by reaction with Na in the high operation temperature environment.

In this study, we used a $CaO–Al_2O_3$ adhesive that has little heterogeneity with Al_2O_3 and that offers stability in a high-temperature environment to examine the bonding properties with α-Al_2O_3 for providing insulation for the BASE. To evaluate the characteristics in the Na atmosphere, novel tube-type impedance measurement method was proposed to detect adhesive leakage and to confirm the applicability of the $CaO–Al_2O_3$ adhesive in the AMTEC system.

2. Material and methods

2.1. $CaO–Al_2O_3$ adhesive bonding

The $CaO–Al_2O_3$ adhesive is manufactured in the form of a paste. The used paste agent contained STD10 (paste agent polymer, KS-Technology, South Korea), mineral spirits (Sigma-Aldrich, USA), and terpineol (Sigma-Aldrich, USA) with a mixture ratio of 9:25:33. The adhesive powder consisting of CaO (Samchun Chem., South Korea) and Al_2O_3 (Samchun Chem., South Korea) was mixed at 1:1 at%, a condition that exhibited the lowest melting point (1415 °C) in the binary phase diagrams. To obtain adequate viscosity, $CaO–Al_2O_3$ and the paste agent were mixed in a ratio of 1.5:1.3 wt%. The paste agent and $CaO–Al_2O_3$ were mixed in a three-role mixer to produce the $CaO–Al_2O_3$ adhesive paste. The paste was applied between the specimens (adherends) and dried for 3 h at 60 °C. After undergoing thermal treatment in an atmospheric-pressure electric furnace for 1 h at 600 °C, the adhesive was heated to the final heat treatment temperature of 1420 °C to induce bonding of the two adherends.

After bonding strength test, the fracture surface was observed using an S-4800 SEM (Hitachi, Japan). Furthermore, EDS analysis was conducted to analyze the components, and XRD analysis of the adhesive was performed using Dmax-2500pc (Rigaku, Japan).

2.2. Bonding strength test of $CaO–Al_2O_3$ adhesive

To evaluate the bonding strength of $CaO–Al_2O_3$, two adherends of 3 mm × 5 mm × 10 mm were bonded together, while maintaining a 3-mm gap, as shown in Fig. 1. The surfaces of the adherends were placed in an acetone solution, and foreign substances were removed using the ultrasonic cleaning before bonding process. The bonded specimen was fixed in a strength measurement device, as shown in Fig. 1 and compressive loading was applied using universal testing machine (MTS Landmark, USA) at a rate of 0.1 mm/min to measure the bonding shear strength. Shear strength was calculated using the formula $\tau = P/A$ (τ: shear strength, P: shear load, and A: shear area), and average value of 10 specimens was used for each experiment condition.

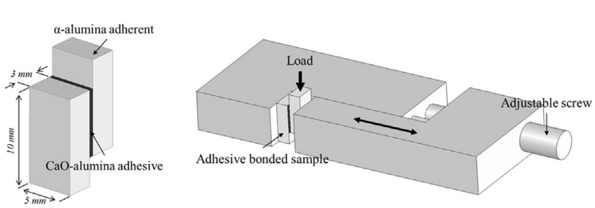

Fig. 1. Bonding shear strength specimen and test apparatus.

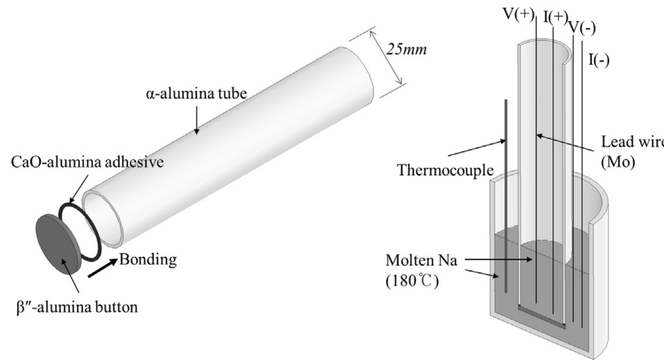

Fig. 2. The Na leakage test method by impedance measurement.

