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Evaluation of Si_3N_4 joints: bond strength and microstructure

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Joining of pressurelessly sintered silicon nitride ceramics was carried out using adhesive slurries in the system Y-Si-Al-O-N in a nitriding atmosphere. The effects of bonding parameters, such as joining temperature (1450–1650 °C), applied pressure (0–5 MPa) and holding time (10–60 min), on the bond strength of joint were evaluated. A typical microstructure of the joint bonded with the optimum adhesive was investigated. The three point bend testing of joined samples with $3 \times 4 \times 36$ mm^3 in dimension was employed to study the bond strength of joints. The results show that an optimum joining process was achieved by holding at 1600 °C for 30 min under an external pressure of 5 MPa and the maximum bond strength was 550 MPa, compared to 700 MPa of unbonded Si_3N_4 ceramic, using the adhesive having the $Si_3N_4/(Y_2O_3 + SiO_2 + Al_2O_3)$ ratio of 0.39. The good bond strength is attributed to the similarity in microstructure and chemical composition between joint zone and ceramic substrate. The fracture modes were classified into two types according to the values of bond strength. © *1999 Kluwer Academic Publishers*

1. Introduction

Structural ceramics joining has been rapidly developed within decades as a new technology to widen the industrial application of structural ceramics. Silicon nitride, because of its superior mechanical properties, is required for advanced structural applications such as heat engines and gas turbines. Joining of Si_3N_4 is a necessary processing step to form complex or larger shapes, or form the attachment of the ceramic to other metal components to produce a good structural integrity.

Of many methods used for joining Si_3N_4, active metal brazing and diffusion bonding have been extensively attracted [1–4]. Recently, PTLPB method for joining Si_3N_4 ceramics is being developed at Berkeley [5, 6]. In general, filler materials might be metals, alloys and glasses [7–22]. Some of these joins have exhibited good bond strength at room temperature, however, the microstructure or nature of the joined layer is greatly different from that of silicon nitride, which (1) introduced thermal cracks in the joint owing to mismatched thermal expansion coefficient; (2) degraded the anti-corrosion ability of the joint, meanwhile, high temperature applications are limited by the lower melt point of the braze. Consequently, using these techniques to join Si_3N_4 to Si_3N_4 greatly affects the attractive materials properties inherent in Si_3N_4 ceramics. Ideally, the joint must have similar material properties and mechanical behavior to unbonded ceramics to be of interest for room-temperature or high-temperature structural applications. To avoid the problems resulting from the dissimilar nature of interlayer and adherend, Bates [23] developed a technique which consisted of joining green parts, using an interlayer of the same nominal composition as the green adherend pieces, followed by codensification of the aggregate body. Although, the results were encouraging and promising, the fabrication cost greatly increased due to the use of hot isostatic pressing(HIP) technique.

Wall [24] successfully joined sialon pieces to make large complex components using β-sialon-glass composite adhesives. The author pointed out that an optimum joint strength could be obtained when using an adhesive with appropriate ratio of β-sialon to glass and that the joint exhibited similar nature of adherend materials. Similarity, in the present study, joining of pressurelessly sintered Si_3N_4 ceramics was conducted using glass-ceramic adhesives in the system Y-Si-Al-O-N as insert interlayer, selected for their superior high temperature performance. The work presented here describes the joining methodology, and the microstructure of these joints, related to bond strength.

2. Experimental produce

2.1. Materials

Samples of silicon nitride, with $20 \times 20 \times 8$ mm^3 in dimension, were prepared by pressurelessly sintering at 1820 °C for 1 h. The sintered density was 3.22 g cm^{-3} as measured by Archimedes' method using distilled water, and the bend strength of Si_3N_4 was about 700 MPa evaluated by three-point method. The chemical composition of the filler materials is listed in Table I.

For the preparation of adhesives, appropriate amounts of α-Si_3N_4, Y_2O_3, SiO_2 and Al_2O_3 were mixed in alcohol with Si_3N_4 balls in a plastic jar for 24 h. The mixture was then dried and blended with water-free alcohol to form a homogenous slurry.

