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Silicon Nitride Joining with Silicate Glass Solder (I)

Nobuya IWAMOTO *, Norimasa UMESAKI** and Yukio HABARA ***

Abstract

$Si_3N_4$-$Si_3N_4$ joining was accomplished by the use of CaO-SiO$_2$-TiO$_2$ glass solder without using applied pressure. The properties of the glasses used and the $Si_3N_4$-glass joining reactions were studied in detail. The strong bond strength obtained from $Si_3N_4$ joints can be put to practical use.

KEY WORDS: ($Si_3N_4$) (Joining) (Glass Solder) (CaO-SiO$_2$-TiO$_2$ System) (Microstructure) (Bond Strength)

1. Introduction

Silicon nitride ceramics are excellent for heat-, corrosion-, abrasion- and insulation-resistance, so these ceramics are being widely considered as materials for components in energy-conversion machines such as heat engines. Therefore, for the purpose of forming complex shapes, the joining of $Si_3N_4$ is a useful and often necessary processing step. In general, joining processes have used wetting by a viscous interfacial phase or sintering/reaction of a powder layer with the solid components to form a bond. 1) Both ways involve the use of applied pressure. The sealing technique with various oxide glass solders is being used to join ceramics and/or metals. It is well known that $Si_3N_4$ is dissolved in oxide glass and that silicon oxynitride glass is consequently formed. 2) This knowledge is now being more effectively applied to the joining of $Si_3N_4$ ceramics. Recently, a method of joining $Si_3N_4$ with oxide glasses was developed. 3)–7) This technique consists of heating a thin layer of glass between the parts to be joined at a temperature and pressure sufficient to reach the molten glass $Si_3N_4$ ceramics, thus creating the bond. 6)

It is well known that the titanium element easily generates nitridation reactions under a nitrogen atmosphere. We have succeeded in getting a strong bond strength of $Si_3N_4$-$Si_3N_4$ ceramic joints are room-temperature by using CaO-SiO$_2$-TiO$_2$ glass solder with nearly eutectic composition without using applied pressure. The results obtained are reported in this paper. In addition, the purpose of the present research was to understand the joining mechanism that took place between $Si_3N_4$ and CaO-SiO$_2$-TiO$_2$ glass solder in detail.

2. Experimental Procedure

2.1 Joining materials and process

A single type of sintered $Si_3N_4$ ($\beta$-$Si_3N_4$, Sumitomo Cement Co., Densification aid components: MgO, Al$_2$O$_3$, Y$_2$O$_3$) was used in this study. Each material was cut into plates of approximately 15 × 30 × 15 mm or 10 × 10 × 20 mm using a diamond cutter, and was then ground using #600 diamond wheels to produce a flat surface (6.5 $\mu$m $R_{max}$ L0.8).

The CaO-SiO$_2$-TiO$_2$ glasses with nearly eutectic composition (25wt% $<$ CaO $<$ 65wt%, 15wt% $<$ SiO$_2$ $<$ 65wt%, 0wt% $<$ TiO$_2$ $<$ 65wt%) were prepared by melting suitable mixtures of analytical grade reagents CaCO$_3$, SiO$_2$ and TiO$_2$ for 30 to 60 min in air 1500°C to 1550°C in a Pt crucible under an electric furnace. In order to make glass samples, the melts were quenched by dipping the Pt crucible partially in cold water. The glass samples obtained were ground to a fine powder using an Al$_2$O$_3$ mortar and pestle for further experiments.

The glass samples were characterized by a variety of property measurement technique. Laser Raman spectra were measured on a JASCO model R-800 double-grating spectrometer at a scattering angle of 90°. The excitation source was the 514.5 nm (19435.6 cm$^{-1}$) line of a NEC GLG-3300 Ar ion laser at a power of from 300 to 400mW. The glass transition temperature ($T_g$), the softening temperature ($T_s$), the crystallization temperature ($T_c$) and the temperature of the melting point ($T_m$) were measured in a DTA apparatus with Al$_2$O$_3$ as the reference. After DTA measurement, an X-ray diffraction experiment was performed on the crystallized samples. The expansion

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93
was measured by using fused SiO₂ as a standard.

