

# Wetting and Bonding Behavior of SUS 304 Metal and Forsterite Ceramic with a PbO-Bi<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>-ZnO Glass Frit

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**Abstract:** The joining behavior of metal to ceramic was investigated using glass frit media. Glass frit with a composition of 71.5PbO-24Bi<sub>2</sub>O<sub>3</sub>-2.5B<sub>2</sub>O<sub>3</sub>-1.5ZnO-0.5SiO<sub>2</sub> in mol. % was designed to bond forsterite ceramic and SUS 304 metal. The glass frit demonstrated a glass transition temperature of 250°C and a thermal expansion coefficient of  $15.9 \times 10^{-6}/^{\circ}\text{C}$ , which is between the values of SUS 304 ( $17.8 \times 10^{-6}/^{\circ}\text{C}$ ) and forsterite ( $9.9 \times 10^{-6}/^{\circ}\text{C}$ ). The contact angle was smaller than 90° at a temperature of 460°C. Redox reaction at the interface between forsterite and SUS304 was found to appear when the electrons in the metal part moved toward the glass part and the oxygen ions in glass moved to the metal side. The decrease of the surface tension due to the PbO solubility on the forsterite side contributed to the better wetting behavior at low temperature. Due to the ionic bonding nature, the glass was able to chemically react with forsterite ceramic and form a rough boundary. The Fe metal in the SUS 304 was oxidized to form FeO ceramic. A thin FeO layer on the SUS 304 surface helped the glass frit to wet the SUS 304, and clear tight bonding between the glass and SUS 304 was achieved.

**Keywords:** Forsterite, SUS 304, Thermal Expansion Coefficient (C.T.E), Ionic Bonding, Joining Glass to Metal

## 1. Introduction

Ceramic-metal bonding with glass frits has many applications such as in gas-containing tubes, electronic vacuum tubes, and electronic packaging. In order to bond the metal and ceramic with glass, the glass should wet both the metal and the ceramic [1, 2]. This implies that, at the processing temperature, the glass should be somewhat fluid. The major problem with such bonds is mechanical fracture resulting from stress accumulated due to mismatch of the coefficients of thermal expansion (CTE) during the cooling process. Therefore, it is difficult to determine the right composition of glass needed to achieve the desired properties. To understand the bonding mechanism, though many experimental and theoretical studies have been conducted [3, 4], many issues still need to be resolved for specific

applications. To fabricate an ionization chamber employing these bonds [5, 6], we designed the glass composition and examined the bonding behavior between metal SUS 304 and forsterite (Mg<sub>2</sub>SiO<sub>4</sub>) ceramic with glass. Figure 1 shows photos of the ionization chamber and its components. To contain the inert gas inside the chamber, forsterite must be tightly bonded with SUS 304 using the bonding glass. It is well known that forsterite is ideal for use in electronic tube parts and circuit substrates due to its low microwave loss, excellent insulation at high temperature, and smooth surface. In addition, forsterite has a suitable CTE so that it bonds easily with metals and glass [7, 8]. In this experiment, we determined the glass composition by combining PbO-B<sub>2</sub>O<sub>3</sub>-ZnO and Bi<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>-ZnO-SiO<sub>2</sub> glasses to result in a high thermal stability and processing temperature below 500°C [9]. The thermal and wetting behaviors of the glass were characterized at various temperatures. We successfully bonded SUS 304 and

forsterite with glass and proposed the bonding mechanism based on the elemental distribution. Where SUS means steel use stainless.

## 2. Experimental Procedure

To characterize the wetting behaviors of the bonding glass on SUS 304 and forsterite, glass powders on the surface of SUS 304 and forsterite were heat-treated at 440-500°C at a rate of 10°C/min for 20 min under a N<sub>2</sub> atmosphere. By applying the bonding glass, bonding between SUS 304 and forsterite was performed at 500°C for 10 min under a N<sub>2</sub> atmosphere. In the process, the bonding glass was packed between SUS 304 and forsterite and was heated at a rate of 5°C/min. The thermal behavior and CTE of the glass were characterized using TG/DTA (SDT Q600, TA Instruments, U.S.A) and a dilatometer (Dil 402 C, Netzsch, EU), respectively. The microstructure and composition were analyzed by SEM/EDS (JSM-6380LV, Jeol, Japan).

