PII: S0955-2219(97)00189-2

Effects of Adhesive Composition on Bond Strength of Joined Silicon Nitride Ceramics

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Abstract

Pressureless sintered silicon nitride ceramics were joined at 1600°C for 30 min under an external pressure of 5 MPa by using mixed powders slurries composed of Y_2O_3, Al_2O_3, SiO_2 and Si_3N_4. The effects of $Si_3N_4/(Y_2O_3 + Al_2O_3 + SiO_2)$ ratio of the adhesive on the bond strength of the joints were investigated. The results showed that the bond strength improved with increasing $Si_3N_4/(Y_2O_3 + Al_2O_3 + SiO_2)$ ratio of the adhesive, because the thermal expansion coefficient of the adhesive was reduced and the nitridation reactions in the adhesive were accelerated by the addition of silicon nitride powders. However, when the silicon nitride content further increased, the bond strength decreased due to the increasing viscosity of the adhesive which had negative effects on the wetting and spreading characteristic of the adhesive. A maximum bond strength of 550 MPa was obtained by joining with an adhesive with the ratio of 0·39; under the experimental conditions, the grain size of the acicular β-Si_3N_4 grains grown in the joint was smaller than those in the joined ceramic. © 1998 Elsevier Science Limited. All rights reserved

1 Introduction

Among structural advanced ceramics, silicon nitride is considered as an important ceramic material for its excellent high temperature strength, resistance to wear and oxidation. In order to widen its applications, it is essential to develop reliable technologies to join this ceramic. At present, two promising methods for joining silicon nitride ceramics are brazing and diffusion bonding.[1] The filler materials can be metals, alloys or glasses,[2] how-ever, the strength of the joints at elevated temperature is rather low because of the relatively low softening temperature of the most commonly used alloy interlayer materials. For materials joined with pure glass, they are more likely to break at the joint due to the low resistance to crack propagation of the layer of glass.[3] So, it is very important to select suitable adhesives for obtaining ceramic joints with high strength at elevated temperatures.

Compared to the oxide glass, oxynitride glass shows much better high temperature performance and higher transition temperature, and its coefficient of thermal expansion slightly decreases with increasing nitrogen content.[4–6] Moreover, silicon nitride ceramics usually contain a small amount of grain boundary glassy phase which belongs to Y–Si–Al–O–N system; thus, suitable oxynitride glasses with the same chemical compositions as those found in the silicon nitride ceramics can be expected to become new adhesives for effectively joining Si_3N_4-based ceramics. Some results of successfully joining silicon nitride ceramics by using oxynitride glasses have been reported.[7–14]

The main purpose of this work is to develop adhesives in the Y_2O_3–Al_2O_3–SiO_2–Si_3N_4 system for joining silicon nitride ceramics. The interlayer material developed possesses a thermal expansion coefficient closely matched to Si_3N_4 and the joints formed have a microstructure similar to that of the ceramics joined. Experimental results of joining silicon nitride ceramics by using five kinds of adhesives with different $Si_3N_4/(Y_2O_3 + Al_2O_3 + SiO_2)$ ratios are described.

2 Experimental Procedures

2.1 Materials
Pressureless sintered silicon nitride doped with Y_2O_3 and Al_2O_3 was chosen for the bonding trials. Samples were cut into $20 \times 20 \times 8$ mm plates, and prior to joining, these plates were polished with 280

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mesh SiC abrasive and then ultrasonically cleaned in acetone.

Five adhesive materials, A, B, C, D and E, were prepared from Si_3N_4 (made in-house, 90% α-phase, 0·56 μm), Y_2O_3 (99·5%, Shanghai Yulong Chemical Factory), Al_2O_3 (99·5%, Suzhou Chemical Factory) and SiO_2 (99·5%, Shanghai Reagent Factory) powders using ball-milling techniques. Adhesives with $Si_3N_4/(Y_2O_3 + Al_2O_3 + SiO_2)$ ratios varied from 0 to 0·82 were prepared as listed in Table 1.

