Journal of the European Ceramic Society 20 (2000) 2685–2689

The wettability of Y–Al–Si–O–N oxynitride glasses and its application in silicon nitride joining

Jian Chen *, Pan Wei, Qiang Mei, Yong Huang

State Key Lab of New Ceramics and Fine Processing, Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, People's Republic of China

Received 29 September 1999; received in revised form 20 March 2000; accepted 28 March 2000

Abstract

In the present work, first, the wettability of Y–Al–Si–O–N oxynitride glasses on Si_3N_4 substrates was investigated. It was found that the wettability of the glass depended on the ratios of Y_2O_3/Al_2O_3, i.e. when the ratio of Y_2O_3/Al_2O_3 increased, the wettability of corresponding glass on Si_3N_4 substrate improved. Based on the wettability work, Si_3N_4 ceramics can be successfully joined using glass with the best wettability. It was proved that a proper joining temperature is important for sound joints; a lower temperature would result in incomplete contact of the glass brazing layer with Si_3N_4 while a temperature higher than 1600° would cause separation of Si_3N_4 joints by complete drainage of brazing glass into bulk Si_3N_4 ceramics. In the range of experiment time, to prolong brazing time is of benefit to the shear strength.

Keywords: Glass; Interface; Joining; Oxynitride glass; Si_3N_4; Wettability

1. Introduction

Silicon nitride ceramics has special status in structural ceramics due to its excellent properties at elevated temperature. However, costly grinding and machining operations mean complex shape of silicon nitride ceramics cannot be made easily considering its hardness. Thus, the joining of silicon nitride has been an active subject of research in the past years.

The most commonly used technique for silicon nitride joining is brazing with metal filler, which is typically an Ag–Cu eutectic alloy that contains 1∼5 wt.% Ti. Although the strength of silicon nitride joints brazed with such joining agents can reach that of bulk silicon nitride, its use temperature is usually limited to 600°C.[1] In past years, much effort has been made to increase the elevated temperature strength of silicon nitride joints by using more refractory braze alloys, such as Pd, Pt,[2] but they are too expensive for application on an industrial scale.

In silicon nitride ceramics processing, it is necessary to add sintering aids, which form a liquid phase with Si_3N_4, SiO_2 on the surface of Si_3N_4 powder to prompt densification during sintering. When cooled, the liquid phase would turn into a glassy phase on the grain boundaries in silicon nitride ceramics; the elevated properties of the ceramics depend on the refractory of the glassy phase. The present work is an outcome of the concept that the prepared oxynitride glass similar to the grain boundary phases in sintered silicon nitride is to be used as silicon nitride joining agents. In principle, such joints would have properties similar to those of bulk silicon nitride; it is expected that Si_3N_4 joining with this kind glass can be used at much higher temperature.

2. Experimental

2.1. Wettability investigation

In this experiment, three kinds of compositions with different Y_2O_3/Al_2O_3 ratios were designed, as shown in Table 1. Powders of Si_3N_4 (Ube-10, 96.5% α-Si_3N_4 phase, Ube Inc. Ltd, Japan), SiO_2 (99.5%, Beijing Chemical Fractory, China), Al_2O_3 (99.5%, Beijing Chemical Fractory, China), Y_2O_3 (99.5%, Shanghai Yuelong Chemical Fractory, China) were mixed by agate ball milling with ethanol for 4 h, and then the dried mixtures

* Corresponding author.

0955-2219/00/$ - see front matter
PII: S0955-2219(00)00115-1

Table 1
The compositions of Y–Al–Si–O–N oxynitride glasses (wt.%)

Sample	Y_2O_3:Al_2O_3: SiO_2:Si_3N_4 (wt.%)	N content (wt.%)	
		Calculate	Analysis
YAl-1	52.9:14.1:22.3:10.7	4.28	4.29
YAl-2	47.9:19.1:22.3:10.7	4.28	4.27
YAl-3	42.1:24.9:22.3:10.7	4.28	4.27

were embedded in a BN lined graphite crucible and melted at 1650°C in a graphite-heated element furnace for 1 h under nitrogen atmosphere. After that, the melt was cooled in the furnace after power cut-off.