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TABLE I Chemical compositions of adhesives

Adhesive	Composition (mol %)				Ratio[a]
	Y_2O_3	Al_2O_3	SiO_2	Si_3N_4	
A	20	20	60	0	0
B	20	20	56	4	0.04
C	31	12	34	23	0.30
D	25	15	32	28	0.39
E	22	17	16	45	0.82

[a]Ratio = $Si_3N_4/(Y_2O_3 + Al_2O_3 + SiO_2)$.

2.2. Joining

The contacting surfaces of the Si_3N_4 substrates were roughly polished using 280 grit SiC, and prior to joining, the samples were ultrasonically cleaned in an acetone bath. The slurry was applied on the surfaces to be joined and an assembly was developed by hand. Joints were usually made by heating in nitriding atmosphere for 30 min at 1600 °C, although temperature ranged from 1450 to 1650 °C and the external pressures from 0 to 5 MPa. The assemblies to be joined were heated at a rate of 10 °C min^{-1} to a fixed temperature then furnace cooled after holding for a desired time.

2.3. Evaluation of strength

The bond strength with adhesive composition, joining temperature, holding time and applied pressure was evaluated by three-point bending test with an Instron-type test machine 1195 at a displacement rate of 0.5 mm min^{-1}. The size of test bars was $3 \times 4 \times 36\ mm^3$. For each test, six specimens were measured.

2.4. Microstructural characterization

Microstructural observations were conducted by a scanning electron microscope (SEM, Shimadzu EPMA-8705QH) equipped with an electron probe microanalyser (EPMA). The microstructures and chemical analyses of the interfacial region were investigated using a transmission electron microscope (TEM, JEM-200CX) and energy dispersive microanalyser (EDX). Reaction products of the fracture surface were identified with an X-ray diffractometer (XRD, D/max-ra).

3. Results

3.1. Adhesive composition

In our previous paper [25], we investigated the effect of adhesive composition on the bond strength of the joints, as seen in Fig. 1. Note that the bond strength increased obviously with the increment of Si_3N_4 concentration in the adhesive, which is up to the maximum bond strength of 550 MPa when the ratio reaches 0.39. Then, there is a drop in strength when the Si_3N_4 content further improves.

3.2. Joining temperature

Fig. 2 shows the effect of joining temperature on the strength. From Fig. 2, we know that the relationship between the joining temperature and bond strength is different for various adhesive composition. At temperatures below 1600 °C, the bond strength improves with the increasing temperature both for the different adhesives, when the temperature is above 1600 °C, the strength of the joint bonded using adhesive B decreases sharply, while for adhesive D, the strength of the joint still increases with increasing temperature.

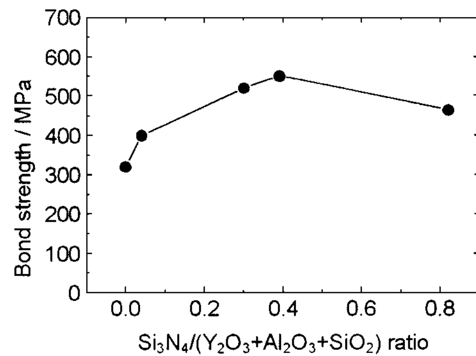


Figure 1 Effect of adhesive composition on the bond strength of joints. Joining condition: joining temperature, 1600 °C; holding time, 30 min; joining pressure, 5 MPa.

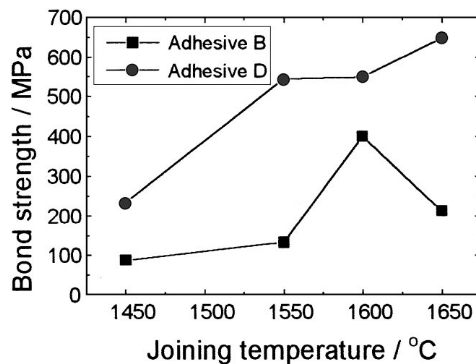


Figure 2 Relation between the average bond strength and the bonding temperature. Joining condition: holding time, 30 min; joining pressure, 5 MPa.