2.2 Joining method

The schematic illustration of the joining procedure is shown in Fig. 1. The mixed powder paste was painted on one side (20×8 mm) of the surface of each Si_3N_4 plate to give a sufficient adhesive coating density (10 mg cm^{-2}). After drying, the adhesive was sandwiched between Si_3N_4 plates, and the assembly was placed into a graphite resistance furnace, then heated to 1600°C with heating rate of 10°C min^{-1} for 30 min in a nitrogen atmosphere (99·5 vol% N_2). An external pressure of 5 MPa was applied to aid the joining process.

2.3 Bond strength

The joined plates were cut into test bars approximately 3×4×36 mm with the joint in the center of the test bar. A 3-point bending test was conducted at room temperature (RT) using a testing machine (Instron 1195). The span of specimens was 30 mm, and the crosshead speed was 0·5 mm min^{-1}.

2.4 Microstructural analysis

Joined specimens were sectioned perpendicular to the joint interface, and microstructural examination of the interface was done using optical microscope (OM) and scanning electron microscopy (SEM).

3 Results and Discussion

3.1 Wetting and spreading

In the Y–Si–Al–O–N system the eutectic temperature lies at approximately 1350°C,[15] hence, the adhesive will certainly melt at the bonding temperature of

Table 1. Chemical composition of adhesives

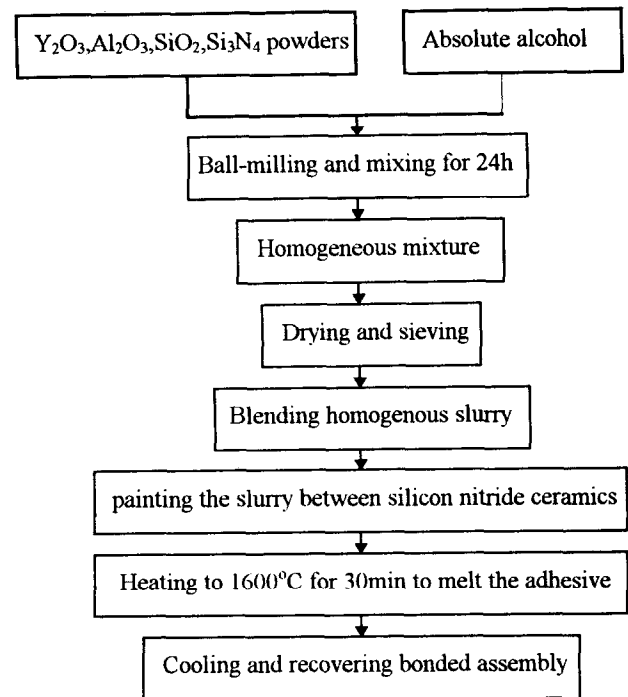| Adhesive	Composition (mol%)				Ratio^a
	Y_2O_3	Al_2O_3	SiO_2	Si_3N_4	
A	20	20	60	0	0
B	20	20	56	4	0·04
C	31	12	34	23	0·30
D	25	15	32	28	0·39
E	22	17	16	45	0·82

^{a}Ratio = $Si_3N_4/(Y_2O_3 + Al_2O_3 + SiO_2)$.

Fig. 1. Schematic illustration of the joining procedure of the silicon nitride ceramics.

1600°C. Wetting and spreading are thus important phenomena in that they play a critical role in distribution and flow characteristic of the liquid which influences the bond strength of the joints. Generally, glasses can wet and bond well to most ceramics,[16] Yamazaki[14] showed that the contact angle of La_2O_3–Y_2O_3–Al_2O_3 glass system was about 10° at 1450°C for 5 min. To evaluate the wetting and spreading behavior of the adhesives investigated, the Si_3N_4 substrates coated with adhesive B, D and E were heat-treated using a heating pattern similar to that used when samples were joined.