The chemical compatibility of the prepared glasses with Si_3N_4 was studied by examining their wettability on Si_3N_4 substrates using the sessile drop method. To avoid possible reactions between nitrogen atmosphere and tantalum, the wettability experiment was conducted under argon atmosphere. The sessile drop apparatus employed consisted of a tantalum resistance furnace fitted with two windows, enabling the illumination of the sessile drop of Y–Al–Si–O–N glass on Si_3N_4 substrate and the projection of its image on a screen. The images were photographed and the diameters and heights of the sessile drops of the glass could be obtained from the films. Through the following formula, the contact angles were calculated:

$$\theta = 2\tan^{-1}(y/x) \quad (\theta < 90^\circ) \tag{1}$$

$$\theta = 90^\circ + \tan^{-1}(y/x) \quad (\theta > 90^\circ) \tag{2}$$

where y is the height and x is the radius of sessile drop, respectively.

2.2. Joining experiments

The Si_3N_4 specimens for joining were prepared by the hot-pressed process, in which Si_3N_4 powder compact was sintered with $Y_2O_3 + Al_2O_3$ (10 wt.%) additives at 1800°C for 1.5 h and then was cut into 5×4×4 and 5×6×4 mm^3 blocks, respectively. After that, these blocks were polished to a final finish with 1 μm diamond paste. Before joining, the ceramics specimens and prepared equal size oxynitride glass blocks used for joining were ultrasonic-cleaned in acetone for 20 min. After that, the small piece of Si_3N_4 ceramics was put on the big one and then the prepared glass block used for joining was put beside the small Si_3N_4 ceramic block in order that, when melting, the glass melt can be absorbed into the welding seam by capillary force. The assembled joints were then put into a furnace equipped with a graphite heater and brazed at different temperature and time in flowing nitrogen atmosphere. The heat rate was 20°C/min.

2.3. Mechanical test and microstructure analysis

Cross-sections of the brazed specimens were made with a diamond saw and polished to a final finish with 0.5 μm diamond paste, examined in scanning electron microscopy (SEM) with an energy dispersive spectroscopy (EDS). The microstructure of the interface was investigated by transmitted electron microscopy (TEM). The TEM specimen was prepared by the standard procedures of grinding, dimpling, and argon-ion-beam thinning. The strength of joints was measured by shear test at a displacement rate of 1 mm/min. The specimen configuration for shear tests and shear test arrangement are shown in Fig. 1.

3. Results and discussion

3.1. Variation of wettability

The wettabilities of three kinds of Y–Al–Si–O–N glasses on Si_3N_4 substrates were examined as described above. Fig. 2 shows the wetting contact angle changes of sample YAl-1 with temperature. It can be seen that there were three stages of contact angle changes of the glass. While the temperature was below 1425°C, the contact angle was kept nearly unchanged, since DTA analysis indicated that the glass completely melted temperature of YAl-1 is 1400°C. It is postulated that the high viscosity of the glass deters it from spreading. When the temperature was higher than 1425°C, there was a sudden fall of contact angle. This is attributed to the decrease of viscosity, and the increment of driving force for spreading with temperature. While the temperature was higher than 1460°C, only a slight fall of contact angle was observed below 1500°C.

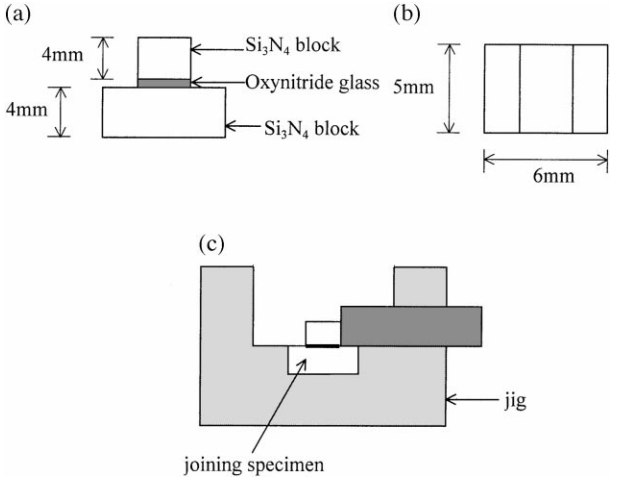

Fig. 1. Specimen configuration for shear tests and shear test arrangement: (a) side view of specimen; (b) top view of specimen; (c) specimen mounted in test jig.

