Enhancement of the bonding strength of Al$_2$O$_3$ ceramics using a reactive intermediate layer formed by aerosol deposition

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ABSTRACT

Bonding with glass frit is important in many applications. Glass frit should wet and react chemically with the substrate. Its glass-wetting properties were improved by applying a lead oxide (PbO) layer fabricated through aerosol deposition (AD) which reacted with the glass frit. The 13 μm-thick PbO AD layer, which was mechanically anchored to the substrate, disappeared during bonding, since the PbO layer became diffused into the glass. The glass pellets on the PbO layer reacted with each other and were spread out at 455°C, which is lower than the equivalent temperature for glass frit on alumina (470°C) without an AD layer because of changes in the glass structure, as confirmed by Fourier-transform infrared (FT-IR) spectroscopy. The coefficient of thermal expansion (CTE) hardly changed. These phenomena increased the bonding strength at the glass-substrate interface of each specimen from 133.61 kPa (without AD) to 180.21 kPa (with AD).

1. Introduction

Alumina ceramics are used in various industries, such as electronics, aerospace and automobiles, due to their excellent mechanical, thermal and chemical properties [1–4]. The difficulty in applying alumina to large or complex structures can be overcome via bonding, which has been the subject of active research. Alumina ceramics can be bonded by active metal brazing, Mo-Mn metallization or glass frit bonding. The latter is economical due to the low cost of the bonding media and is suitable for joining the same or different materials in air condition at low temperatures [5,6].

The chemical reaction between the glass and the substrate is important for high bonding strength, and when occurring at the interface, it is more active at low viscosities. The viscosity of glass is decreased by increasing the bonding temperature to above the glass transition temperature, causing the glass to wet the substrate surface [7,8]. Activating a chemical reaction at the interface necessitates considering the composition match between the glass and the substrate. In addition, once bonding is halted by cooling after the chemical reaction at high temperature, the difference in the CTE between the glass and the substrate greatly affects the bonding strength. It is therefore very important to lower the bonding temperature.

Lowering the glass bonding temperature necessitates considering the glass structure and composition, which can be modulated by adding a modifier such as alkali, rare alkali, bismuth or lead. This destroys the continuity of the glass structure and weakens the oxide bonds in the glass, as a result of which the modifier reduces the melting temperature of the glass system.

AD involves the spraying of a powder onto a substrate in a vacuum chamber to prepare a coating layer. The ceramic particles are broken by strong collisions with the substrate, thus coating onto the substrate. In AD, the ceramic composition and type of substrate do not need to be considered before coating and the type of substrate, as any ceramic coating layer can be fabricated by AD on various substrates [9–14]. Our previous study reported the glass bonding behavior after reaction with lead oxide (PbO) on 304 stainless steel (STS304) [7], but it did not discuss the bonding strength or the effects or it of the thermal properties. In the present study, glass bonding was applied to alumina, and the effect on the wetting properties and bonding strength of the reaction with the AD PbO layer on the substrate were investigated.

2. Experimental

2.1. Aerosol deposition (AD)

The coating chamber vacuum was kept at 2 × 10⁻² bar during the coating process. PbO powders and nitrogen gas were mixed in the aerosol chamber and sprayed onto the alumina substrate in the coating chamber.
through a nozzle slit with dimensions of $5 \times 1 \text{ mm}^2$. The substrate was moved twice at a speed of $5 \text{ mm/s}$ along the $x$-axis.

### 2.2. Glass fabrication & bonding

Glass with a composition of $38\text{Bi}_2\text{O}_3 -0.9\text{Al}_2\text{O}_3 -22.9\text{B}_2\text{O}_3 -33.7\text{ZnO} -4.5\text{BaO}$ was selected, because it is a crystallized glass capable of low-temperature bonding. The glass was prepared from pure $\text{Bi}_2\text{O}_3$ (99.9%), $\text{Al}_2\text{O}_3$ (99.9%), $\text{B}_2\text{O}_3$ (99.9%), $\text{ZnO}$ (99.9%), and $\text{BaO}$ (99.9%) in an electric resistance furnace at 1050°C for 2 hours under an air atmosphere. The fabricated glass contained a large amount of bismuth, and crystallization occurred at a low temperature. Glass powders were fabricated by crushing the glass cullet followed by sieving. The diameter of the glass frit particles was 20 to 30 $\mu$m. The glass frit pellets with a 2 mm $\Phi \times 4 \text{ mm}$ were placed on the PbO layer and annealed at 430°C at a constant heating rate of 10°C/min for 20 minutes. For comparison, other glass frit pellets were placed on alumina (Figure 1).

