Silicon Nitride Joining with Silicate Glass Solder (I)

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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 (β-Si_3N_4, Sumitomo Cement Co., Densification aid components: MgO, Al_2O_3, Y_2O_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 μm R_{max} L0.8).

The CaO-SiO_2-TiO_2 glasses with nearly eutectic composition (25wt% $\leqslant$ CaO $\leqslant$ 65wt%, 15wt% $\leqslant$ SiO_2 $\leqslant$ 65wt%, 0wt% $\leqslant$ TiO_2 $\leqslant$ 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° 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_2O_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 400 mW. 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_2O_3 as the reference. After DTA measurement, an X-ray diffraction experiment was performed on the crystallized samples. The expansion

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was measured by using fused SiO_2 as a standard.

Fig. 1 indicates the outline of a Si_3N_4 joining process developed by use. Glass paste mixed with screen oil was painted on one side of the surface of each Si_3N_4 plate. After drying, a sandwich of glass solder was put between Si_3N_4 plates, and then Si_3N_4 joining was carried out by heating for 10 to 30 min at 1400° to 1600°C under various atmospheres (N_2, Ar, N_2 of 5 kg/cm^2, $5H_2/95N_2$, 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: 100$\mu m\phi$).

2.3 Bond strength test

The joint plates were cut into test bars of approximately $5 \times 4 \times 60$ mm or $3 \times 3 \times 60$ 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%SiO_2-35wt%TiO_2 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 $Si_2O_5^{2-}$ sheet, the SiO_3^{2-} chain, the $Si_2O_7^{6-}$ dimer and the SiO_4^{4-} monomer.[8] This result implies a relatively low viscosity of the glasses in the molten state and thus good wetting between the molten glasses and Si_3N_4 in the joining process. Furthermore, the Raman spectrum obtained suggests that Ti^{4+} ions with four-fold oxygen coordination (TiO_4 tetrahedron) and six-fold oxygen coordination (TiO_6 octahedron) may coexist in the glass.

Fig. 3 shows the DTA curve of 30wt%CaO-35wt%SiO_2-35wt%TiO_2 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_c = 870°C and 940°C due to crystallization, and then four endotheric peaks at T_m = 1261° to 1378°C

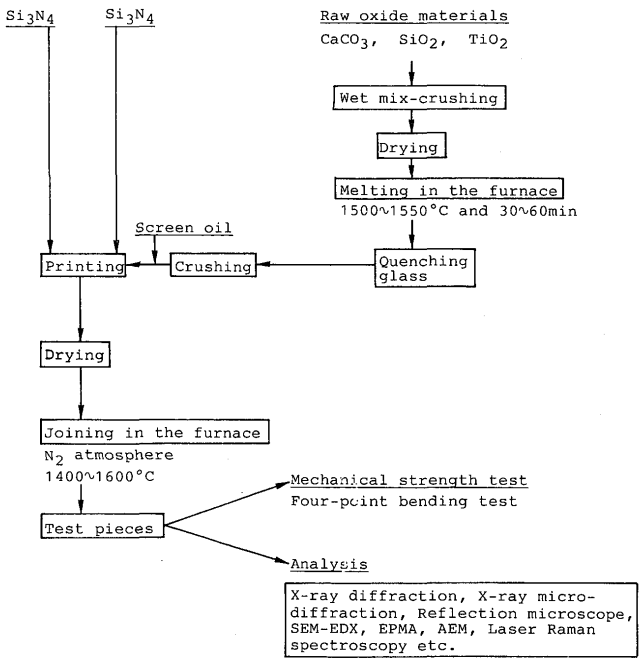

Fig. 1 Process of Si_3N_4 joining.

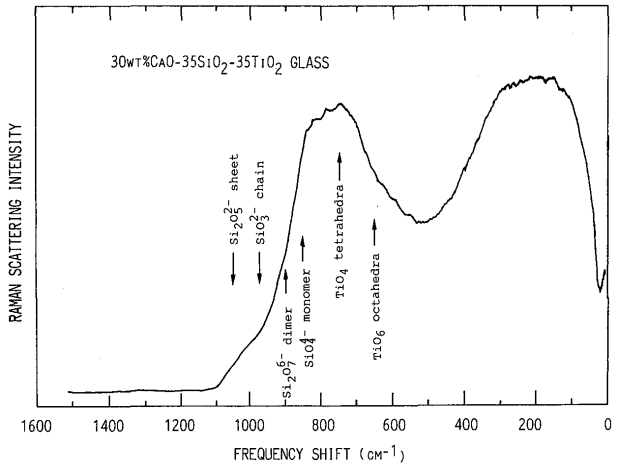

Fig. 2 Raman spectrum of 30wt%CaO-35wt%SiO_2-35wt%TiO_2 glass.