## 3. Results and Discussion

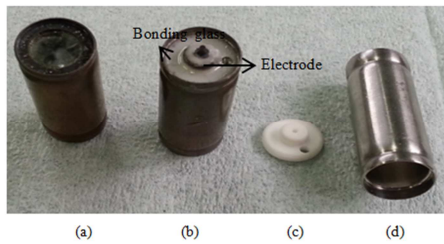
Figure 2 shows the X-ray diffraction (XRD) pattern of the bonding glass. XRD patterns showed the broad peak indicating the amorphous phase. It is known that the composition with large amount of PbO or Bi<sub>2</sub>O<sub>3</sub> can easily generate the crystalline phase but even though the total amount of second oxides as PbO and Bi<sub>2</sub>O<sub>3</sub> was over 90 mol %, a glass phase was successfully fabricated by controlling the cooling rate [9, 10]. For the glass to be utilized for bonding, it must be somewhat fluid at the processing temperature. Differential thermal analysis of the glass was conducted, and the results are presented in Figure 3. The glass transition temperature ( $T_g$ ) was identified at 250°C, softening occurred ( $T_s$ ) at 370°C, and crystallization ( $T_c$ ) occurred at 490°C and 564°C. With regard to the relief of stress accumulated during the cooling process, the CTE of glass should be matched with those of SUS 304 and forsterite. If we consider the structure of the gas tube in Figure 1, a larger CTE of SUS 304 compared to forsterite is more desirable to induce compressive stress upon the forsterite. This accumulated compressive stress will effectively seal the gas inside the SUS tube. Though it was not presented here, the CTE of the bonding glass was measured to be  $15.9 \times 10^{-6}/^{\circ}\text{C}$ , which is between the values of SUS 304 ( $17.8 \times 10^{-6}/^{\circ}\text{C}$ ) and forsterite ( $9.9 \times 10^{-6}/^{\circ}\text{C}$ ). The major difficulty in joining ceramic with metal results from the dissimilar natures of the atomic bonds between the two materials. To seal the forsterite and SUS 304 tightly with bonding glass, the glass should be able to wet both materials. Figure 4 shows the wetting behavior of the bonding glass on forsterite and SUS 304. The bonding glass showed different wetting behaviors depending on the substrates. Below 460°C, it can be seen that the bonding glass did not wet the forsterite and SUS 304 well. When the temperature increased over 460°C, the contact angle decreased dramatically, and the bonding glass spread on the SUS 304 like a liquid. Comparing the contact angle at 460°C, the contact angle between the glass and SUS

304 became smaller than that between the bonding glass and forsterite. This difference behavior in contact angle depending on the kind of substrates indicates that the underlying mechanism differs significantly depending on the chemical bonding of substrates.

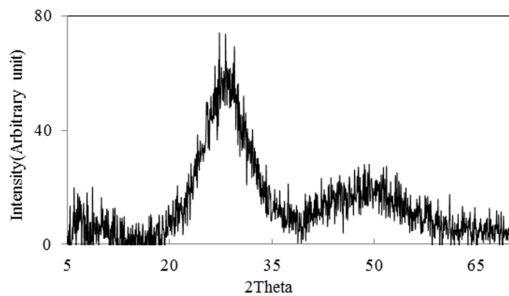
To investigate the chemical reaction between bonding glass and substrates, we observed the bonding interface with scanning electron microscope (SEM) and analyzed the element distribution with energy dispersive X-ray spectroscopy (EDS). Figure 5(a) shows the SEM and EDX results of bonding between glass and SUS 304. SEM image showed that the interface was flat and smooth and a tight bond was formed without void. The EDX results show that while elements from the glass were not detected inside SUS 304, as shown in spectra 3 and 2 in Figure 5(a), but interestingly a significant amount of Fe was detected inside the glass region, as observed in spectrum 4 in Figure 5(a). This Fe distribution in glass indicates that the elements from the glass did not diffuse into SUS 304 but the elements from SUS 304 did diffuse into the glass. Thermodynamically, metallic Fe is less stable than oxides such as FeO, Fe<sub>2</sub>O<sub>3</sub>, and Fe<sub>3</sub>O<sub>4</sub> in the bonding process [11, 12], hence metal oxide can be easily formed on the surface of SUS 304. As glass is basically a kind of metallic oxide compound and has ionic bonding nature, the iron oxide formed on the metal surface could help the glass to wet the SUS 304 and accelerate the chemical reaction with the glass. Considering that the bonding process was conducted under a N<sub>2</sub> atmosphere, it can be inferred that oxygen for the formation of iron oxide on the SUS 304 surface should be supplied from the glass, which is a kind of metallic oxide. Luo *et al.* observed the borosilicate glass-Kovar bonding and explained the bonding with an oxidation-reduction mechanism [11, 12]. At the interface, the neutral metal was oxidized into metal cations by supplying free electrons to the glass. The glass, which accepts electrons from the metal, donates an oxygen anion to balance the charge neutrality. Then, the metal cation, i.e. Fe<sup>2+</sup> or Fe<sup>3+</sup> reacts with the oxygen anion to form the ionic metal oxide such as FeO, Fe<sub>2</sub>O<sub>3</sub> or Fe<sub>3</sub>O<sub>4</sub> [11, 13]. For the bonding between the glass and forsterite materials, as these two materials are ionic compounds, which are composed of anions and cations, it is expected that the bonding glass will chemically react easily with ceramic forsterite. Figure 5(b) shows the glass and forsterite interface where the materials are bonded tightly without any voids. The interface has a rough boundary, which implies that the glass chemically reacted with forsterite. This rough interface is beneficial in increasing the bonding strength between the glass and forsterite. When measuring the distribution of elements, Mg from the forsterite was observed in all spectra, as was Pb or Bi from the glass. This elemental redistribution implies that the bonding between the glass and forsterite was enabled by interchanging the elements in each material. In our previous study, we reported that metal Pb accelerated the bonding between SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-R<sub>2</sub>O ceramics and PbO-Bi<sub>2</sub>O<sub>3</sub>-B<sub>2</sub>O<sub>3</sub>-ZnO-SiO<sub>2</sub> glass by forming a new crystal phase at a temperature lower than the glass transition temperature [9, 13]. As discussed in the previous paragraph, in