2.3. Evaluation of resistance properties of $CaO–Al_2O_3$ adhesive in Na condition

It is impossible to detect liquid or gas Na leakage by the bonding shear strength test method alone. Therefore, to detect leakage when the bonding part is exposed to liquid Na, the use of the experimental setup shown in Fig. 2 was proposed. A β''-Al_2O_3 button with a 25 mm diameter is attached to α-Al_2O_3 having an internal diameter of 23 mm and openings on both sides and submerged in molten Na over 180 °C. Molten Na is also placed inside the bonded tube, along with electrodes for measuring the impedance and a thermocouple for measuring the temperature. Without any Na leakage in the initial state, the detection device shows the resistance of β''-Al_2O_3 itself. When Na leakage occurs, the conduction of Na creates a short circuit that drastically reduces the resistance and this characteristic provides information regarding the adhesive's Na resistance and its long-term stability.

3. Results and discussion

3.1. Bonding properties of $CaO–Al_2O_3$

Fig. 3 shows the fracture surface after the bonding strength test of the specimen bonded at the processing temperature of 1420 °C using the $CaO–Al_2O_3$ adhesive. Fig. 3a shows the surface of the adherend and Fig. 3b the fracture pattern of the surface on which the adhesive was applied. Fractures shown in Fig. 3b were observed throughout the surface coated with the adhesive, but the surface of the adherend was not exposed on the fracture surface. This is a case of cohesive failure, which occurs in adhesives with strong bonding characteristics.

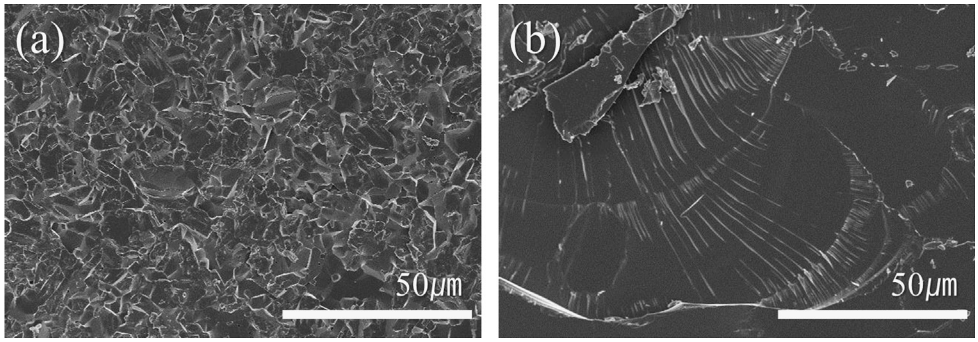

Fig. 3. Fracture surface after shear strength test (a) Al_2O_3 adherend side and (b) cohesive failure surface at adhesive bonded area.

Furthermore, the fracture surface bonded with CaO–Al_2O_3 did not display interfacial or adhesive failure, which involves debonding of the interface between the adhesive and the adherend. In cohesive failure, no damage occurs between the adhesive and the adherend; shear fracture only occurs in the adhesive itself, demonstrating high bonding strength between the adhesive and the adherend [5]. In this study, cohesive failure could be achieved because of using an adhesive containing CaO, which lowers not only the sintering temperature of Al_2O_3 in the adhesive during the bonding process but also decreases the sintering temperature of Al_2O_3 in the adherend material, it forms a melting zone between the adhesive and the adherend material [6]. When interfacial failure occurs on a bonded interface that is exposed to high temperature and other adverse conditions, the bonding strength deteriorates from the interface and results in debonding. The result showed that the CaO–Al_2O_3 adhesive will offer sufficient reliability even when it is exposed to AMTEC operation conditions of the high-temperature Na gas environment, because of strong interface bonding with typical cohesive failure, indicating an outstanding bonded interface.

The fracture surface of the adhesive, shown in Fig. 3b, did not have any pores. This pore free adhesive layer could be obtained because CaO–Al_2O_3 exists in the $12CaO \cdot 7Al_2O_3$+ liquid state at the sintering temperature of 1420 °C, allowing it to be evenly spread on the bonding surface. Excellent wetting characteristics with the adherend yields optimal bonding effects of an adhesive, and the SEM fractography showed that the wetting characteristics between the CaO–Al_2O_3 adhesive and the α-Al_2O_3 adherend were outstanding. This property will be effective in restraining the leakage of Na gas and pressure in AMTEC system applications, for which gas-tightness is a critical factor [7].