3.3. Applied pressure

Fig. 3 shows the effect of applied joining pressure on the bond strength. As seen in the figure, the bond strength of the joints increases greatly with increasing external pressure. However, the degree of compressive

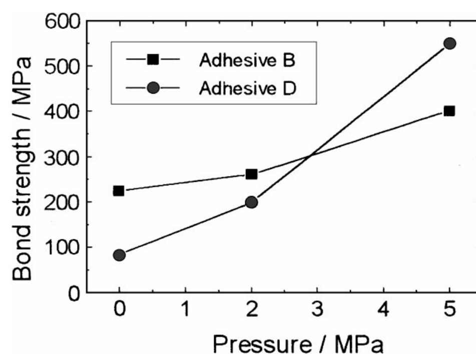


Figure 3 Effect of joining pressure on the bond strength. Joining condition: joining temperature, 1600 °C; holding time, 30 min.

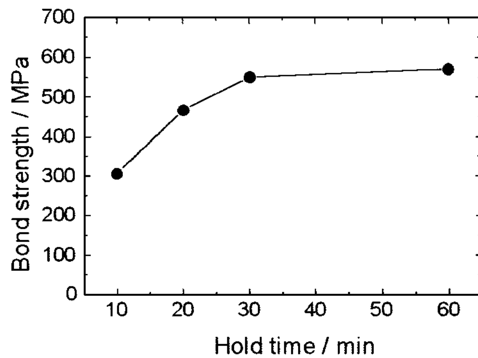


Figure 4 Effect of holding time on the bond strength. Joining condition: joining temperature, 1600 °C; joining pressure, 5 MPa.

deformation increases as the pressure improves. Using a 5 MPa bonding pressure a 2.5% reduction in the height of the sample was observed. At higher bonding pressure, the amount of deformation became even larger.

3.4. Holding time

Fig. 4 shows the effect of holding time on the strength. It is clearly seen from the figure that the bond strength increases with increasing holding time, but there is a little change in strength when the holding time is over 30 min. It is then considered that holding time in excess of 30 min is sufficient to a strong joint.

3.5. Microhardness

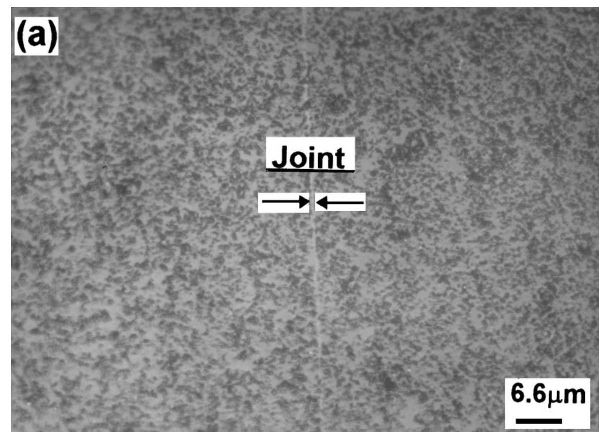
Table II lists the result of hardness test of samples joined using adhesive D at 1600 °C for 30 min under a pressure of 5 MPa. The hardness is lower for indentations made in the parent β-Si_3N_4 than that in the joint, even lower at the vicinity of the interface. This means that (1) the glass has been nearly exhausted during the joining process and (2) the joint has more denser microstructure than the parent Si_3N_4 ceramic.