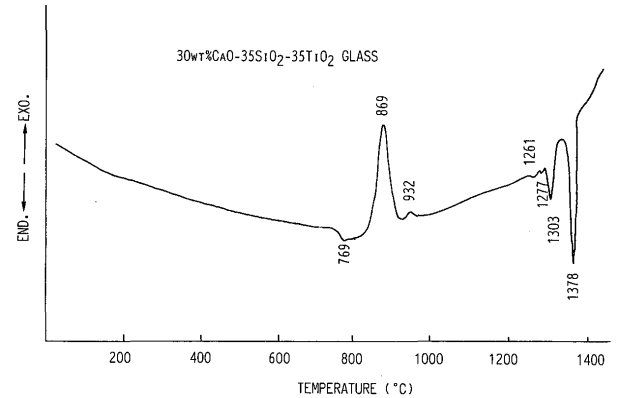

Fig. 3 DTA curve of 30wt%CaO-35wt%SiO_2-35wt%TiO_2 glass.

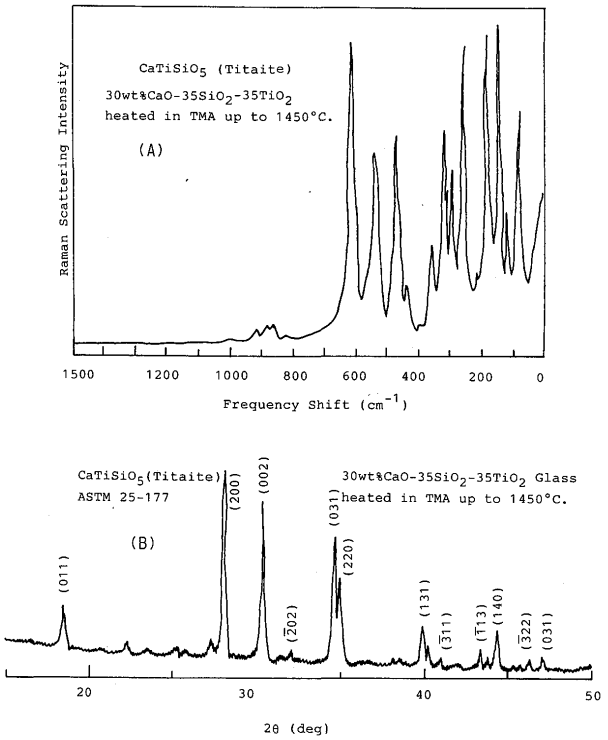

Fig. 4 Raman spectrum (A) and X-ray diffraction pattern (B) of 30wt%CaO-35wt%SiO_2-35wt%TiO_2 glass crystallized by the DTA test.

due to melting. After DTA measurement, the $CaTiSiO_5$ titanite phase crystallized from the glass was confirmed by Raman spectroscopy and X-ray diffraction (see **Fig. 4**).

Fig. 5 shows the thermal expansion curve of 30wt% CaO-35wt%SiO_2-35wt%TiO_2 glass. The thermal expansion coefficient for the temperature interval between room-temperature and 628°C was found to be $\alpha_g = 1.29 \times 10^{-6}$/°C. This value is about 1/3 that of the Si_3N_4 ($\alpha_c = 2.8 \sim 3.0 \times 10^{-6}$/°C) used, and compressive stress between the Si_3N_4 and the glass is consequently produced. Johnson and Rowcliffe[7] reported that the difference in the thermal expansion coefficients between

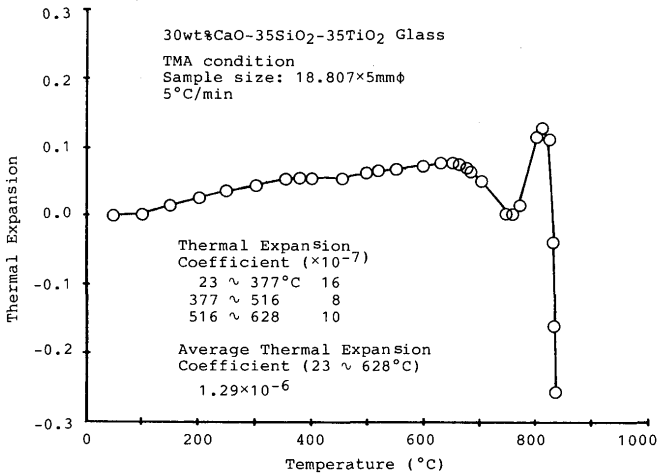

Fig. 5 Thermal expansion curve of 30wt%CaO-35wt%SiO_2 -35wt%TiO_2 glass.