The results are shown in Fig. 2. Adhesive B with pure-glass forming composition is shown to be fully melted and flowed well over the substrate at the joining temperature. However, there are obvious cracks in the glass layer formed due to the difference in the coefficients of thermal expansion of the glass and Si_3N_4 during cooling. This result indicates that residual stress is developed in the joint with the pure-glass adhesive. It is clearly seen from Fig. 2(d) that frothing is produced when the surface is coated with adhesive D and E. The frothing phenomenon is caused by the volatile decomposition of Si_3N_4 with N_2 gas as a major volatile species.[17] Moreover, the frothing is more serious with increasing Si_3N_4 content of the adhesive. Accordingly, with increasing the amount of Si_3N_4, the wetting and spreading of the adhesive is not good. This is due to the increased amount of solid phase (α-Si_3N_4) in the joining composition during joining process, and consequently the
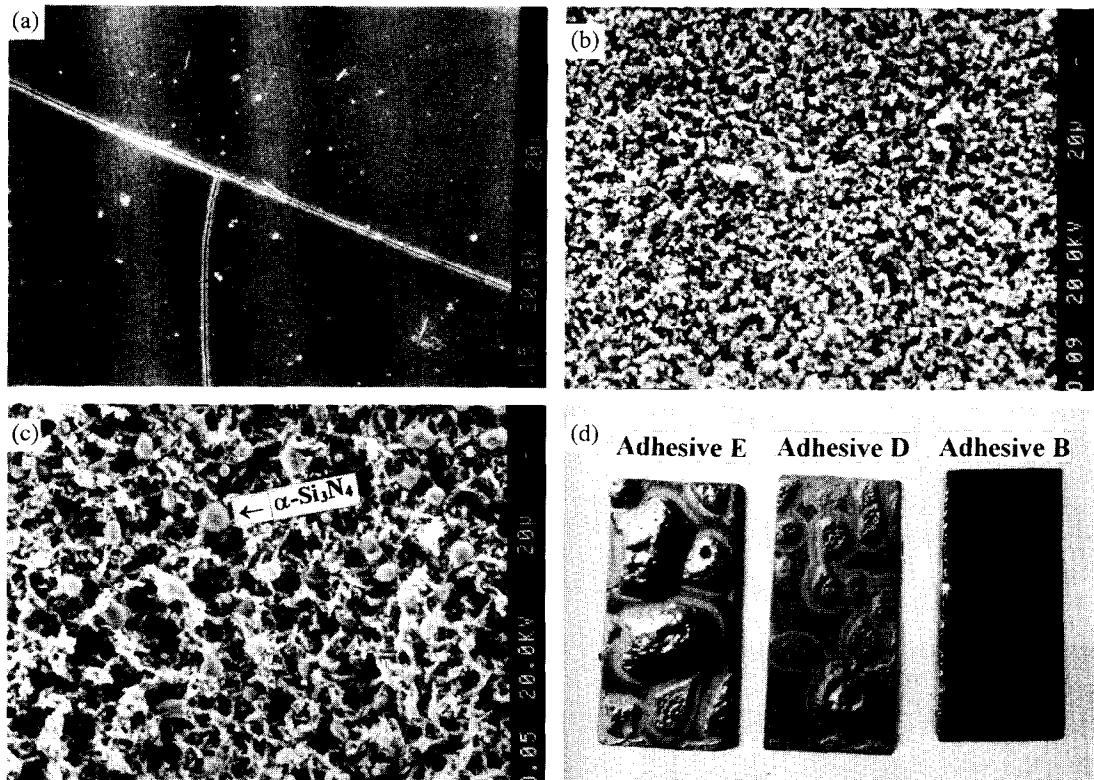
Fig. 2. Si_3N_4 substrates coated with adhesive powder and heat-treated at 1600°C for 30 min: (a) adhesive B; (b) adhesive D; (c) adhesive E.

increase in adhesive viscosity.[3] But no thermal expansion mismatch cracking exists in the coating layer. By the addition of Si_3N_4 powder to the glass solder, more nitrogen atoms enter the $Si(O_4)$ tetrahedral units by substituting for oxygen atoms which leads to the decrease of thermal expansion coefficient.[4]

The adhesive with $Si_3N_4/(Y_2O_3 + Al_2O_3 + SiO_2)$ ratio of 0·82 does not exhibit any thermal expansion mismatch cracking, but many unreacted Si_3N_4 particles [see Fig. 2(c)] are obviously found in the adhesive coating which increase the viscosity of the adhesive, therefore hindering the spreading across the substrate surface.