4. Discussion

4.1. Bonding parameter

As the results mentioned above, we know that except for adhesive composition, the bonding parameters such as joining temperature, applied pressure and holding time, play key roles in the mechanical properties of joints. It is well known that the eutectic temperature in the system of Y-Si-Al-O-N is around 1350 °C [26], therefore, the joining temperature should be higher than this to form liquid phase. At lower temperature, the adhesive can not melt completely and its viscosity is so high that the chemical reaction between the adhesive and ceramic is not vigorous, then the bond strength is not strong. With increasing the temperature, adhesive B forms a pure oxynitride glass liquid, and adhesive D which originally contains a large amount of α-Si_3N_4 ingredient becomes a mixture of solid phases (α-Si_3N_4, β-Si_3N_4) and glass liquid. At 1600 °C, the joined sample with adhesive B exhibits a maximum bond strength of 401 MPa on average. At still higher temperature, the viscosity of adhesive B becomes very small, and the liquid joining composition drains into the Si_3N_4 and/or flows out of the joint [27, 28], in addition, vaporization of liquid glass occurs. Therefore, little joining composition remains between two Si_3N_4 ceramics, resulting in a very thin joint (see Fig. 5a), thus, the strength degradation is probably caused by the incomplete solder coverage of Si_3N_4. While for adhesive D, the joining process is more like sintering process due to the large amount of Si_3N_4 in the adhesive, consequently, higher temperatures enhance the densification of the joined layer which in turn improves the bond strength. The upper limit temperature is limited by the decomposition of Si_3N_4 and the vaporization of the liquid phase, which should be below 1650 °C.

Applied pressure is an another process parameter. Kanzaki *et al.* [29] reported that the bond strength of joints by direct diffusion bonding at 20 MPa and 1873 K was 540 MPa, compared with that of 360 MPa of the joint bonded without pressure. The effect of pressure



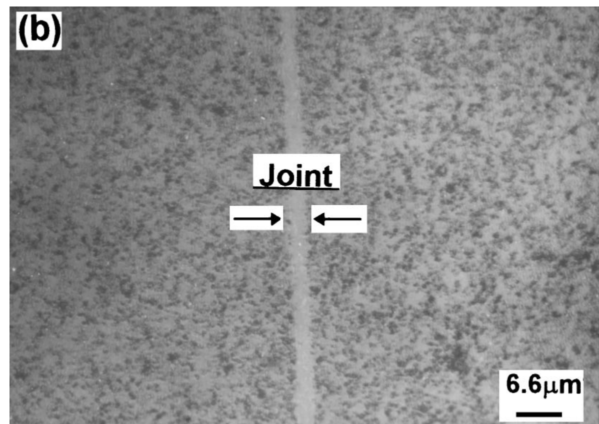


Figure 5 Optical microscopies of joined Si_3N_4: (a) adhesive B, (b) adhesive D. Joining condition : joining temperature, 1600 °C; holding time, 30 min; joining pressure, 5 MPa.

TABLE II Result of hardness test of joined sample (Load 100 g)

Location	Hardness (GPa)		
	Min.	Max.	Aver.
Si_3N_4 substrate	17.2	18.2	17.9
Joint zone	21.4	22.9	22.0