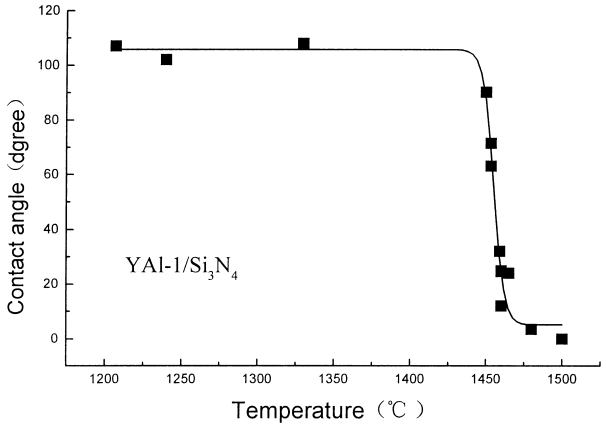

Fig. 2. Variation of contact angle of sample YAl-1 with temperature.

The wetting behaviour changes of the other two kinds of glasses are similar to that of YAl-1; however, as the ratios of Y_2O_3/Al_2O_3 changed, the wettability of Y–Al–Si–O–N glasses was different. Fig. 3 shows the variation of contact angle of Y–Al–Si–O–N glass with ratios of Y_2O_3/Al_2O_3 at 1500°C. It can be seen that the contact angle of Y–Al–Si–O–N glass decreases with increment of Y_2O_3/Al_2O_3. K-Diedrich et al.[3] reported that the surface tension of oxynitride glasses is nearly twice as high as the corresponding oxide glasses due to the incorporation of nitrogen, so it is important to keep the nitrogen content in glasses the same. This is not difficult to get, since the additions of Si_3N_4 and SiO_2 are the same in glass batches, and these three kinds of glasses were melted simultaneously at the same temperature in one furnace. The right column in Table 1 shows the analysis nitrogen contents in these three kinds of glasses. It is found that the nitrogen content varies very little and, thus, the effect of nitrogen content variation on the wettability can be neglected.

The main cause for the changes of contact angles of the glass with ratios of Y_2O_3/Al_2O_3 is now under investigation. Recently, Kitayama et al.[4] found that β-Si_3N_4 seed in Y_2O_3–SiO_2–Si_3N_4 liquid with Y_2O_3/SiO_2 molar ratio of 2/1 grew much larger than in the liquid with Y_2O_3/SiO_2 molar ratio of 1/2, indicating that the solubility of Si_3N_4 in the Y_2O_3 richer Y_2O_3–SiO_2–Si_3N_4 liquid is higher. Kramer et al[5] reported that when he studied the grain growth of silicon nitride dispersed in Y–Al–Si–O–N oxynitride glasses, only grains with diameters larger than 0.1 μm grow, while those grains smaller than 0.1 μm would dissolve in the glass. On account that TEM observation found no reaction phases at the interface (as shown in Fig. 7), it is believed that the dependence of wetting contact angle on Y_2O_3/Al_2O_3 is due to the difference of Si_3N_4 dissolution rates into glass at the interface. Thus, it can be postulated that the different mass transportation between Si_3N_4 substrates and oxynitride glasses with different Y_2O_3/Al_2O_3 ratio would result in the interfacial energy variation. We do not have more knowledge about the variation of the glass surface tension with the ratios of Y_2O_3/Al_2O_3 but, comparing with that of the interfacial tension, the devotion of the surface tension to wetting of the glass melt on Si_3N_4 substrate is small.

Besides Si_3N_4 joining, the different wettabilities of Y–Al–Si–O–N oxynitride glass with various ratios of Y_2O_3/Al_2O_3 are also very important in deciding the ratio of Y_2O_3/Al_2O_3 in Si_3N_4 sintering additives. From the wettability results it can be concluded that higher Y_2O_3 contents in $Y_2O_3 + Al_2O_3$ sintering additive are beneficial to producing dense Si_3N_4 ceramics, which is why Y_2O_3 richer sintering additives are widely used in Si_3N_4 ceramics fabrication.[6–8]

3.2. Joining investigations and microstructures

Based on the wetting results, Y–Al–Si–O–N oxynitride glass with the best wettability was chosen as Si_3N_4 joining agent. Unlike other studies,[9,10] pre-melting oxynitride glass joining agents would lower joining temperature and relieve the pressure applied on the assembled joints during joining, which is beneficial to