Si_3N_4 and glass can cause thermal fracture as a result of the mismatch. As opposed to the glasses used by them[7] is almost double that of hot-pressed Si_3N_4,[7] and tensile stress between the Si_3N_4 and the glass is consequently produced. It seems that tensile stree develops thereby causing thermal expansion cracks.

3.2 Si_3N_4-glass reactions

Si_3N_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_3N_4 joint are described in this section.

Fig. 6 shows an optical micrograph of the joint region in the bonded Si_3N_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_3N_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_3N_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

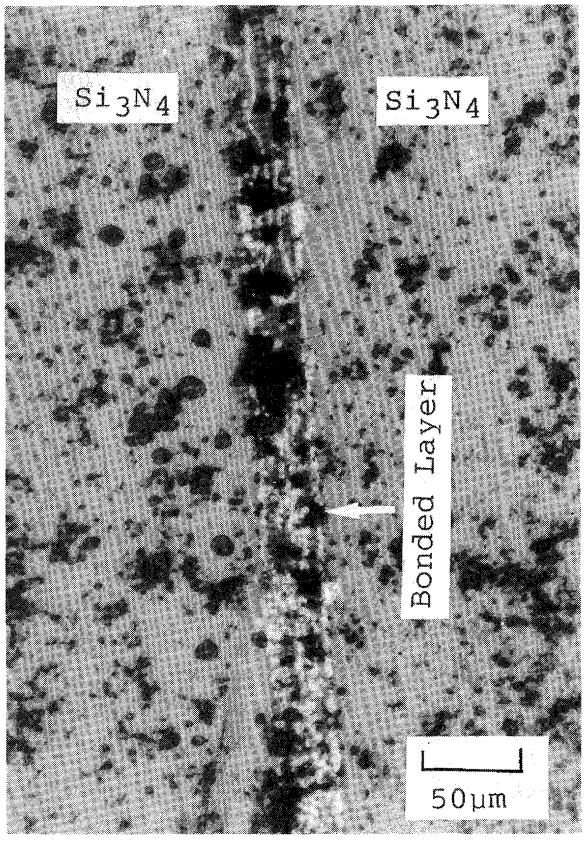

Fig. 6 Optical micrograph of joint region.