### 2.3. Analysis methods

The microstructures of the glass-substrate cross-sections were observed by field emission scanning electron microscopy (FESEM, Hitachi S-4300SE, Japan). The elemental distribution at the glass-substrate interfaces was characterized by energy dispersive X-ray spectroscopy (EDXS, Hitachi S-4300SE, Japan). Hot-stage microscopy (HSM, Misura HSM, Expert System Solutions, Italy) was used to observe the changes in the glass structure at high temperatures. The wetting angle between the substrate and the glass pellets was measured using HSM images during heat treatment and the contact area ratio ($a/a_0$) was calculated using images from samples maintained at 430°C for 20 minutes (Figure 2). The changes in the glass structure were analyzed by Fourier-transform infrared (FT-IR) spectroscopy (VERTEX 80V, BRUKER, Germany). The CTE was measured by dilatometry (DIL 402, NETZSCH, Germany). To fabricate specimens for the CTE measurement, glass powder and a glass/PbO mixed powder were melted at 600°C for 2 hours, poured into a black smoke mold and removed after cooling. The CTE of each glass pellet was measured using a dilatometer (High Temp. Dilatometer, NETZSCH, Germany). The shear bonding strength between the substrate and the glass pellets after bonding was measured with a shear force measuring system (Dage 4000, Nordson DAGE, UK). The shear force was applied with a load of 5 kg at 1 mm per minute. To assure results, each specimen was measured 5 times and the average value was used.

### 3. Results & discussion

The film fabricated by AD was observed by SEM to analyze the cross-sections of the PbO film and the
result of the bonding process and the images obtained are shown in Figure 3. The AD film was dense with a thickness of ~13 μm, suggesting that the PbO film adhered strongly to the substrate. (Figure 3(a)) After the bonding process, no PbO film was observed anywhere. This means that the PbO layer was diffused into the glass during the bonding process. (Figure 3(b))

The changes in the wetting angle in the of the glass pellets on the substrate during bonding (430 ~ 510°C) were observed using HSM, as shown in Figure 4. The wetting angle of each specimen was 90°C at 430°C, and it increased with increased in temperature. The wetting angles of the glass pellets on alumina with PbO film and alumina without PbO film were maximized at 123°C at 455°C and at 153°C at 470°C, respectively. The temperature maximized wetting angle was the temperature at which the glass frits began to wet the substrate. This temperature decreased by 15°C in the presence of the PbO film. This indicated that the PbO film lowered the temperature at which the glass started to wet the substrate. The right side of the figure shows the wetting behavior of glass on alumina with PbO film and on alumina without PbO film at 475°C. The glass pellets on alumina without PbO film wet the substrate and showed a half ball shape, but the glass pellets on alumina without PbO film did not completely wet the substrate.

Figure 5 shows cross-sectional SEM images and the component distribution of the glass after bonding at 430°C for 20 minutes. The white crystalline phase with a circular shape can be observed in Figure 5(a). The white crystalline phase with a circular shape which consisted of more Zn, Al and fewer Ba, Bi components (Figure 1(b)) can be observed in the glass. However, no phases are observed in glass reacted with PbO. (Figure 5(c)) The major component of glass (Bi) and Pb were diffused into the alumina. And the AD layer disappeared when the two phases were present in the glass. The viscosity of the glass could be reduced by crystalline phases [15–17].

Borate glass can form two structures: a tetrahedral (3D) structure and planar (2D) structure. The planar structure contained more non-bridged oxide (NBO), which has a lower bonding strength than the tetrahedral structure. The bonding of planar structures can be more easily broken at low temperature than that of tetrahedral structures. As a result, the triangle structure, which has more NBO, was wetted at lower temperatures.