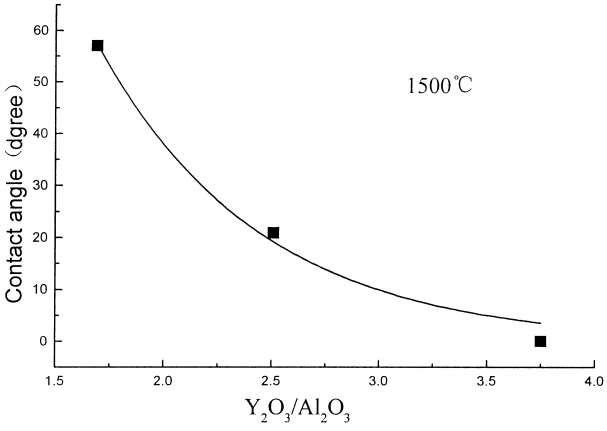

Fig. 3. Variation of contact angle as a function of ratios of Y_2O_3/Al_2O_3 when experiment temperature maintained at 1500°C.

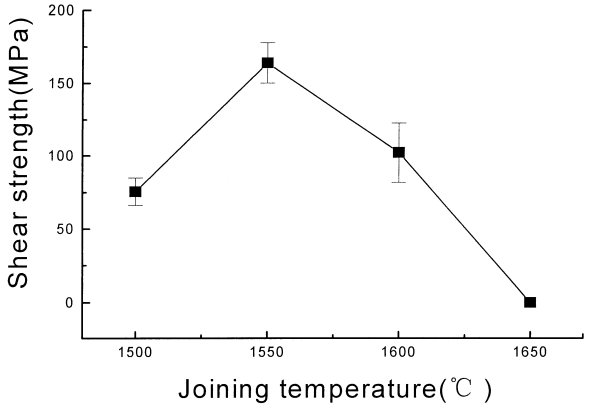

Fig. 4. Effect of joining temperature on shear strength of Si_3N_4 joints (the joining time is 30 min).

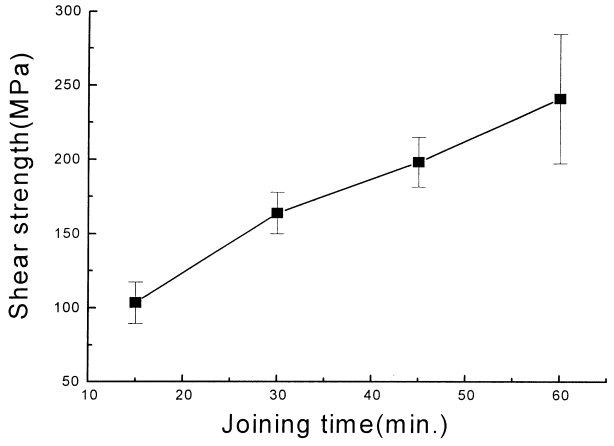

Fig. 5. Effect of joining time on shear strength of Si_3N_4 joints (the joining temperature is 1550°C).

fabricating complicated shapes of Si_3N_4 products. In addition, pre-melting oxynitride glass exhibited better wettability on Si_3N_4 substrates compared with in-situ synthesis of glass joining layer using powder paste, for example. Xie et al.[11] reported that the undissolved α-Si_3N_4 phase in powder paste would deter melting glass from spreading. Fig. 4 shows the effect of joining temperature on the shear strength of the joints. As can be seen in this figure, when the joining temperature increased, the strength increased and reached 164 MPa at 1550°C, but further increase of temperature resulted in the decrease of Si_3N_4 joining strength. At 1500°C, a non-uniform continuous glassy layer was observed. Besides this, there were some voids present at the joining interface. It is obvious that, at lower temperature, although the capillary force of the glass pulled the two Si_3N_4 blocks together, the higher viscosity of the glass prevented the glass from easily going into the weld seam by capillary forces and inhibited contact with Si_3N_4. When the temperature was raised to 1550°C, the viscosity of the glass decreased, leading to an intimate bond. In this case, the joining interface was difficult to ascertain in places. However, if the temperature was too high, for example when it reached 1650°C, the viscosity of the glass decreased too much, hence the glass would be drained away from the interfacial region under the larger capillary forces in bulk Si_3N_4 and this would lead to separation of the joints. Thus, in order to get sound joints, a proper joining temperature was desirable.