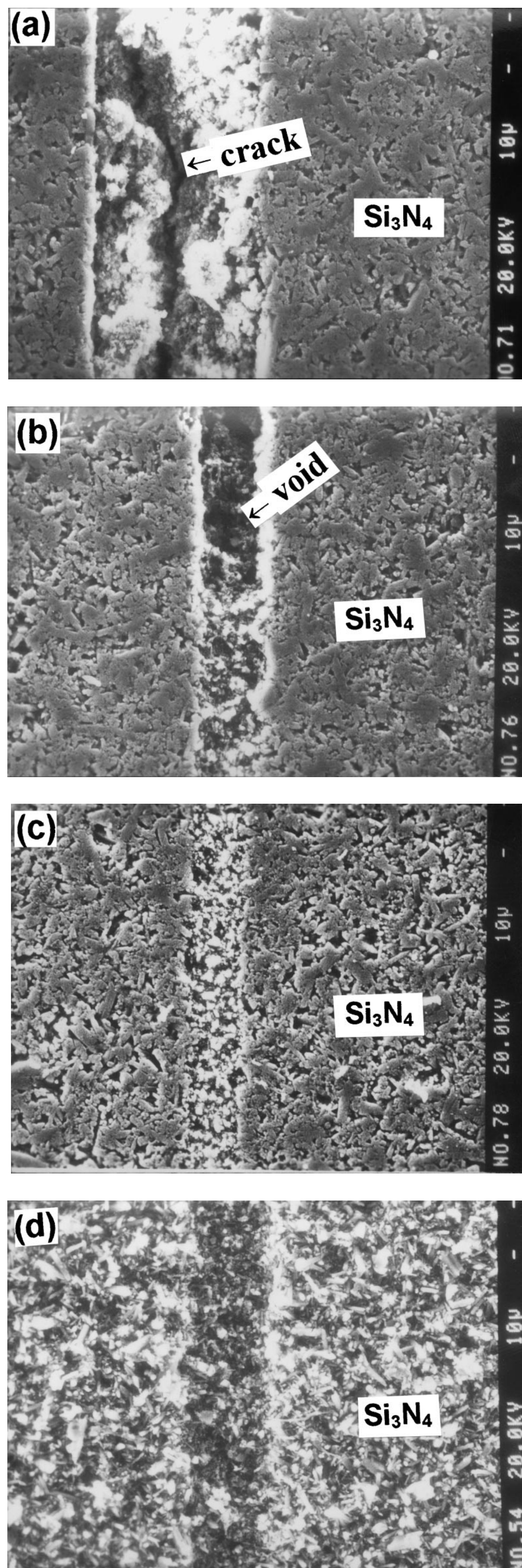


Figure 6 Microstructures at bonding interface in specimens joined with adhesive D. (a) 1450 °C, 30 min, 5 MPa (b) 1600 °C, 30 min, without pressure (c) 1600 °C, 30 min, 2 MPa (d) 1600 °C, 30 min, 5 MPa.

is then clearly deduced from that experimental results. Fig. 6 shows the microstructures of joints bonded with various pressures. As seen from the figure, without applied pressure, large voids were observed in the joint, but the joint is dense when a small uniaxial joining pressure of 2 MPa is applied. Accordingly, the external pressure, acting as a force to achieve close contact at the interface, has shown a positive effect on the even spreading of the highly viscous adhesive, promotes the densification and the elimination of voids in the joint, the bond strength increases correspondingly. On the other hand, higher pressure can cause the deformation of the joined body, this should be avoided.

A long holding time can be beneficial to the out-diffusion of liquid joining composition into the adjacent parent Si_3N_4 material, resulting in the densification of the joint.

In general, optimization can be achieved through manipulation of the joining temperature, holding time, and applied pressure. In this paper, optimal strength for the joints ($543 < \delta < 650$ MPa) is achieved by joining at high temperature ($1550 < T < 1650$ °C) for 30 min under an external pressure of 5 MPa when adhesive D is applied.