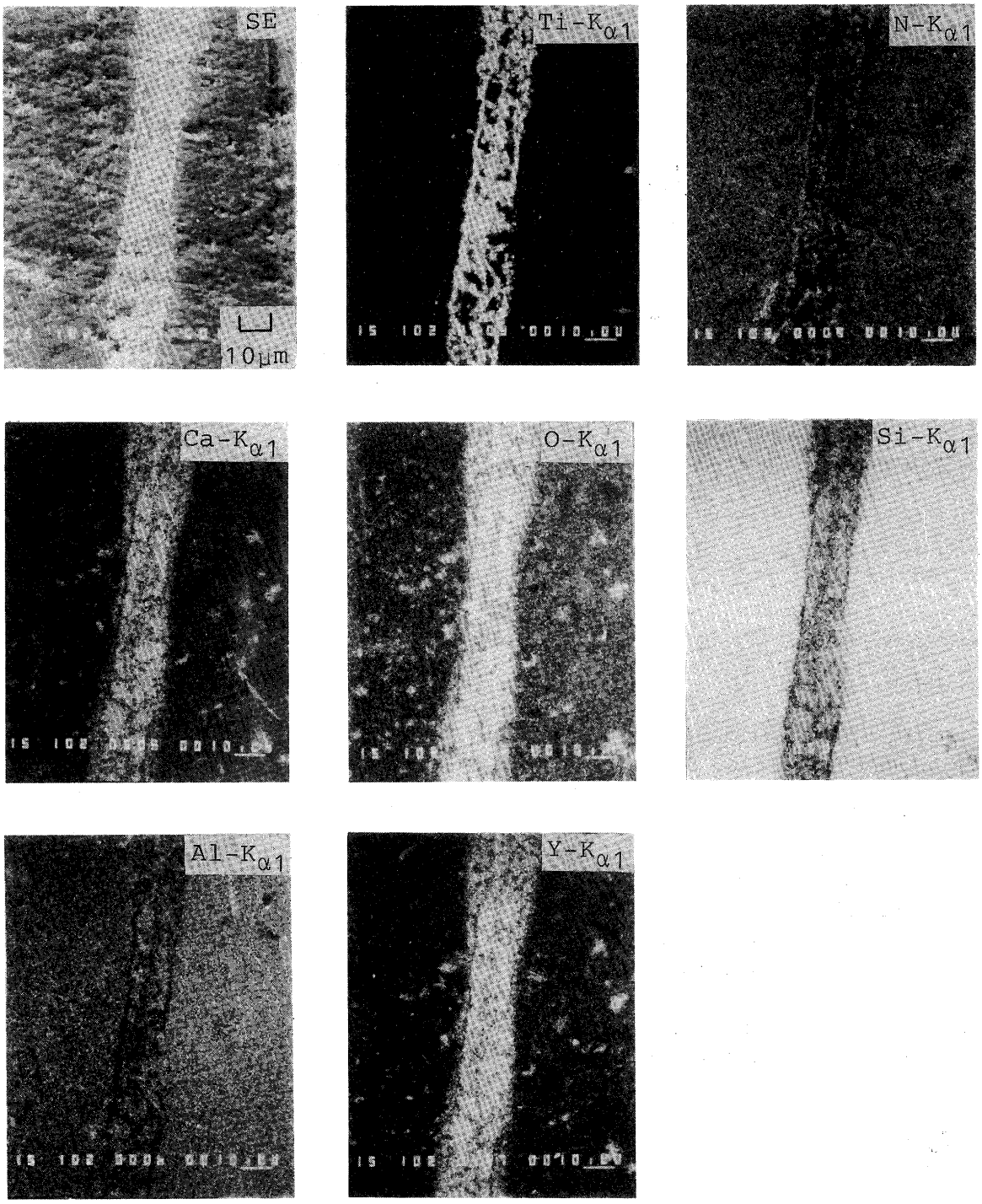

Fig. 7 EPMA micrographs of joint region in the bonded Si_3N_4.

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 ~ 3μm 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 β-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

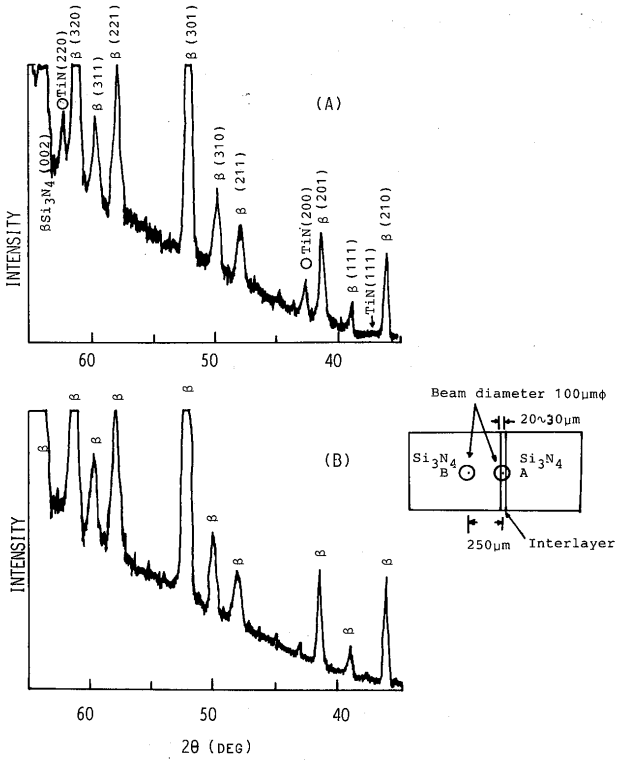

Fig. 8 X-ray microdiffraction patterns of joint region in the bonded Si_3N_4.