SUS 304 and glass bonding, the glass donates an oxygen anion to accept electrons from the metal. Consequently, cations such as Pb<sup>2+</sup> or Bi<sup>3+</sup> in the glass are reduced to Pb or Bi metal. It was reported that even a tiny amount of MgO (100~150 ppm) dramatically reduced the surface energy of Al<sub>2</sub>O<sub>3</sub> with the formation of segregates at the interface [14, 15]. In our experiment, this reduced Pb or Bi metal reduced the surface energy of forsterite, and the glass wetted the forsterite well, leading to tight bonding between the glass and forsterite.

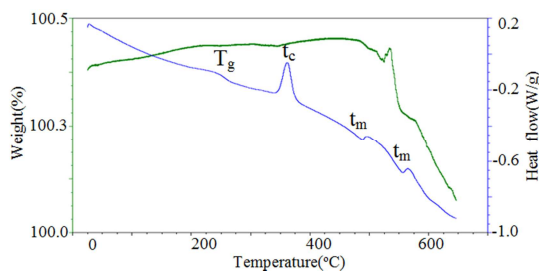
In Figure 6, a schematic of the bonds between ceramic forsterite and SUS 304 with bonding glass is presented. In fact, bonds are strongly dependent on the bonding nature of materials and the bonding mechanism can be explained with the atomic transfer between two different materials. For metal-glass bonding, Fe metal donated electrons and accepted an oxygen anion from the glass to make a metal oxide. Due to the ionic bonding nature, the metal oxide on the surface of SUS 304 helped the bonding glass to wet the SUS 304. Meanwhile, for the glass-forsterite bonding, the cations in the glass were reduced by accepting electrons from the metal. This reduced metal lowered the surface energy of forsterite and accelerated the chemical reaction at a lower temperature.



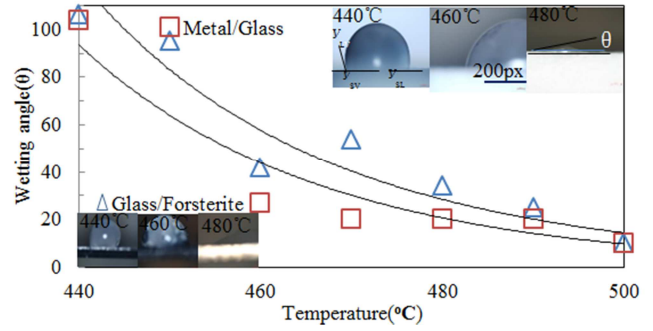
**Figure 1.** Photo of the ionization chamber and its components: (a) Mica window, (b) Assembled shape, (c) Forsterite piece, and (d) Body (SUS 304).