Table 1 shows the results of EDS analysis performed on the fracture surface, indicating a high level of oxygen but little difference from stoichiometric weight percent of $12CaO \cdot 7Al_2O_3$. Solubility to oxygen was reported during the melting and heat-treatment processes of $12CaO \cdot 7Al_2O_3$, and high oxygen content also measured in this study because the molten adhesive absorbed and contained oxygen during the bonding process, confirming that $12CaO \cdot 7Al_2O_3$ was completely dissolved under the temperature condition of the bonding process [8].

Table 1
EDS results of CaO-alumina adhesive bonded surface.

Element	Measured wt%	Stoichiometric wt% of $12CaO \cdot 7Al_2O_3$
O	46.91	38.10
Al	23.51	27.27
Ca	29.59	34.63
Total	100.00	100.00

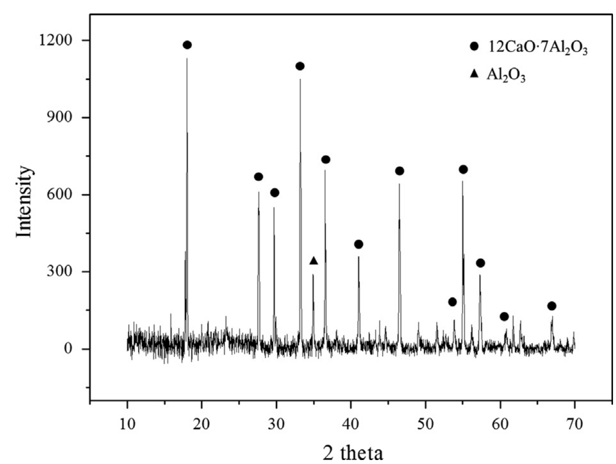

Fig. 4. XRD peak result of CaO–Al_2O_3 adhesive bonded surface.

To observe the crystallinity and phase of the CaO–Al_2O_3 adhesive after the bonding process, XRD diffraction analysis was performed, the results of which are shown in Fig. 4. The results coincide with the standard peak pattern of $12CaO \cdot 7Al_2O_3$ displayed circular small mark at peak. The results confirm that the adhesive investigated in this study by mixing CaO and Al_2O_3 at 1:1 at% yielded $12CaO \cdot 7Al_2O_3$ with high crystallinity [9].

Although the minimum bonding process temperature of CaO–Al_2O_3 is 1415 °C, bonding can also occur at higher temperatures, and the experiments of temperature conditions for the optimal bonding process were needed. The bonding process at 1420, 1450, and 1500 °C were performed with CaO–Al_2O_3 paste and then, the bonding shear strength using the method shown in Fig. 1 was evaluated to obtain the

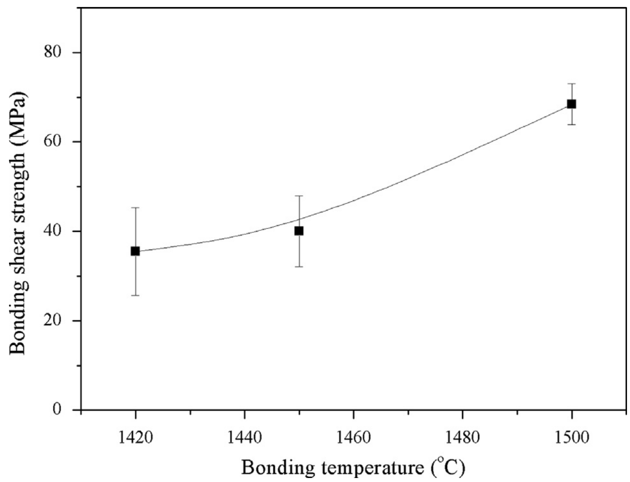

Fig. 5. Bonding shear strength according to process temperature.