Fig. 1 indicates the outline of a Si₃N₄ joining process developed by use. Glass paste mixed with screen oil was painted on one side of the surface of each Si₃N₄ plate. After drying, a sandwich of glass solder was put between Si₃N₄ plates, and then Si₃N₄ joining was carried out by heating for 10 to 30 min at 1400°C to 1600°C under various atmospheres (N₂, Ar, N₂ of 5 kg/cm², 5H₂/95N₂, air and a vacuum of 5 × 10⁻³ torr). No external pressure was used in joining the two plates.

2.2 Microstructural analysis

The joint cross section produced were metallographically polished and then observed by means of an optical microscope, EPMA and SEM-EDX. Slices of the typical joint cross sections were ground, polished, and then Ar-ion-thinned to prepare electron-transparent samples for TEM observation. The transmission electron microscope (AEM) was performed on a HITACHI H800 200 kV TEM-EDX. A few joint regions were examined analysis (Beam diameter: 100μm).

2.3 Bond strength test

The joint plates were cut into test bars of approximately 5 × 4 × 60 mm or 3 × 3 × 60 mm with the plane of the joint in the center of the test bar. The bond strength of each joint was measured by a four-point bending machine with a span length of 30 mm using a loading rate of 0.5 mm/min.

3. Results and Discussion

3.1 Properties of the glass solder

Fig. 2 shows the Raman spectrum of a typical 30wt%CaO-35wt%SiO₂-35wt%TiO₂ glass. As shown in this figure, the weak Raman bands in the frequency range from about 800 to 1200 cm⁻¹ are due to the Si-O stretching vibration of depolymerized silicate anions such as the Si₂O₅⁻ sheet, the SiO₂⁻ chain, the Si₂O₅²⁻ dimer and the SiO₂⁻ monomer. This result implies a relatively low viscosity of the glasses in the molten state and thus good wetting between the molten glasses and Si₃N₄ in the joining process. Furthermore, the Raman spectrum obtained suggests that Ti⁴⁺ ions with four-fold oxygen coordination (TiO₄ tetrahedron) and six-fold oxygen coordination (TiO₆ octahedron) may coexist in the glass.

Fig. 3 shows the DTA curve of 30wt%CaO-35wt%SiO₂-35wt%TiO₂ glass for the temperature interval between room-temperature and 1400°C. The glass transition temperature T_g (= 750°C) and the glass softening temperature T_s (= 770°C) were observed by this DTA measurement. As shown in this figure, there were exothermic peaks at T_g = 870°C and 940°C due to crystallization, and then four endothermic peaks at T_m = 1261°C to 1378°C.
Si$_3$N$_4$ and glass can cause thermal fracture as a result of the mismatch. As opposed to the glasses used by them, it is almost double that of hot-pressed Si$_3$N$_4$, and tensile stress between the Si$_3$N$_4$ and the glass is consequently produced. It seems that tensile stress develops thereby causing thermal expansion cracks.

3.2 Si$_3$N$_4$-glass reactions

Si$_3$N$_4$ joined with 35wt%CaO-40wt%SiO$_2$-25wt%TiO$_2$ glass at 1500°C for 30 min under N$_2$ gas at 5 kg/cm$^2$ gave a higher bond strength. The results obtained from the microstructural analysis regarding this Si$_3$N$_4$ joint are described in this section.

Fig. 6 shows an optical micrograph of the joint region in the bonded Si$_3$N$_4$. This picture indicates the formation of the condensed joint region with a thickness of about 20μm. The joint is characterized by the golden thin-layer, which consist of titanium nitride (for details, please see below).

The EPMA micrographs of the joint region in the bonded Si$_3$N$_4$ and the corresponding X-ray maps for selected elements Ti, N, Ca, O, Si, Al and Y are shown in Fig. 7. The X-ray map for the element Ti illustrates that the Ti is clearly distributed in the joint region, and does not diffuse into Si$_3$N$_4$ throughout the molten glass. Because the distribution of the element Ti is almost in accord with that of the element N, the result indicates that the elements Ti and N form a titanium nitride compound. On
the other hand, the X-ray maps for the elements Ca and O illustrate that the Ca and O are relatively distributed over all in the joint region, and the distribution of these elements extends for about $2 \sim 3 \mu m$ from the bonding interface to $Si_3N_4$. In addition, the elements Ca and O are slightly soluble in the Ti-rich nitride compound in the joint region, as can be seen in these pictures. As previously mentioned, the elements Al, Y and Mg are densification aid components for the $Si_3N_4$ ceramics used. It is well known that these densification aid elements are present in glassy joining phases between $\beta-Si_3N_4$ grains. The fact that should be taken notice of is the behavior of Y in the joint region. The X-ray map for the element Y illustrates that Y diffuses from the $Si_3N_4$ grain boundaries to the joint region during joining, and consequently is densely distributed over all into the joint region.