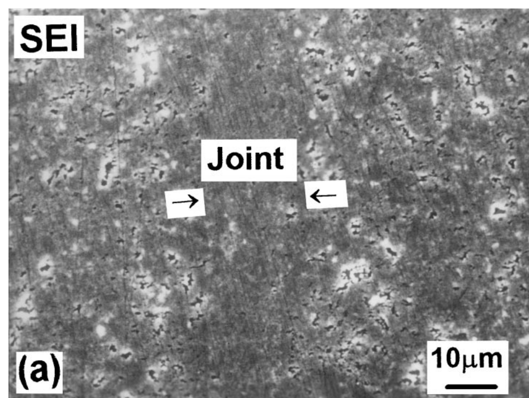
4.2. Microstructure of joints

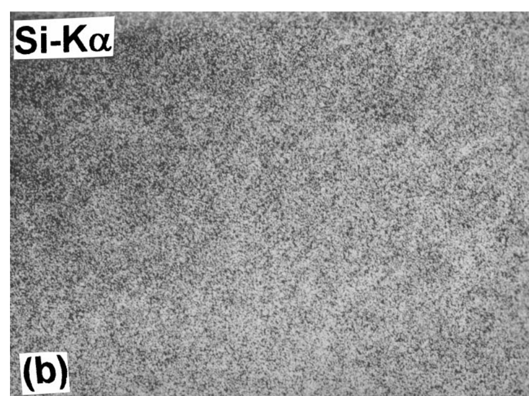
Fig. 7 shows the secondary electron image (SEI) and area elemental distribution of joined Si_3N_4 with adhesive D at 1600 °C for 30 min under a pressure of 5 MPa. The concentration distribution of Si element is uniform across the whole sectioned surface, however, the elements Y and Al are enriched at the Si_3N_4/interlayer interface. This indicates that (1) the diffusion of elements is obvious during the joining process and beneficial to enhancement of the bond strength, (2) the amount of glass is slight higher in the joint zone, especially at the vicinity of the interface.

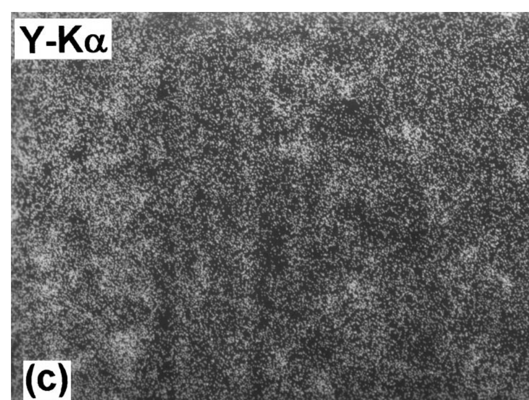
Fig. 8 shows the interfacial morphology of the joint etched in molten NaOH. From Fig. 8 the following points can be made. (1) The boundary between the parent Si_3N_4 and the newly formed material in the joint is not easy to distinguish. (2) The grains in the joint have a small grain size than those in the parent Si_3N_4. Moreover, there has been a high degree of intergrowth of the β-Si_3N_4 grown within the joint with that in the parent Si_3N_4 ceramic. (3) the main crystalline phase in the joined layer is consisted of elongated β-Si_3N_4, indicating that the transformation of α-Si_3N_4 to β-Si_3N_4 is completed during joining process, and β-Si_3N_4 grains in the joint develop well.

Fig. 9 shows the results of SEM and EDX analysis. Note that there is no appreciable difference in chemical composition between the joining zone (including grains and grain boundaries) and the original body. This is consistent well with Fig. 7. Therefore, the properties of the joint are not so different from those of the parent material due to the similarity in microstructure and composition between the joint and adherend.

The joinining process is summarized in the following. For joining with adhesives containing a small amount of α-Si_3N_4 powder, when the joining temperature is over the eutectic temperature (about 1350 °C) of Y-Si-Al-O-N system, the oxide components of the adhesive react and form a pure liquid glass [8], the glass flows to wet the substrate and so-called liquid phase







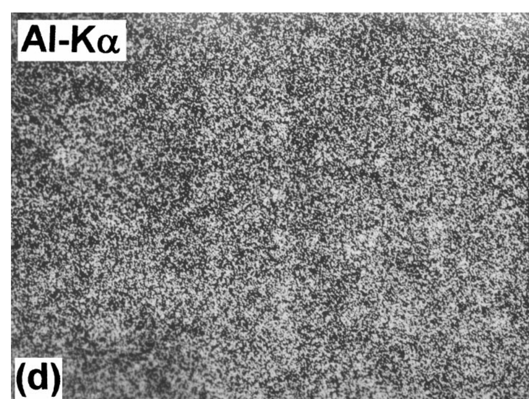


Figure 7 SEM image and area elemental distribution at the interface of Si_3N_4/Si_3N_4 sample joined with adhesive D. Joining condition: joining temperature, 1600 °C; holding time, 30 min; joining pressure, 5 MPa.