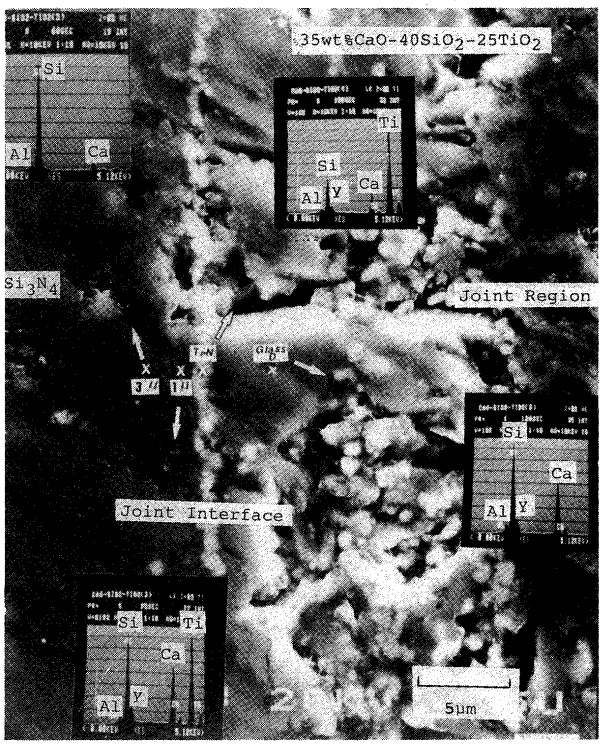

Fig. 9 SEM micrographs of joint region in the bonded Si_3N_4.

Si_3N_4 dissolves in the molten glass, and the titanium nitride precipitates as a result of the following reaction between the Si_3N_4 and Ti^{4+} ions in the molten glass:

$$Si_3N_4 + 4Ti^{4+} \rightarrow 3Si^{4+} + 4TiN \quad (1)$$

$$3Si^{4+} + 3O^{2-} \rightarrow 3SiO\ (gas). \quad (2)$$

O^{2-} is free oxygen existing in the molten glass. It is generally accepted that the introduction of oxides such as CaO and TiO_2 to SiO_2 melt breaks the Si-O-Si bridging bonds connecting SiO_4 tetrahedra of three-dimensional network units, creating non-bridging (O^-) and free (O^{2-}) 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-Si_3N_4 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 Si_3N_4-glass interface. This picture reveals that there is a thin-layer based on Al-Si-Y-Ca-Ti between the Si_3N_4 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 Si_3N_4 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 components 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 Al_2O_3 and/or TiO_2 tends to enhance immiscibility in complex silicate systems.[9] Furthermore, a miscibility gap is found in the systems SiO_2-Y_2O_3[10] and SiO_2-TiO_2.[11] Therefore, the formation of Glasses A and B in the oxynitiride 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

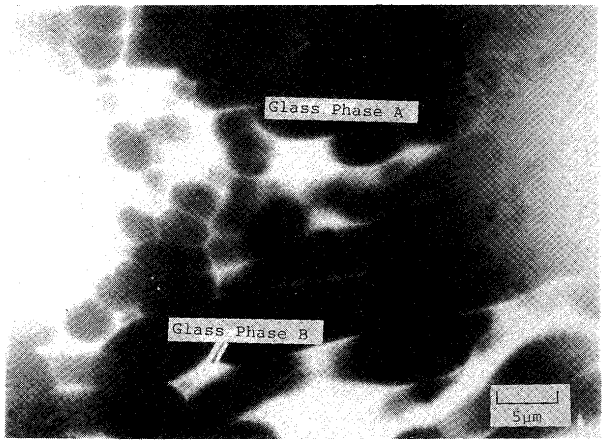

Fig. 10 Transmission micrograph of the oxynitride glassy layer.

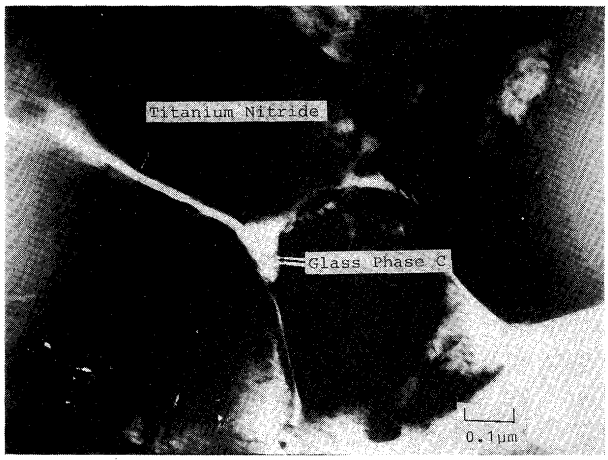

Fig. 11 Transmission micrograph of the layer-like TiN precipitates.

mainly made of Ti-rich TiO_2-SiO_2 glass.

