Joining of Si_3N_4 to Si_3N_4 with Partially Crystallized Cordierite Glass or Oxynitride Glass Solders

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(Received December 4, 1997)

ABSTRACT

Crystallization heat treatment was applied to the joint of silicon nitrides with a cordierite glass containing ZrO_2, in order to improve the toughness of a joint. The crystallization depended on the layer thickness of the joint and did not occur when the thin layer was less than 30 μm. Although crystallization resulted in the strengthening of the joint, the highest bending strength was obtained when the joint had a thickness of less than 30 μm. Several oxynitride glass solders were then prepared and some properties, such as thermal expansion coefficient, Vickers hardness, glass transition temperature and their wettability with Si_3N_4 were measured.

Joining of Si_3N_4 to Si_3N_4 was carried out at a temperature between 1573 and 1873 K with oxynitride glass solders. The best joint was achieved for the condition in which the solder glass penetrated slightly into the Si_3N_4 matrix and the resulting dissolution of the matrix produced a rough joined interface. A maximum bending strength of 400 MPa was obtained. This value corresponds to 73% of that for Si_3N_4 matrix and was maintained up to 1073 K.

1. INTRODUCTION

Since the strength of glass ceramics is much greater than that of glass itself, it can thus be expected that the strength of the joint with a glass will be increased by the crystallization of the glass layer of the joint. Among the huge number of investigations on Si_3N_4 joining /1/, only two papers /2,3/ report work in which the crystallization is applied to the strengthening of the joint of silicon nitride by the use of the reaction product. One /2/ utilized Si_3N_2O as the crystalline phase produced by the reaction between Si_3N_4 and SiO_2 in a glass solder of the MgO-Al_2O_3-SiO_2 system and the other /3/ used TiN which was prepared from the reaction between Si_3N_4 and TiO_2 in the solder of the CaO-SiO_2-TiO_2 system. Both reactions take place above a temperature of 1773 K. However, the utilization of the reaction product to strengthen the joint is not without difficulties, such as the need for higher temperatures, the lack of size uniformity of the reaction products, the toughness of the compound itself, and so on.

To avoid these shortcomings, the crystallization of cordierite glass has been used to join silicon nitride to silicon nitride in this paper. On the other hand, oxynitride glasses (whose composition was the same as the cordierite glass except for the nitrogen concentration) were used as the solders for comparison, since oxynitride is well known for its good mechanical properties resulting from the introduction of nitrogen into a silica network /4/.

The crystallization of cordierite glass applied to the joining of silicon nitride was not completely successful since the nitrogen from silicon nitride matrix dissolved in the solder glass. However, crystallization did result in the strengthening of the joint when the crystallization was properly achieved.

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2. EXPERIMENTAL

2.1 Sample of cordierite glass and its characteristics

The selected chemical composition of cordierite glass was 49 SiO_2 24 Al_2O_3 -20 MgO -7 ZrO_2 (mass%) with a melting point below 1673 K. A glass sample was prepared by melting mixed chemicals SiO_2, $MgCO_3$, Al_2O_3 and ZrO_2 in a Pt crucible in air. The glass for soldering was crushed into powder, sieved to under 100 mesh.

The glass transition and crystallization temperatures of the prepared glass were determined using a scanning calorimeter and the crystallized phase was identified using an x-ray diffraction technique. The thermal expansion coefficient of the glass was measured by a dilatometer. These property values are summarized in Table 1, including the chemical compositions of the glass and silicon nitride used in these experiments.

For the crystallization of the soldered layer a two-step heat treatment was applied after joining. The temperature of the first step for the nucleation of crystals was fixed at 1173, which is slightly higher than Tg. The temperature of the second step for a crystal growth process was taken as 1473 K which is much higher than Tc by ca. 150 K. After several preliminary tests, a heat treatment time of 5.4 ks was selected for the nucleation process and 1.8 ks for the crystal growth. Under these conditions, the heat treated glass crystallized to cordierite.

2.2 Oxynitride glasses and their characteristics

A part of the SiO_2 in the cordierite glass was converted to Si_3N_4 for the preparation of oxynitride glass. Using a RF furnace, all chemicals were melted together in a graphite crucible lined with BN under a nitrogen atmosphere at 1873 to 1973 K for 7.2 ks. The glass solder was prepared by crushing the glass ingot. The chemical compositions of the solder glasses including analysed nitrogen concentration are shown in Table 2; the nitrogen was analysed by an argon-carrier extraction method. Glass transition temperatures, the thermal expansion coefficients and Vickers hardness of the prepared samples were also measured. The results are shown in Table 3.