When changing joining time at 1550°C, we got various values of shear strength at different time (as shown in Fig. 5). In the experiment range of joining time, the strength of Si_3N_4 joints increased with joining time. SEM observation found that when the joining time was

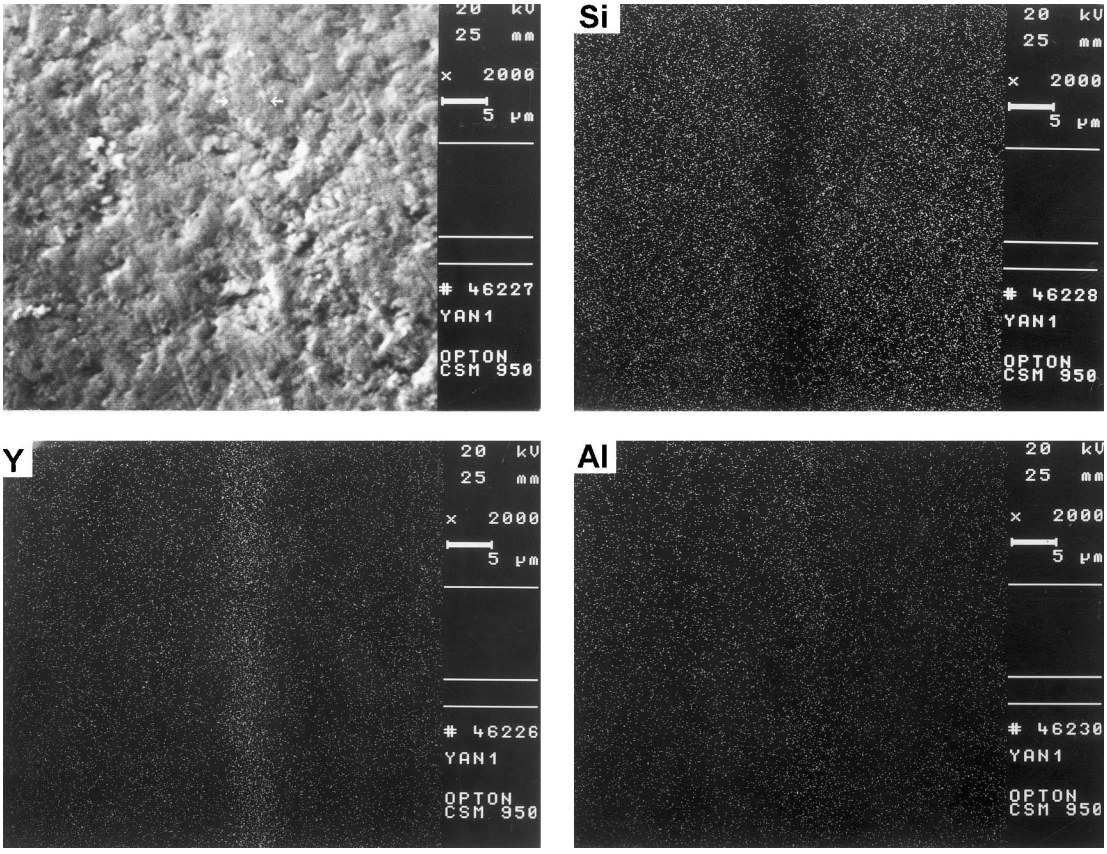

Fig. 6. Cross-sectional SEM micrographs of Si_3N_4 joints and its corresponding composition maps.

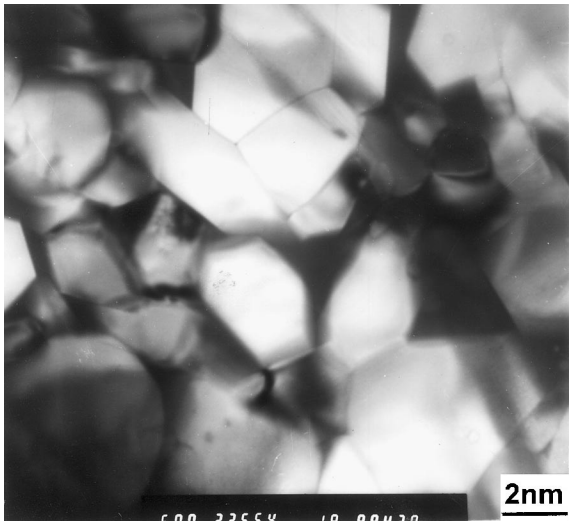

Fig. 7. TEM micrograph of Si_3N_4 microstructure near joining interface.

prolonged, the contact of oxynitride glass with Si_3N_4 would be more intimate, which led to the increase of shear strength. As shown in Fig. 6, it can be seen that the joined region is so uniform that it is difficult to find where the joining interface is in the second electron image unless it was investigated by using element X-ray maps.