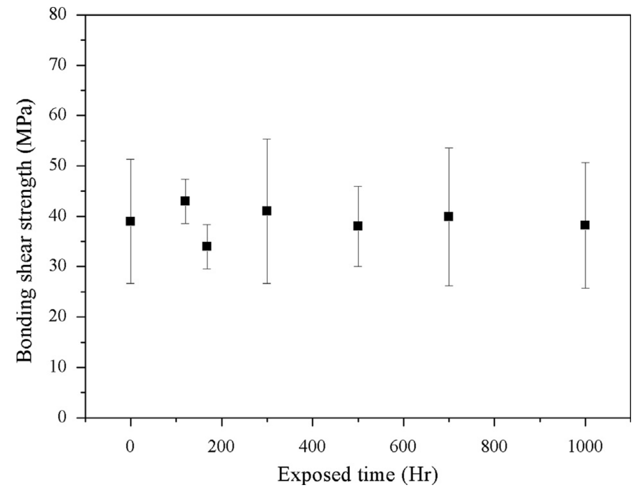

Fig. 6. Bonding shear strength after molten Na exposure.

optimal boding process condition. The results are shown in Fig. 5. As the bonding process temperature increased, bonding strength also increased from 35 to 40 and 68 MPa, and the standard deviation within each strength value decreased. Previous studies report that as the heat treatment temperature increases, the viscosity of $12CaO \cdot 7Al_2O_3$ decreases, and this property improved the wettability and increased the bonding strength [10,11]. Based on a study of the bonding properties of Si_3N_4, Fei reported that the bonding layer's thickness is related with the adhesive's viscosity, wettability, and interface energy. In particular, Fei suggested that by lowering the adhesive's viscosity, the wettability can be increased and the bonding layer's thickness can be reduced, thus improving the bonding shear strength. Similarly, it can be considered that increasing the bonding process temperature of $CaO–Al_2O_3$ improved the wettability and reduced the bonding layer's thickness, thus resulting in the improvement of the bonding shear strength [12,13]. Although improvement in the bonding strength based on the experimental result at each bonding temperature was confirmed, bonding with the $CaO–Al_2O_3$ adhesive is optimal at a relatively low temperature of 1420 °C because if the bonding temperature approaches the sintering temperature of 1600 °C, grain growth of the BASE can be accelerated and cause degradation of the physical properties in machinery.

3.2. Na resistance properties of $CaO–Al_2O_3$ adhesive

3 mm × 5 mm × 10 mm specimens bonded using the $CaO–Al_2O_3$ paste at 1420 °C were exposed to molten Na at 180 °C for 1000 h to examine the changes in bonding strength. For each evaluation, 10 specimens were taken out of the molten Na and tested, and the results are shown in Fig. 6. Specimens bonded with the $CaO–Al_2O_3$ adhesive maintained bonding shear strength of 40 MPa even after being exposed to Na for an extensive period. As explained above, this is due to the strong bonding between the adhesive and the adherend, preventing molten Na from penetrating into the interface and causing degradation. Furthermore, it has been reported that Na does not react with either Al_2O_3 or CaO, using the $CaO–Al_2O_3$ adhesive highly reliable in the Na environment [14].

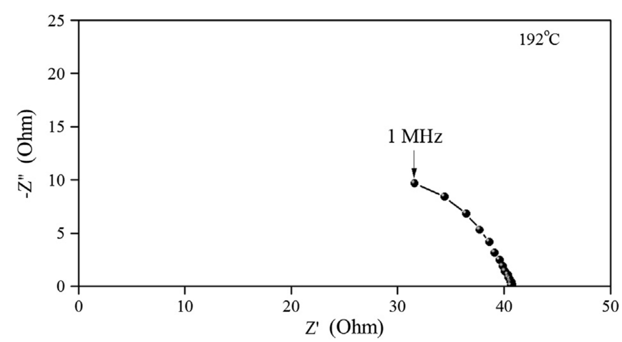

Fig. 7. AC impedance spectra of β''-Al_2O_3 with Na electrodes.