The joining temperatures were determined by measuring the contact angle between the oxynitride glass and Si_3N_4 using the sessile drop method in a temperature range of 1473 to 1873 K. Results are shown in Fig. 1 as a function of temperature. Wetting of the glass was observed above 1673 K.

2.3. Joining

The joining procedure was the same as that used in previous work /5/. The thickness of the solder layer was changed for the cordierite glass at four levels from 15 to 150 μm but was kept constant at 30 μm for the oxynitride glasses. Joining temperatures were chosen at four levels, with 100 K intervals, between 1473 and 1873 K. For cordierite glass solder, the heat treatment followed immediately after the joining process.

The joint was cut and polished both for testing the bending strength and for SEM-EDX observation. The bending strength of the joint was measured by a four-point-bending test at room temperature and by a three-point-bending test at high temperatures up to 1273 K. SEM-EDX observation was carried out near the joined interface and along the fracture surface of the joining after the bending test.

3. RESULTS AND DISCUSSION

3.1. Joining the crystallized cordierite glass

It was observed that the crystallization of a joined layer depends on the thickness of the solder layer. No crystals could be observed in the thin layers with a thickness of less than 30 μm. In the thicker layers (with a thickness of more than 30 μm), a small amount of precipitated crystals was found in the joined layer and the amount of the crystals was found to increase with increasing thickness of the layer. For example, Fig. 2 shows the SEM images of the solder layer formed between Si_3N_4 matrixes joined at 1673 K and then heat treated at 1173 K for 5.4 ks and at 1473 K for 1.8 ks, with cordierite glasses of varying thicknesses. In these photographs, the white spots are crystals of ZrO_2, added as a nucleation reagent, and the black crystals are cordierite.

Table 1
Analysed chemical composition, thermal expansion coefficient (α), bending strength (BS) and glass transition (Tg) and crystallization (Tc) temperatures of the samples

sample	chemical composition/mass %						α (323-1073K)/K	BS/MPa	Tg/K	Tc/K
	Si_3N_4	SiO_2	Al_2O_3	MgO	CaO	ZrO_2				
Si_3N_4	92		5.0	2.5	0.4		33.9×10^{-7}	468		
solder(gl)		51.2	23.3	18.6		7.0	47	115	1093	1331
solder(cry)							35	240		

Table 2
Analysed chemical composition (mass %) of oxynitride glass solders

sample	Si_3N_4	SiO_2	Al_2O_3	MgO	ZrO_2	N(batch)	N(analysed)
ON-0	0	47.7	24.9	20.8	6.8	0	0
ON-1	3.5	41.9	26.3	21.3	7.6	1.76	1.41
ON-2	7.6	38.4	24.8	19.9	7.4	3.5	3.05

Molecular forms are calculated from the analysed values of cations, oxygen and nitrogen.

Table 3
Glass transition temperature (Tg), thermal expansion coefficient (α) and Vickers hardness (Hv) of oxynitride glass solders

sample	Tg/K	α (323-1073K)/K	Hv/GPa
ON-0	1069	47×10^{-7}	6.8
ON-1	1094	41.5	7.5
ON-2	1136	35	8.2

Table 4
Estimated residual stress (σ) and elastic modulus (E) in the joints produced at 1773 K with oxynitride glass solders

sample	N /mass %	⊿α /K	E/GPa	σ /MPa
ON-0	1.4	13×10^{-7}	91.2	178
ON-1	2.3	7	95.7	100
ON-2	3.3	~0	100.7	~0

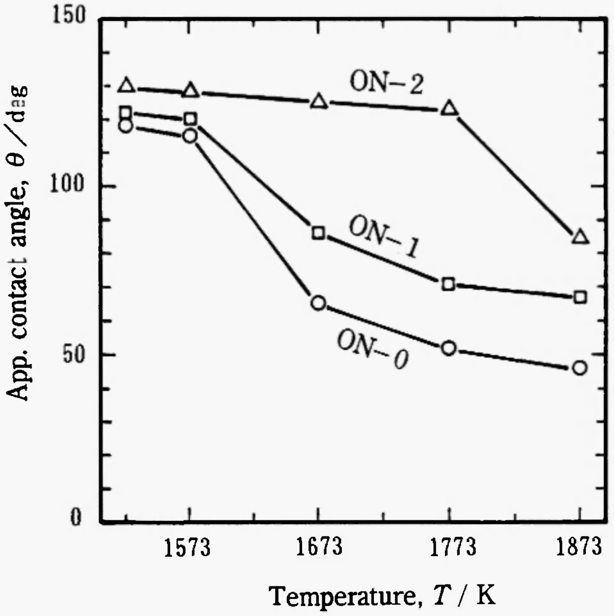


Fig. 1: Apparent contact angle between solders and silicon nitride substrate as a function of temperature.