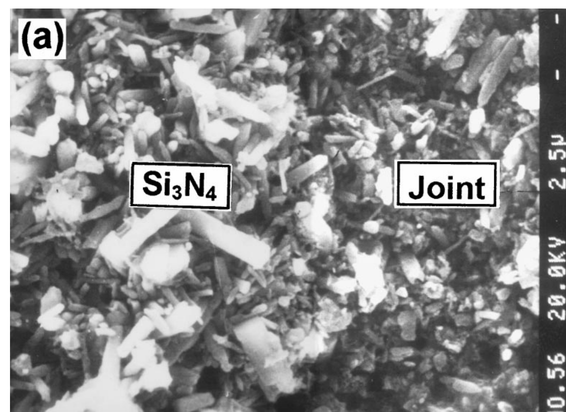


Figure 8 Interfacial morphology of the joint bonded with adhesive D: (a) sample etched in molten NaOH, (b) well developed β-Si_3N_4 grains in the joint. Joining condition: joining temperature, 1600 °C; holding time, 30 min; joining pressure, 5 MPa.

bonding proceeds. The molten glass dissolves the β-Si_3N_4 grains at the areas of contact and penetrates the Si_3N_4 ceramic, followed by crystallization of H phase (discuss later) from the liquid. An intimate bond is thus formed by the capillary force of the glass layer. For joining with adhesives containing a large amount of α-Si_3N_4 powder, in the initial stage of bonding process, the liquid glass is formed as described above, but α-Si_3N_4 does not react with the liquid until the joining temperature exceeds 1450 °C. As the temperature further increases, that is up to 1600 °C, α-Si_3N_4 is dissolved by the liquid followed by the precipitation of β-Si_3N_4 when the nitrogen and silicon content of the liquid reaches saturation, this process is somewhat like the liquid phase sintering of Si_3N_4. The newly formed β-Si_3N_4 grains grows across the joint and forms a network with the β-Si_3N_4 in the parent material which is contacting the joint, therefore, a sound joint is developed.

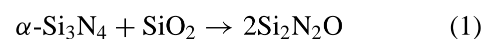
4.3. Fracture behavior

The fracture modes of the joined body can be classified into two types according to Fig. 10. Mode I, for strong bonds, fracture initiated near the interface, then the propagating crack deflected away from the joint and propagated within the Si_3N_4 somewhat parallel to the interface, as shown in Fig. 10b, fracture occurred directly in the parent Si_3N_4 ceramic especially for a stronger joint, as shown in Fig. 10a. Mode II, in case of low-strength joints, however, cracks started at the joint interface and the fracture path moved abruptly across the joint from one side to the other (see Fig. 10c and d),

Figure 9 TEM of joined sample bonded with adhesive D and corresponding EDX analysis, TEM for (a) joint (b) parent Si_3N_4, EDX results for (c) β-Si_3N_4 in the adherend material (d) β-Si_3N_4 in the joint (e) intergranual glassy phase in the adherend material (f) intergranual glassy phase in the joint.

which could imply that the critical crack propagation is difficult and that a number of defects with nearly critical size do exist. Therefore, it is considered that, under the same joining condition, adhesive composition plays a key role in the residual stress level and distribution in the joint, which in turn influences the fracture behavior.

XRD analysis on fracture surfaces exposes the phases present in the joints, as shown in Fig. 11. When the sample joined using adhesive B, two main crystalline phases are identified as β-Si_3N_4 and N-apatite $Y_{10}[SiO_4]_6N_2$ (H phase), while in case of adhesive D only peaks of β-Si_3N_4 are identified. "H" phase is formed by the possible reaction as follows [30]:



$$\alpha\text{-}Si_3N_4 + SiO_2 \rightarrow 2Si_2N_2O \quad (1)$$

$$9Si_2N_2O + 5Y_2O_3 \rightarrow Y_{10}[SiO_4]_6N_2 + 4\beta\text{-}Si_3N_4 \quad (2)$$

The peaks of β-Si_3N_4 are part from the parent Si_3N_4 ceramic and part from the newly formed Si_3N_4 grains in