Although experimental results confirmed that the $CaO–Al_2O_3$ adhesive maintains its bonding strength even when exposed to Na, gas-tightness is also of utmost importance in the practical AMTEC environment. Therefore, to evaluate whether the $CaO–Al_2O_3$ adhesive maintains gas-tightness in the Na environment the new experimental setup shown in Fig. 2 was suggested. For the comparison of the gas-tightness, a glass sealant for bonding at 870 °C was evaluated simultaneously, the main composition of which are SiO_2 and BaO. The impedance pattern of β''-Al_2O_3 on the molten Na electrodes is plotted in Fig. 7 by a single arc. The capacitance calculated from the arc is 1.20×10^{-9} F, which appears to be attributable to the grain boundary component. Because molten Na was used as electrodes in the experiment, the impedance part in the electrodes was very small due to high level of activity of electrode. Fig. 8 shows the changes in the resistances of β''-Al_2O_3 bonded with the $CaO–Al_2O_3$ adhesive and the glass sealant. Resistances are displayed in normalized values for simple comparison of the two specimens. It can be seen that the β''-Al_2O_3 bonded with $CaO–Al_2O_3$ maintains its resistance even after being exposed to Na for more than 400 h because gas-tightness is maintained around the bonded area. On the

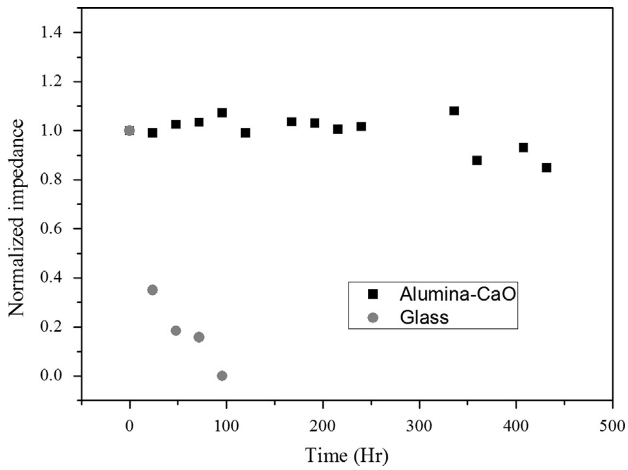

Fig. 8. Impedance result of the tube leakage test method.

other hand, the resistance of the β″-Al_2O_3 bonded with the glass sealant is the same value at first few hours but it decreased to almost 0 after 100 h. This signifies that the glass sealant is not capable of maintaining gas-tightness in molten Na and that a short circuit was created. Unlike the CaO–Al_2O_3 adhesive, the glass sealant contains a significant amount of SiO_2, which, when exposed to Na, causes corrosion and expedites decrease of resistance from Na leakage, resulting in a short circuit [14]. SiO_2 reaction with Na produces 1/2$Na_2Si_2O_5$ and 1/4Si whose reaction induces Na diffusion into glass adhesive layer. Na diffusion into adhesive layer resulted in a reduction of SiO_2 content that can degrade gas or liquid tightness [15]. It can be concluded that the glass sealant made from SiO_2 is not adequate for the Na environment because a short circuit can fail AMTEC operation. On the other hand, the CaO–Al_2O_3 adhesive showed high resistance in reaction with molten Na, demonstrating the possibility of its application for maintaining gas-tightness and preventing short circuits in the AMTEC system.

4. Conclusion

This study proposed a novel CaO–Al_2O_3 adhesive that can replace the traditional glass sealant used for insulation bonding of the BASE, an essential technology for the implementation of the AMTEC system. The bonding strength was evaluated and degradation in the Na atmosphere, which is the operating environment of the AMTEC system. The CaO:Al_2O_3 = 1:1 adhesive displayed typical cohesive failure and excellent bonding characteristics. The bonding strength was maintained for 1000 h even under exposure to the Na environment.

Furthermore, a novel impedance measurement technique to detect leakage in the Na atmosphere was proposed based on which we were able to confirm that the CaO–Al_2O_3 adhesive used in this study offers better sealing than the conventional glass sealant.

Through this basic research on AMTEC sealing adhesive, the possibility was obtained that CaO–Al_2O_3 adhesive can be used effectively in the AMTEC system.

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