The increase in viscosity and associated decrease in the wetting and spreading ability of the adhesive with increasing $Si_3N_4/(Y_2O_3 + Al_2O_3 + SiO_2)$ ratio would not affect bonding if an external pressure is exerted to the assembly during the joining process.

3.2 Bond strength and fractograph

Bond strengths as a function of $Si_3N_4/(Y_2O_3 + Al_2O_3 + SiO_2)$ ratios are plotted in Fig. 3. As shown in the figure, the joint using adhesive A without Si_3N_4 powder exhibits the lowest bond strength with an average value of 320 MPa. A maximum strength of 550 MPa is obtained as the ratio reaches 0·39, i.e. for adhesive D. As the Si_3N_4 content increases, the adhesive will not form pure-glass liquid but contains both liquid and solid

phases at the joining temperature, more nitrogen content is introduced into the liquid phase by the reaction between α-Si_3N_4 and liquid phase, thus decreasing the thermal expansion coefficient of the adhesive. Furthermore, the addition of Si_3N_4 powder tends to accelerate nitridation reaction at the joint region during joining process.[12] As a result, the joint region is dense and has less defects, which is contributive to increasing bond strength. However, the bond strength decreases when using adhesives with $Si_3N_4/(Y_2O_3 + Al_2O_3 + SiO_2)$ ratio in excess of 0·39. This is probably due to the lack of liquid-forming components which limits the
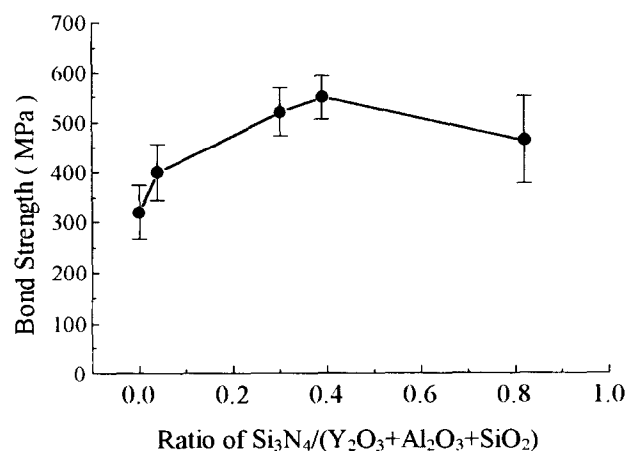

Fig. 3. Effects of $Si_3N_4/(Y_2O_3 + Al_2O_3)$ ratio of the adhesive on bond strength.

densification of the adhesive in the joint and redu-
ces the transformation extend of α-Si_3N_4 to β-
Si_3N_4.

The fracture mode of the joined specimens
depends on the values of bond strength. For the
sample with low bond strength, fracture initiates
predominantly from defects in the joint, and frac-
ture path moves abruptly across the joint from one
side to the other. While for the sample with high
bond strength, fracture initiates at the interface
between the silicon nitride ceramics, then propa-
gates through Si_3N_4. The propagation of cracks
from the interface into the silicon nitride suggests
the formation of a tougher bonded interface, com-
pared with the silicon nitride. Figure 4 shows the
fractrograph of the joined Si_3N_4 using adhesive D.
From the micrograph, the microstructure of the

joined layer is similar to that of ceramic matrix. It
is considered that the similarity in microstructure is
the main reason leading to the higher bond
strength.