Since the crystallization of this glass by the two-step heat treatment was perfect, the difficulty of the crystallization in these joined layers could be attributed to the effect of nitrogen dissolved into the solder layer which arose from the silicon nitride matrix during the joining. The crystallization of the cordierite glass containing nitrogen at various concentrations was then tested with the same heat treatment. Figure 3 shows the relation between the (100) intensity and the nitrogen concentration of the glasses; it is evident that the (100) intensity decreases with increasing nitrogen concentration. This suggests strongly that nitrogen hinders the crystallization of cordierite. Since the source of nitrogen is the silicon nitride matrix, then the nitrogen concentration in the solder would be expected (i) to be highest at the interface between Si_3N_4 and the solder, and (ii) to decrease with increasing distance from the interface. Thus, it is safe to conclude that the nitrogen tends to disturb the crystallization of cordierite glass.

The bending strength of the joint is shown in Fig. 4

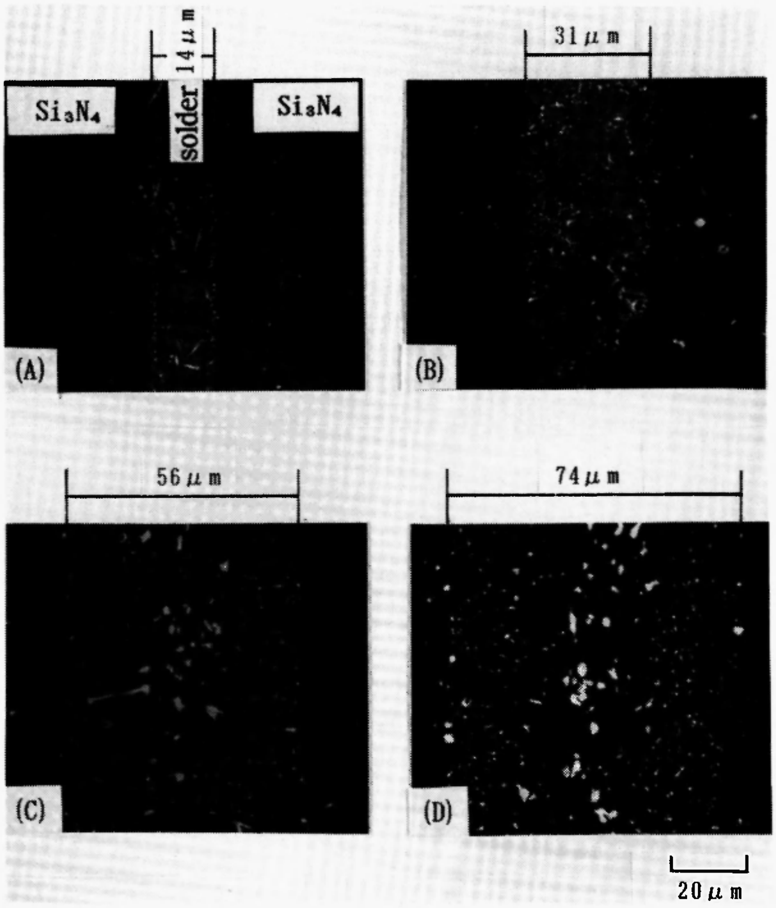


Fig. 2: SEM micrographs of the joined layer as a function of a solder layer thickness.