The structure of borate glass was changed by reaction with Pb ions according to the following reaction:

$$BØ_4^- \rightarrow BØ_2O^-$$

where Ø is the oxygen bond bridging boron and O is NBO. The NBO was increased by this process, and the bonding strength of each ion was reduced. As a result, the tetrahedral structure was changed to a planar structure, and the wetting properties of the borate glass were improved [7,18].

Figure 3. Cross-sectional SEM images of the (a) as-deposited PbO layer fabricated by AD and (b) post-bonding process.

Figure 4. Wetting angle changes during annealing (420 ~ 520°C).
Figure 6 shows infrared spectra of the glass powder and glass/PbO mixed powder (10:1 vol%). Each powder was heated to 500°C for reaction. The glasses were maintained at 500°C for 20 minutes. Borate glass can occur in the form of planar $\text{B}_3\text{O}_3^-$ and/or tetrahedral $\text{B}_4\text{O}_4^-$. In the IR spectra, the planar $\text{B}_3\text{O}_3^-$ shows four fundamental bands at around 950, 750, 1250 and 600 cm$^{-1}$. The tetrahedral $\text{B}_4\text{O}_4^-$ unit also exhibits four bands at around 1000, 900, 600 and 550 cm$^{-1}$ [19]. The absorption band at 950 cm$^{-1}$ became more intense and the absorption bands at 750, 1250 and 600 cm$^{-1}$ occurred in the reaction with PbO. On the other hand, the absorption band at 900 cm$^{-1}$ became less intense due to the reaction with PbO. These results show that the number of planar borate structures was increased and the number of tetrahedral borate structures was reduced through reaction with PbO. The absorption band at ~500 cm$^{-1}$ was assigned to the stretching vibrations of Bi-O bonds in strongly distorted BiO$_6$ octahedral units, B-O-B bond-bending vibrations, and this band was overlapping with the band due to PbO$_4$-BiO$_6$ structural units [20]. It became more intense when reacted with PbO. The absorption band at ~710 cm$^{-1}$ was assigned to the bending vibrations of B-O-B in BO$_3$ planar units [19]. The band at ~1320 cm$^{-1}$ was assigned to B-O stretching vibrations of trigonal $\text{B}_3\text{O}_3^-$ units in metaborates, pyroborates and orthoborates [21]. The absorption band at ~840 cm$^{-1}$ and the shoulder at around 1234 cm$^{-1}$ found in this glass system were assigned to the B-O stretching vibrations of BO$_3$-O$^-$ units with non-bridging oxygen atoms [22,23]. The absorption band at ~840 cm$^{-1}$ was assigned to vibrations of some boron atoms attached to NBO in the form of BO$_4$ vibration [22].

To observe the effect of heat treatment at the same temperature on the shape of glass pellets, the bonding process was conducted by holding the temperature at 430°C for 20 minutes and the results were observed by HSM. The shape of the glass pellets during the holding
time is shown in Figure 7(a). The height of the glass pellets on alumina without PbO decreased, but the contact area was not affected. The contact area of glass pellets on alumina with PbO increased over time. To analyze the wetting properties under the holding temperature conditions, the changes in the contact area ratio ($a/a_0$, $a_0$: initial contact area/$a$: contact area during bonding) over time are shown in Figure 7(b). Initially, the contact area ratio of glass pellets on alumina without PbO decreased up to 6 minutes, after which it retained the same value ($a/a_0 \sim 0.94$). The contact area ratio of glass pellets on alumina with PbO decreased until

![Figure 7](image.png)

Figure 7. High-temperature (a) images during heating (holding temperature at 430°C for 20 min), (b) changes in the area ratio with the holding temperature, and (c) cross-sectional images of the specimens (pure glass (left) and glass reacted with PbO (right) held at 430°C for 20 minutes).
2 minutes, however and then increased up to 20 minutes (a/a0 ~ 1.20). Figure 7(c) shows cross-sectional images of specimens (glass pellets on alumina without PbO (left) and with PbO (right) heated at 430°C for 20 minutes). Glass pellets on alumina without PbO had more pores than glass pellets on alumina with PbO due to the viscosity of the glass. Since pores in glass move out of low-viscosity materials easily, the viscosity of glass pellets on alumina without PbO was clearly higher than that of glass pellets on alumina with PbO. The chemical reaction between the substrate and the glass proceeded actively in the high-viscosity material, and the bonding strength between the substrate and the glass increased.