Fig. 5. Optical micrograph of the joints: (a) adhesive B; (b)
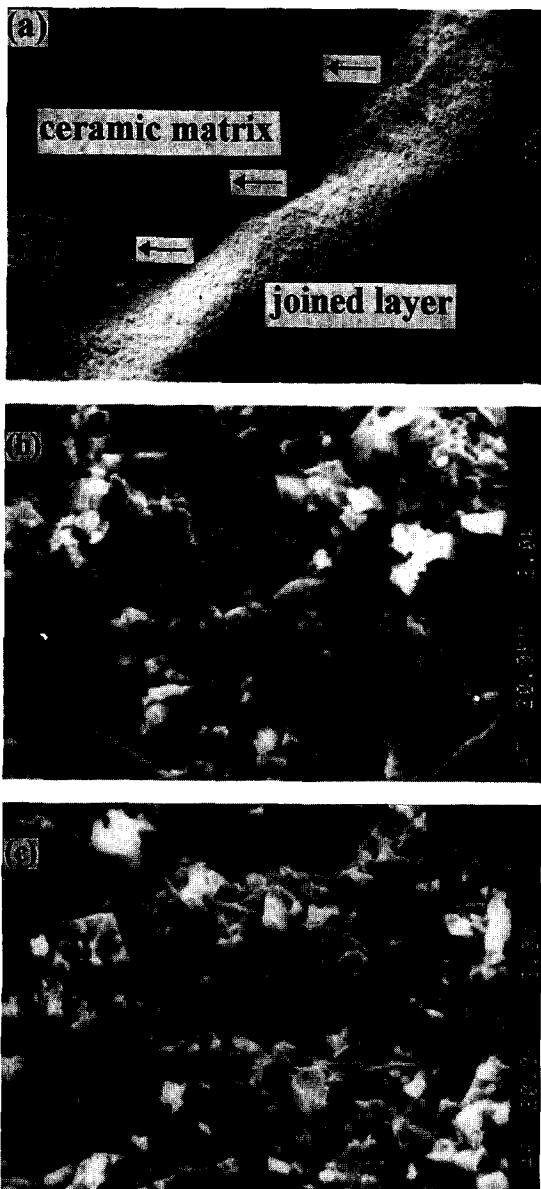adhesive D.

Fig. 4. Fracture surface of sample bonded with adhesive D:
(a) low magnification (fracture began from the left in the
photographs); (b) SEM micrograph of ceramic matrix; (c)
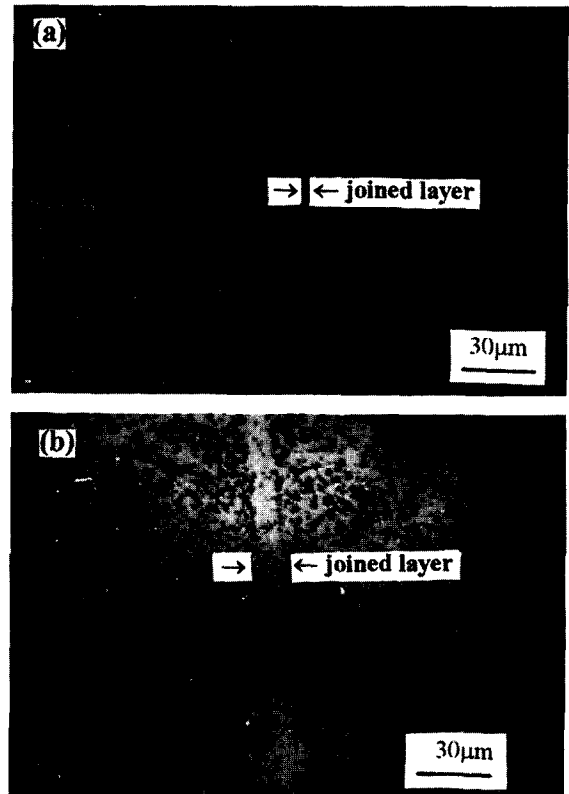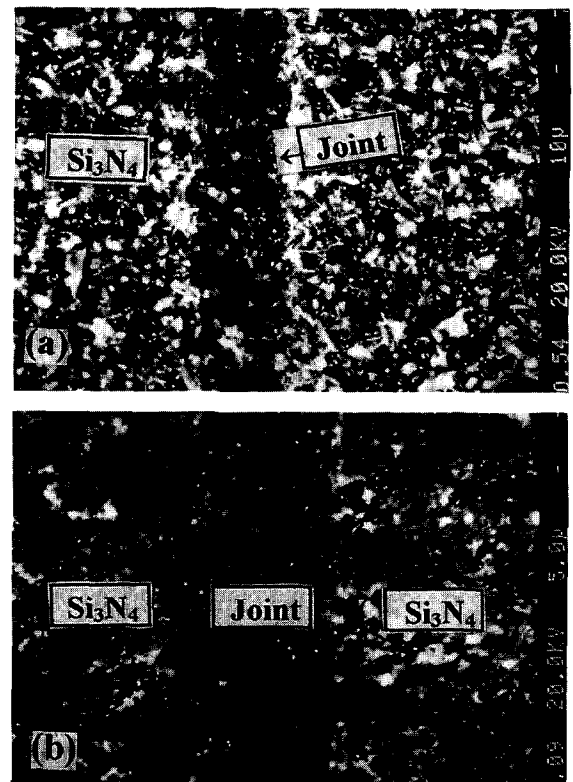SEM micrograph of joined layer.