**Fig. 8** shows the X-ray microdiffraction patterns of the joint region in the bonded $Si_3N_4$. As shown in Fig. 8 (A), the above-mentioned layer-like compound was identified as titanium nitride TiN. It can be considered that the
Si₃N₄ dissolves in the molten glass, and the titanium nitride precipitates as a result of the following reaction between the Si₃N₄ and Ti⁴⁺ ions in the molten glass:

\[ \text{Si}_3\text{N}_4 + 4\text{Ti}^{4+} \rightarrow 3\text{Si}^{4+} + 4\text{TiN} \]  
\[ 3\text{Si}^{4+} + 3\text{O}^{2-} \rightarrow 3\text{SiO} \text{(gas)} \]

O²⁻ is free oxygen existing in the molten glass. It is generally accepted that the introduction of oxides such as CaO and TiO₂ to SiO₂ melt breaks the Si-O-Si bridging bonds connecting SiO₄ tetrahedra of three-dimensional network units, creating non-bridging (O²⁻) and free (O²⁻) oxygen. No band for the (111) plane of the precipitated TiN (Crystal structure: NaCl type) appears in the obtained X-ray micro-diffraction pattern, as can be seen in Fig. 8 (A). This is caused by the distortion of the TiN crystalline structure due to other elements (O, Si, Al, Y, Ca and Mg) dissolved in TiN precipitates. The only identified crystalline species in the joint region are β-Si₃N₄ and TiN. Consequently, the joint consists of the layer-like TiN precipitates and glassy matrix.

Fig. 9 shows the SEM-EDX micrograph of the bonded Si₃N₄ glass interface. This picture reveals that there is a thin-layer based on Al-Si-Y-Ca-Ti between the Si₃N₄ and the TiN precipitates. As previously mentioned, the layer region dissolves oxygen and nitrogen, and is of the glassy phase. It is, therefore, considered that the thin-layer consists of oxynitride glasses based on the Al-Si-Y-Ca-Ti system. The presence of the glassy thin-layer probably makes it possible to accomplish our Si₃N₄ joining.

Fig. 10 shows the transmission micrograph of the oxynitride glassy layer existing in the bonded interface found by SEM-EDX observation. As shown in this picture, the microstructure is characteristic of the intergranular phase and the boundary phase. The electron diffraction patterns obtained from both phases indicate the diffuse rings due to the non-crystalline structure. We now call the intergranular glass phase Glass A, and the boundary glass phase Glass B. Fig. 11 shows the transmission micrograph of the layer-like TiN precipitates. The microstructure also consists of the TiN grains (grain size: 0.5 ~ 1μm) and the boundary glass phase (Glass C). Table 1 indicates the mean chemical compositions of the TiN precipitates and Glasses A, B and C determined by AEM analysis. As illustrated by the values in Table 1, Glasses A and B are made from the component Al-Si-Ca-Ti-Y of the same type, whereas the contents of the main components Al, Si, Ti, and Y in Glass A are evidently distinct from those in Glass B. It is well known that the addition of Al₂O₃ and/or TiO₂ tends to enhance immiscibility in complex silicate systems. Furthermore, a miscibility gap is found in the systems SiO₂-Y₂O₃ and SiO₂-TiO₂. Therefore, the formation of Glasses A and B in the oxynitride glassy layer is considered as being a result of the phase separation phenomena. On the other hand, the precipitated TiN slightly contains the impurities Al, Si, Ca and Y, but over 90% of it comes from the component Ti. Glass C is
Table 1 Mean chemical compositions of TiN precipitates and glass phases A, B and C determined by AEM analysis.

<table>
<thead>
<tr>
<th>Element</th>
<th>TIN precipitate&lt;sup&gt;1&lt;/sup&gt;</th>
<th>Glass A&lt;sup&gt;2&lt;/sup&gt;</th>
<th>Glass B&lt;sup&gt;3&lt;/sup&gt;</th>
<th>Glass C&lt;sup&gt;4&lt;/sup&gt;</th>
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<tr>
<td>Al</td>
<td>2.4</td>
<td>34.5</td>
<td>22.2</td>
<td>4.1</td>
</tr>
<tr>
<td>Si</td>
<td>4.2</td>
<td>32.2</td>
<td>36.8</td>
<td>31.4</td>
</tr>
<tr>
<td>Ca</td>
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<td>3.3</td>
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<tr>
<td>Ti</td>
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<tr>
<td>Y</td>
<td>2.3</td>
<td>21.3</td>
<td>18.6</td>
<td>4.5</td>
</tr>
<tr>
<td>Fe</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.6</td>
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Data based on average values of <sup>1</sup>: 7-points; <sup>2</sup>: 10-points; <sup>3</sup>: 5-points; <sup>4</sup>: 7-points.