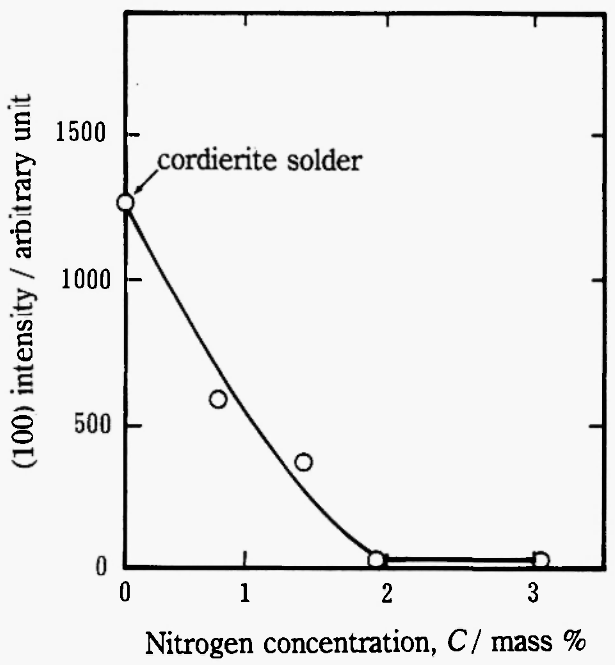


Fig. 3: (100) intensity of cordierite as a function of nitrogen concentration in the glass solder.

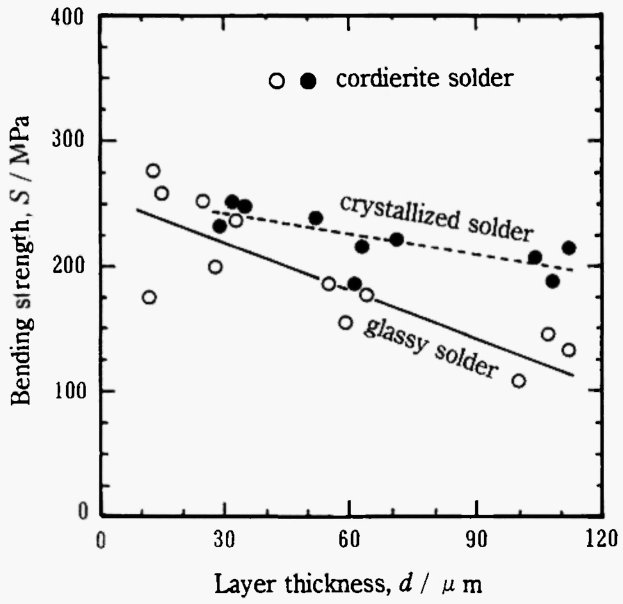


Fig. 4: Bending strength of the joint at room temperature as a function of a joined layer thickness for glassy and crystallized cordierite glass solders.

as a function of the thickness of the joined layer. It can be seen from Fig. 4 that the bending strength of the joint decreases markedly with increasing thickness of the joined layer for a joint not subjected to heat treatment but decreases only slightly for the joint where a crystallizing heat treatment was carried out. In other words, the crystallization of the joined layer was effective for the strengthening of the joint. However, since the crystallization of the joined layer was not perfect due to the dissolution of nitrogen, a joint with enough strength could not be obtained.

It is noteworthy that the highest bending strength was achieved in the thinnest solder layer tested here, though the scattering of the strength is rather large due to the difficulty in obtaining uniform spreading of the small amount of solder over the joining surface. This observation is compatible with the fact that nitrogen is known to strengthen the structure of oxide glass from the work carried out on oxynitride glasses /4/.

3.2. Joining with oxynitride glass

The bending strength of the joints produced from oxynitride glasses with different concentrations is shown in Fig. 5 as a function of the joining temperature. As shown in Fig. 1, the wetting of the solder glass on the silicon nitride substrate was poor at 1573 K but improved to good above 1673 K for the On-

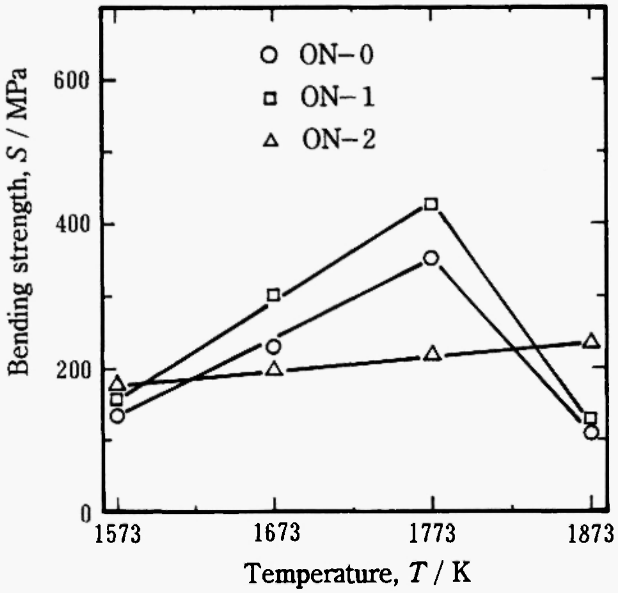


Fig. 5: Average bending strength of the joints at room temperature as a function of joining temperatures. Bending strength was taken as the mean of the results obtained on five samples.