Fig. 6. SEM micrograph bonded sample using adhesive D: (a)
molten NaOH etched; (b) mechanically polished.

3.3 Microstructural observation of the joints

Figure 5 shows the optical micrograph of the polished Si_3N_4 joints. Under the same joining temperature, holding time and pressure, the joint thickness for the material joined using adhesive B is only about $2\mu m$, in Fig. 5(a). This bonding thickness is due to the fact that the fluid adhesive penetrates into the ceramic matrix. When adhesive D is used, the thickness of joined layer is about $12\mu m$. It is considered that the joining composition has an effect on the joint thickness which in turn affects the bond strength. Figure 6 shows the SEM micrograph of the Si_3N_4 joint. It is clearly seen from Fig. 6(a) that the grain size of Si_3N_4 grains in the joint is smaller than that of Si_3N_4 grains in the matrix. This is related to the lower joining temperature and shorter holding time compared with the heat treatment of sintering the ceramic. In addition, Fig. 6(b) shows that the joint is more denser than the adherend material. Consequently, it is considered that these features of the joint may contribute to the formation of high-strength joint.

4 Conclusion

Si_3N_4–Si_3N_4 joining was accomplished by using mixed powder slurries composed of Y_2O_3, Al_2O_3, SiO_2 and Si_3N_4 which reacted with the Si_3N_4 substrate and densified at 1600°C under N_2 atmosphere. Some conclusions can be drawn, i.e.:

1. The pure-glass forming compositions wetted and spread to/across Si_3N_4 well. However, with increasing the Si_3N_4 content, there existed more solid phase in the adhesive which decreased the wetting and spreading characteristic of joining composition, and hence increased the viscosity of the adhesive.

2. With increasing Si_3N_4 powder in the adhesive, the bond strength of the joints increased. When the $Si_3N_4/(Y_2O_3 + Al_2O_3 + SiO_2)$ ratio reached 0·39, a maximum bond strength of 550 MPa was obtained, which was approximately 80% of that of unbonded materials. There was a drop in strength when using the adhesive with ratio over 0·39.

3. Microstructural analysis showed that the grain size of Si_3N_4 grains in the joint region was smaller than that of Si_3N_4 grains in the matrix due to the lower joining temperature and shorter holding time, and that the joint was more denser than the adherend material.

4. Fracture mode of the samples depended on the values of joint strength. For the sample with low joint strength, fracture occurred directly through the joined layer, while for the sample with high joint strength, fracture initiated at the interface of the joined layer and propagated through Si_3N_4 which suggested the formation of a tougher bonded interface.

Acknowledgement

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