After bonding, the length difference between a substrate and glass due to the difference in the CTE can be expressed by the following equation:

\[
\Delta l_{\text{sub}} - \Delta l_{\text{glass}} = l_0 \times (a_{\text{sub}} - a_{\text{glass}}) \times \Delta T
\]

The left term of Equation (1) is proportional to the residual stress at the interface and proportional to the initial contact length \(l_0\), the difference CTE \(\Delta a\) between bonding material and the substrate, and the temperature difference \(\Delta T\) between the bonding temperature and room temperature. As the factors decreased, the stress caused by differences in thermal expansion could be reduced.

The CTE values for glass and PbO-reacted glass are shown in Figure 8. The CTE values for pure glass and PbO-added glass were 5.55 × 10\(^{-6}\) and 5.40 × 10\(^{-6}\)/K, respectively. The viscosity of the glass was reduced by the reaction with PbO, which improved the wettability of the glass pellets on alumina with PbO. The CTE of the glass was only slightly affected due to reaction with PbO, however indicating that the stresses formed on the glass-alumina interface were only slightly affected.

The shear bonding force of the glass/substrate interface was measured. The shear forces of glass pellets on alumina without PbO and with PbO were 4.3N and 9.1N, respectively. The contact areas of glass pellets on alumina without PbO and with PbO were 32.2 × 10\(^{-6}\) and 50.2 × 10\(^{-6}\) m\(^2\), respectively. For comparison with the correct value, the bond stress of the interfaces was calculated using the contact area. The shear stress (kPa) is indicated in Table 1. However, the shear stress of glass reacted with a PbO bonding specimen (180.21 kPa) was 1.3 times higher than that for a pure glass-bonding specimen (133.61 kPa). And the shear stresses of the specimens were 179.21, 183.33, 170.55, 190.69 and 177.28 kPa (bonding specimens with glass reacted with PbO)/110.49, 168.21, 120.67, 140.21 and 128.49 kPa (bonding specimens with pure glass). The standard deviations for each specimen were 7.46 kPa and 22.19 kPa, respectively. These differences in shear force were attributed to the reaction with PbO. As the PbO diffused into the glass, the viscosity of the glass decreased, which activated ion exchange at the interface. Consequently, the bond strength was increased and the stress at the interface was reduced by AD.

4. Conclusions

The glass-bonding temperature was lowered by PbO interlayers formed by AD. SEM, EDX, HSM, FT-IR and the shear force measuring system showed that the thermal properties of the glass were improved by a chemical reaction between the PbO AD layer and the glass. The ~13μm-thick interlayer formed by AD disappeared after bonding, and Pb components were present throughout the glass. The structure of the glass was changed by the addition of Pb ions, which in turn increased the amount of NBO in the glass structure. As a result, the viscosity of the glass was reduced and the contact area was broadened. Through this mechanism, ion exchange between the glass and the PbO AD layer proceeded more actively at the same temperature. Meanwhile, the CTE values for pure glass and PbO-added glass were 5.55 × 10\(^{-6}\) and 5.40 × 10\(^{-6}\)/K, respectively. The CTE of glass was hardly affected by the reaction with PbO. As a result, the shear stress of pure glass-alumina (180.21 kPa) was larger than that of glass reacted with PbO-alumina (133.61 kPa). These results revealed that a PbO AD layer changed the thermal properties of the glass and increased the bonding strength.

Table 1. Shear stress required for breakage of the glass-substrate interface of each specimen.

| Without PbO layer | With PbO layer |
|-------------------|----------------|
| Shear stress (kPa) | 133.61 ± 22.10 | 180.21 ± 7.46 |

**Disclosure statement**

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