0 and ON-1 solders. For the ON-2 solder, the wetting only started above 1873 K. The bending strength of the joints reflects these wetting conditions, the strength of the joints obtained using a joining temperature of 1673 K was found to be weak but increased with temperature for ON-0 and ON-1 solders. Figure 6 shows the change of nitrogen concentration in the joined glass layer during the joining. The increase of nitrogen concentration between 1673 and 1773 K was about 1% in ON-0 glass and about 0.6% in ON-1 glass. Since the increase of nitrogen concentration in ON-2 glass was very small, then the nitrogen concentration in ON-2 glass, about 3 mass%, may be regarded as the solubility limit in this glass. Figure 7 shows the SEM micrographs of the interfaces of the joint with three kinds of oxynitride glass solders. In Fig. 7A and 7B, the very rough interface and a glass-penetrated region in the matrix can be observed. On the other hand, Fig. 7C shows a relatively smooth interface which indicates that there was little dissolution of nitrogen from the matrix. This observation is consistent with both the change of nitrogen shown in Fig. 6 and the behaviour of the apparent contact angle shown in Fig. 1.

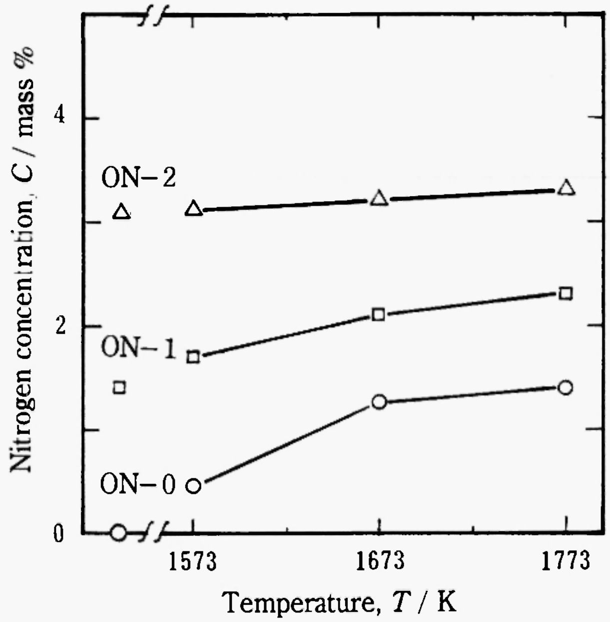
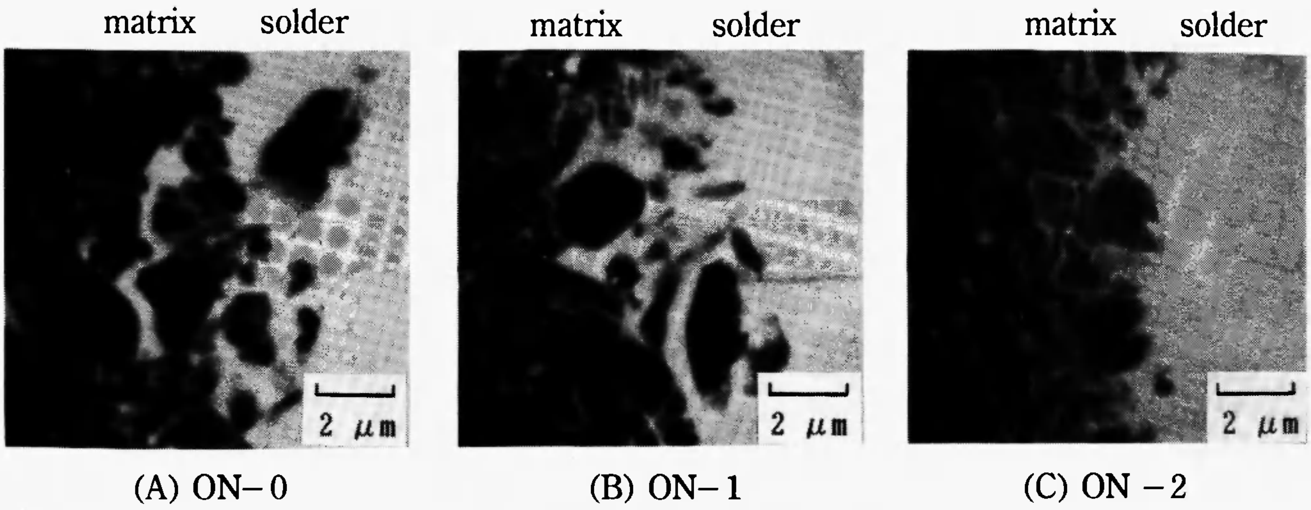