Unlike another study,[12] TEM observation on the interface of the joints found no Si_2N_2O phase, as shown in Fig. 7. This may be due to the joining agents having already been pre-melted, hence there was no possibility for the reaction between SiO_2 and Si_3N_4 to occur or, as explained by Mecartney et al.,[13] that the concentration of nitrogen in the glass was not high enough for forming the Si_2N_2O phase. Anyway, complete or nearly complete crystallization of the joints to increase its strength is an object yet to be achieved.

4. Conclusion

In the present work, the wettability of Y–Al–Si–O–N glasses with various ratios of Y_2O_3/Al_2O_3 was studied. It was found that the wettability of Y–Al–Si–O–N glasses improved with the increment of Y_2O_3/Al_2O_3. Using glass with the best wettability as brazing agent, sound Si_3N_4 joints can be fabricated at 1550°C for 1 h. A lower temperature would result in incomplete contact of glass brazing layer with Si_3N_4 while a temperature higher than 1600°C would cause separation of Si_3N_4 joints by complete drainage of the brazing glass. In the range of experiment time, prolonged brazing time is of benefit to the shear strength. TEM observation did not find a new reaction phase occurred at the interface besides the dissolution of small β-Si_3N_4 grain into brazing glasses.

Acknowledgements

This work was supported by NSFC (Grant No.59632090). JCh would like to thank Ms. Wang Min for her encouragement and helpful discussion in this research.

References

1. Debedoe, D., Holland and Hanson, W., Bonding silicon nitride using glass-ceramics. *Key Eng. Mater*., 1995, **100**, 233.
2. Paulasto, M., Kivilagti, J. K. and Peteves, S. D., Joining of silicon nitride via a trasient liquid. *Scripta Metal. et Mater*., 1995, **32**, 1209.
3. K-Diedrich, H., Eckebracht, H. A. and H. Frischat, G., Viscosity and surface tension of oxynitride glass melts. *J. Am. Ceram. Soc*., 1995, **78**, 1123.
4. Kitayama, M., Hirao, K., Toriyama, M. and Kanzaki, S., Control of β-Si_3N_4 crystal morphology and its mechanism (part 1). *J. Ceram. Soc. of Japan*, 1999, **107**, 930.
5. Kramer, M., Hoffmann, M. J. and Petzow, G., Grain growth studies of silicon nitride dispersed in and oxynitride glass. *J. Am. Ceram. Soc*., 1993, **76**, 2778–2784.
6. Boskovic, S., Sintering of Si_3N_4 in the presence of additives form Y_2O_3–SiO_2–Al_2O_3 system. *J. Mater. Sci*., 1990, **25**, 1513.
7. Bodur, C. T., Szabo, D. V. and Kromp, K., Effects of heat treatments on the microstructure of a ytttrial/aluminia-doped hot-pressed Si_3N_4 ceramic. *J. Mater. Sci*., 1993, **28**, 2089–2096.
8. Falk, L. K. L. and Dunlop, G. L., Crystallization of the glassy phase in an Si_3N_4 material by post-sintering heat treatments. *J. Mater. Sci*., 1987, **22**, 4369–4376.
9. Walls, P. A. and Ueki, M., Joining Sialon ceramics using composite β-sialon-glass adhesives. *J. Am. Ceram. Soc*., 1992, **75**, 2491–2497.
10. Mecartner, M. L., Sinclair, R. and Loehman, R. E., Silicon nitride joining. *J. Mater. Sci*., 1985, **68**, 472–478.
11. Xie, Rongjun, Huang, Liping, Fu, Xiren and Chen, Yuan, Effects of adhesive composition on bond strength of joined silicon nitride ceramics. *J. Eur. Ceram. Soc*., 1998, **18**, 901–905.
12. Baik, S. and Raj, R., Liquid-phase bonding of silicon nitride ceramics. *J. Am. Ceram. Soc*., 1987, **70**, C–105.