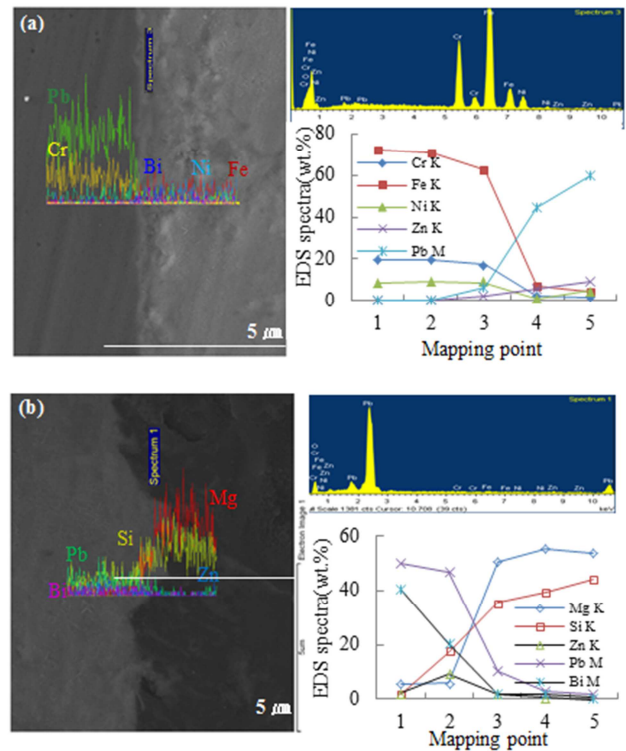
**Figure 2.** XRD patterns of the bonding media, 71.5PbO-24Bi<sub>2</sub>O<sub>3</sub>-2.5B<sub>2</sub>O<sub>3</sub>-1.5ZnO-0.5SiO<sub>2</sub> (mol.%) glass system.



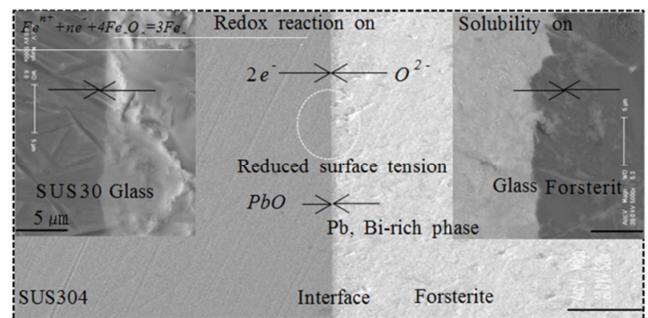
**Figure 3.** Tg/DTA curves of 71.5PbO-24Bi<sub>2</sub>O<sub>3</sub>-2.5B<sub>2</sub>O<sub>3</sub>-1.5ZnO-0.5SiO<sub>2</sub> (mol.%) glass system, where  $T_g$ ,  $t_c$ , and  $t_m$  represents the glass transition temperature, softening point, an  $t_m$  melting temperature, respectively.



**Figure 4.** Contact angle of metal/glass/forsterite, and schematic diagrams of sessile drop configurations. The contact angle is identified as  $\theta$ . 440~500°C interval 10°C held for 20 min in a furnace containing N<sub>2</sub>.



**Figure 5.** Cross sectional SEM and line scanning images, and EDS results (a) SUS 304/glass (b) Glass/forsterite interlayer.



**Figure 6.** Schematic of the wetting and bonding mechanism between SUS 304/lead-bismate glass as bonding glass/forsterite. Left was represented SUS 304/glass side, middle was bonding glass, and right was glass/forsterite side, as determined from the SEM images, respectively. There are three figures illustrated here.

## 4. Conclusion

The wetting and joining behaviors of 71.5PbO-24Bi<sub>2</sub>O<sub>3</sub>-2.5B<sub>2</sub>O<sub>3</sub>-1.5ZnO-0.5SiO<sub>2</sub> in mol. % glass to achieve bonding with forsterite ceramic and SUS 304 metal were investigated to fabricate an ionization chamber. The glass transition was measured to be 250°C, which is significantly lower than that of normal glass. The thermal expansion coefficient of the glass was  $15.9 \times 10^{-6}/^{\circ}\text{C}$ , which is between the values of SUS 304 ( $17.8 \times 10^{-6}/^{\circ}\text{C}$ ) and forsterite ( $9.9 \times 10^{-6}/^{\circ}\text{C}$ ). Due to the ionic bonding nature of glass, it easily wetted and reacted with the forsterite ceramic at temperatures of 440-500°C. However, the wetting behavior of the glass was dependent on the temperature on SUS 304. The elemental distribution analysis and SEM images support that the high temperature accelerated the oxidation of Fe in SUS 304, producing FeO that bridged the bond with glass.

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