3.3 Bond strength of Si_3N_4 joints

We have succeeded in getting Si_3N_4 joints with strong bond strength by our joining technique+. **Table 2** lists the values of the bond strength of the typical Si_3N_4 joints at room-temperature measured by a four-point bending test. The bonded Si_3N_4 is so strong as to be able to be put to practical use (see **Fig. 12**).

Table 1 Mean chemical compositions of TiN precipitates and glass phases A, B and C determined by AEM analysis.

Element	TiN precipitate*1	Glass A*2	Glass B*3	Glass C*4
Al	2.4	34.5	22.2	4.1
Si	4.2	32.2	36.8	31.4
Ca	1.1	1.6	3.3	6.0
Ti	90.3	10.1	19.2	53.5
Y	2.3	21.3	18.6	4.5
Fe	—	—	—	0.6

Data based on average values of *1: 7-points; *2: 10-points; *3: 5-points; *4: 7-points.

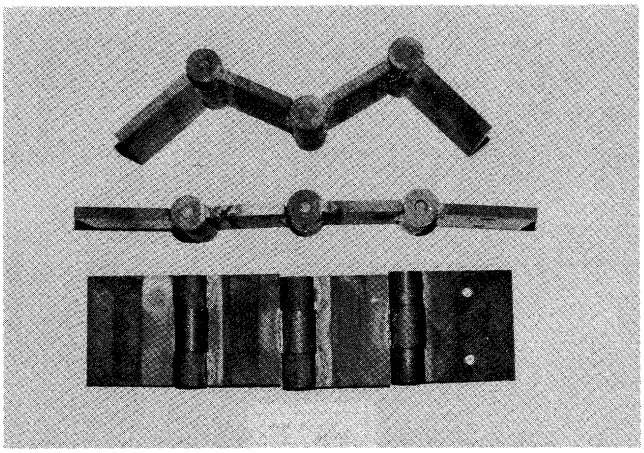

Fig. 12 Curtain for the hot blast stove in steelmaking.

As illustrated by the values in Table 2, the bond strength increased by the addition of α-Si_3N_4 powder to 35wt%CaO-40wt%SiO_2-25wt%TiO_2 glass solder. By the addition of Si_3N_4 powder to the glass solder, the thermal expansion coefficient of the glass is matched closely to that of the Si_3N_4 ceramics used. Therefore, the addition of Si_3N_4 tends to decrease the residual stress resulting from mismatching, and consequently will lead to a higher bond strength of the Si_3N_4 joints. Futhermore, the addition of Si_3N_4 tends to accelerate nitridation reactions at the joint region during the joining process.

Table 2 Bond strength (kg/mm²) of the Si_3N_4 joints*1.

	N_2-atmosphere 35wt%CaO-40SiO_2-25TiO_2					30CaO-35SiO_2-35TiO_2		5 kg/cm² N_2	
α-Si_3N_4 *2	0	10	20	30	40wt%		1		35CaO-40SiO_2-25TiO_2
1.	28.8	27.0	21.1	25.3	26.9	1.	30.5	1.	31.6
2.	25.6	30.3	22.9	23.7	12.5	2.	16.1	2.	20.3
3.	21.6	21.3	38.4	29.4	19.5	3.	14.4	3.	25.9
4.	19.6	18.0	25.3	32.5	20.5	4.	33.4	4.	24.6
Av.	24.0	24.3	26.9	27.7	19.9	Av.	23.6	Av.	25.6 kg/mm²

*1: Reacting at 1500°C × 30 min in each atmosphere.
*2: α-Si_3N_4 powder: particle size 10μm ⩾ 97%; α-powder ratio ⩾ 90%.

+ The test bars were joined under the following atmospheres: N_2, N_2 of 5 kg/cm², Ar and $5H_2/95N_2$.

4. Conclusion

Si_3N_4-Si_3N_4 joining was accomplished using glass interface layers in the CaO-SiO_2-TiO_2 system that reacts with the Si_3N_4 surface at temperature of 1400°–1600°C under N_2 atmosphere and densified.

Information of the microstructure of the joint region in the bonded Si_3N_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 Si_3N_4 ceramics used were densely distributed over all into the joint region by the diffusion from the Si_3N_4 garin 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 Si_3N_4 and TiN precipitates.

We have succeeded in getting the Si_3N_4 joints with strong bond strength by our joining technique. Furthermore, we confirmed that the bond strength increased by the addition of α-Si_3N_4 powder to the CaO-SiO_2-TiO_2 glass solder.

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