Fig. 6: Change of nitrogen concentration in the solder layer as a function of joining temperatures.

Inspection of Fig. 5 indicates that the origin of the increase of the joint strength can be attributed to two factors: (1) strengthening of the solder glass itself resulting from the dissolution of nitrogen (as shown by the increase of Tg and Hv with nitrogen concentration in Table 2) and (2) the anchor effect of the penetrated solder into the matrix with a rough interface. Both factors explain the increase of the bending strength up to a joined temperature of 1773 K.

Residual stress in the joint is also an important factor for the soundness of the joint. Consequently, this parameter was estimated by using the following equations which are based on the thermal expansion coefficients listed in Table 3:



(A) ON−0 (B) ON−1 (C) ON −2

Fig. 7: SEM micrographs of the interface between silicon nitride matrix and oxynitride solder glass joined for 1.2 ks at 1773 K.

$$\sigma = E\varepsilon$$
$$\varepsilon = \Delta\alpha\Delta T$$

where σ is a residual stress at the interface, E is elastic modulus of the glass, ε is strain resulting from the differences in expansion coefficients of glass and matrix, $\Delta\alpha$ is the difference of the thermal expansion coefficients, and ΔT is a temperature difference between joining and room temperatures.

A value of $E = 5.085 \times [\text{mass\%N}] + 84.2$ was used for oxynitride glass for the Si-Al-Mg-O system, as given by Homeny and McGarry /6/. Table 4 shows the results of the calculation. The fact that the residual stress of ON-0 glass is much larger than that of ON-1 glass may partially interpret the relative weakness of the bending strength of the joint with ON-0 solder when compared with that for ON-1 solder.

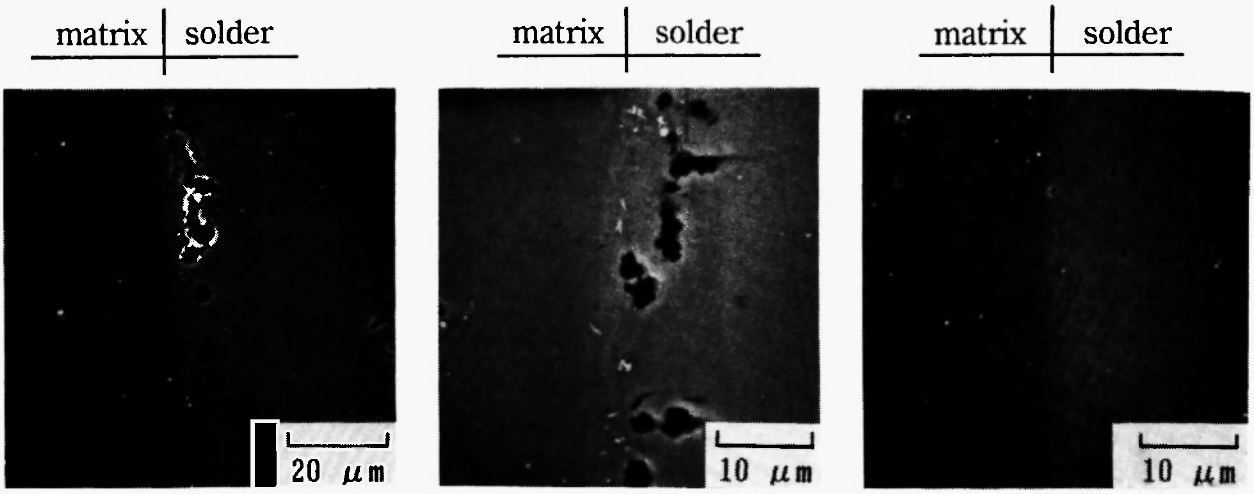
A decrease in bending strength at 1873 K is caused by void formation, as shown in Fig. 8. Large voids, about 10 and 2 ~ 5 μm in diameter, were formed in front of the joined interface at a joining temperature of 1873 K with ON-0 and ON-1 solders, respectively. These voids were probably produced by reactions such as:

$$Si_3N_4 + 3MgO \rightarrow 3SiO(g) + 3Mg(g) + 3N_2(g)$$
$$Si_3N_4 + 3SiO_2 \rightarrow 6SiO(g) + 2N_2(g)$$

These generated voids will make the joint fragile as shown in Fig. 5.

3.3. Bending strength at high temperatures

Bending strength at high temperatures is shown in Fig. 9 where the bending strengths of (i) Si_3N_4, (ii) Si_3N_4 joined with ON-1 solder and (iii) joined with the crystallized cordierite glass are plotted against temperature. As can be seen from Fig. 9, the joint formed with ON-1 glass lost its strength at 1273 K which is little higher than Tg of this oxynitride glass. However, the crystallized joint kept its strength up to 1373 K, although the strength gradually decreased from 1273 K. It was shown that the crystallization of the solder layer is an effective way of keeping the strength at temperatures above Tg even though the absolute value of the strength at room temperature is much smaller than that joined with ON-1 glass. Since there was no good way of controlling the crystallization of the joint in this experiment, further improvement of joining by crystallization was not performed. However, further investigations to find the optimum conditions for crystallization of oxynitride glass to provide the high temperature use of a joint beyond Tg temperature would be worthwhile.



(A) ON–0 (B) ON–1 (C) ON–2

Fig. 8: SEM micrographs of the joint interfaces obtained for 1.2 ks at 1873 K with oxynitride glass solders.

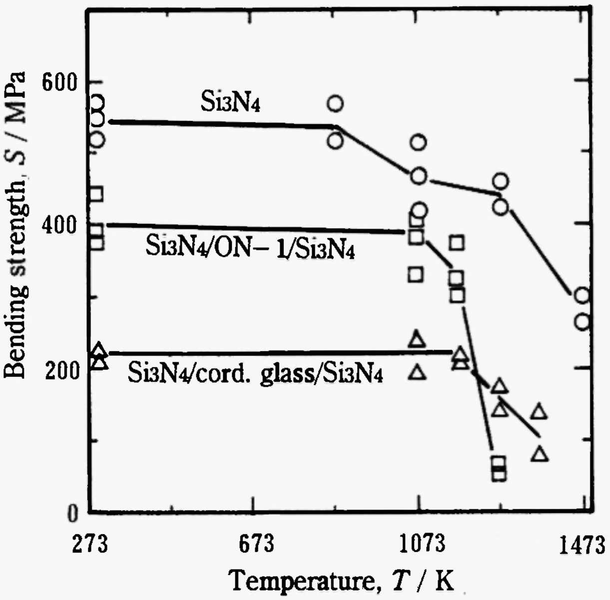


Fig. 9: Bending strength of the joint at high temperatures.

4. CONCLUSION

Two kinds of experiments have been carried out for the joining of Si_3N_4 to Si_3N_4. One involved joining with a crystallized cordierite glass and the other joining with oxynitride glasses having different nitrogen concentrations. Crystallization of the cordierite glass after joining to silicon nitride was not completely successful due to the dissolution of nitrogen into the glass solder layer from the silicon nitride matrix during the joining. Although strengthening of the joint by the crystallization could be observed, the strongest joint was achieved by the thinner solder layer with a thickness of 30 μm containing dissolved nitrogen.

The joining of silicon nitrides was carried out with oxynitride glasses whose composition was based on the cordierite composition containing nitrogen at two levels. The bending strengths of the joints were measured both at room and high temperatures and SEM observations of the joined interface and of the fracture surface were carried out. The best joining was obtained for the conditions where suitable penetration of the solder glass into the silicon nitride matrix occurred and the dissolution of the silicon nitride resulted in a rough interface between the matrix and the solder. A maximum bending strength of 400 MPa when tested at room temperature was recorded for a joint produced at 1773 K with 2.35 N containing oxynitride glass solder and this strength was maintained up to 1073 K, which is slightly below the glass transition temperature of this solder.

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