3.3 Bond strength of Si₃N₄ joints

We have succeeded in getting Si₃N₄ joints with strong bond strength by our joining technique<sup>*</sup>. Table 2 lists the values of the bond strength of the typical Si₃N₄ joints at room-temperature measured by a four-point bending test. The bonded Si₃N₄ is so strong as to be able to be put to practical use (see Fig. 12).

As illustrated by the values in Table 2, the bond strength increased by the addition of α-Si₃N₄ powder to 35wt%CaO-40wt%SiO₂-25wt%TiO₂ glass solder. By the addition of Si₃N₄ powder to the glass solder, the thermal expansion coefficient of the glass is matched closely to that of the Si₃N₄ ceramics used. Therefore, the addition of Si₃N₄ tends to decrease the residual stress resulting from mismatching, and consequently will lead to a higher bond strength of the Si₃N₄ joints. Furthermore, the addition of Si₃N₄ tends to accelerate nitridation reactions at the joint region during the joining process.

Table 2 Bond strength (kg/mm²) of the Si₃N₄ joints<sup>*</sup>.

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<tr>
<th>N₂-atmosphere</th>
<th>α-Si₃N₄&lt;sup&gt;2&lt;/sup&gt;</th>
<th>35CaO-35SiO₂-25TiO₂</th>
<th>5 kg/cm² N₂</th>
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<tr>
<td>35wt%CaO-40SiO₂-25TiO₂</td>
<td>0</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>1.</td>
<td>28.8</td>
<td>27.0</td>
<td>21.1</td>
</tr>
<tr>
<td>2.</td>
<td>25.6</td>
<td>30.3</td>
<td>22.9</td>
</tr>
<tr>
<td>3.</td>
<td>21.6</td>
<td>21.3</td>
<td>38.4</td>
</tr>
<tr>
<td>4.</td>
<td>19.6</td>
<td>18.0</td>
<td>25.3</td>
</tr>
<tr>
<td>Av.</td>
<td>24.0</td>
<td>24.3</td>
<td>26.9</td>
</tr>
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</table>

<sup>*1</sup>: Reacting at 1500°C X 30 min in each atmosphere.
<sup>*2</sup>: α-Si₃N₄ powder: particle size 10μm > 97%; α-powder ratio > 90%.

The test bars were joined under the following atmospheres: N₁, N₂ of 5 kg/cm², Ar and 5H₂/95N₂.
4. Conclusion

$\text{Si}_3\text{N}_4$-$\text{Si}_3\text{N}_4$ joining was accomplished using glass interface layers in the CaO-SiO$_2$-TiO$_2$ system that reacts with the $\text{Si}_3\text{N}_4$ surface at temperature of 1400$^\circ$C–1600$^\circ$C under N$_2$ atmosphere and densified.

Information of the microstructure of the joint region in the bonded $\text{Si}_3\text{N}_4$ was obtained by several microscopic measurements. EPMA observation indicated that the elements Ti and N formed a layer-like titanium nitride compound in the joint region, and that the densification aid elements Al and Y for the $\text{Si}_3\text{N}_4$ ceramics used were densely distributed over all into the joint region by the diffusion from the $\text{Si}_3\text{N}_4$ garn boundaries. The Ti-rich layer-like compound was identified as distorted TiN crystalline by X-ray microdiffraction measurement. SEM-EDX and AEM observations revealed that there was a thin-layer, which consists of a few oxynitride glasses based on Al-Si-Y-Ca-Ti system, between the $\text{Si}_3\text{N}_4$ and TiN precipitates.

We have succeeded in getting the $\text{Si}_3\text{N}_4$ joints with strong bond strength by our joining technique. Furthermore, we confirmed that the bond strength increased by the addition of $\alpha$-$\text{Si}_3\text{N}_4$ powder to the CaO-SiO$_2$-TiO$_2$ glass solder.

References