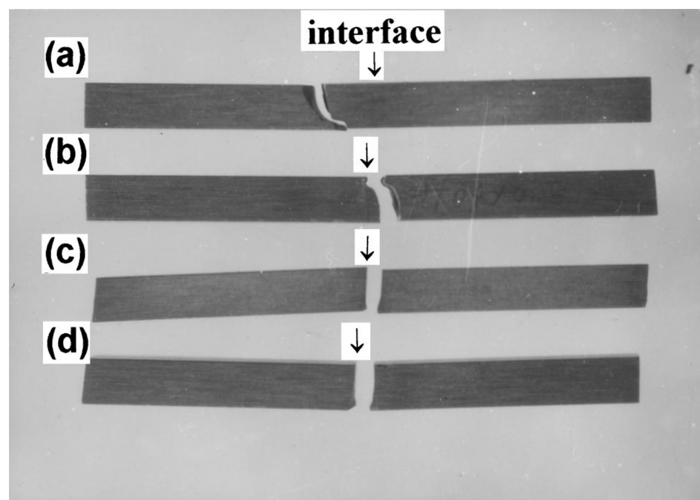


Figure 10 Optical microscopy of broken joined samples indicating two types of fracture modes: (a) adhesive D 594 MPa, (b) adhesive D 549 MPa, (c) adhesive B 420 MPa, (d) adhesive E 350 MPa.

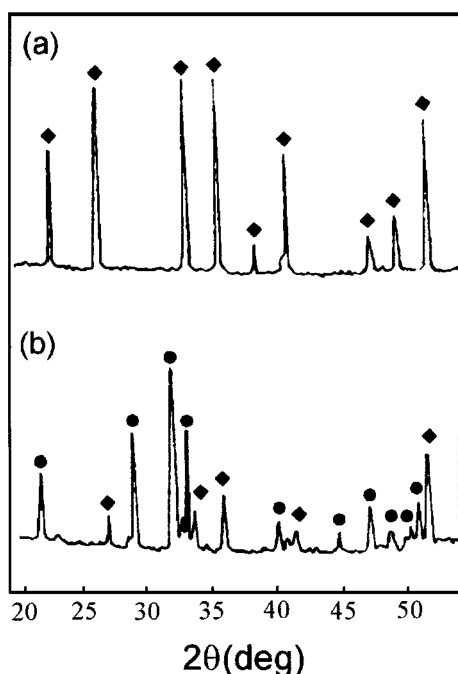


Figure 11 X-ray diffraction of the fracture surface of Si_3N_4/Si_3N_4 joint broken at the interface: (a) adhesive B, (b) adhesive D. Joining condition: joining temperature, 1600 °C; holding time, 30 min; joining pressure, 5 MPa. ◆ **H**, ● β-$\mathbf{Si_3N_4}$.

the joint during joining process. From the XRD result, it is further confirmed that the good joint strength (corresponding to fracture mode I) of samples joined using adhesive D is attributed to the similar microstructure and composition between the joint and parent Si_3N_4 ceramic.

5. Conclusion

The bond strength and microstructure of Si_3N_4/Si_3N_4 joints joined with the adhesive in the system Y-Si-Al-O-N under various joining conditions have been reported. The main results are:

1. Appropriate adhesive in the system Y-Si-Al-O-N could be used to produce Si_3N_4/Si_3N_4 joints with high bond strength. A maximum bond strength of 550 MPa, approximately 80% of that of monolithic Si_3N_4 ceramic, was obtained when an optimum joining process was achieved by holding at 1600 °C for 30 min under an applied pressure of 5 MPa, using adhesive with its ratio of $Si_3N_4/(Y_2O_3 + SiO_2 + Al_2O_3)$ reaching 0.39.
2. Similarity in microstructure and chemical composition between joint zone and ceramic substrate was produced during the joining process which was analogous to sintering process, leading to an imitate, strong and satisfying bond.
3. Fractographic evidence showed that fracture behavior depended on the bond strength of the joined samples or the residual stress level in the joint zone.

Since the nature of the joined layer is very similar to and the bond strength of the joint is approaching to that of the monolithic silicon nitride ceramic when using adhesive D as insert materials, it can be expected that the joint is refractory enough for high temperature applications. Further work on evaluation of the heat and oxidation resistance of the joined body will be reported in near future.

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