

Joining of Si_3N_4 using $\text{Ag}_{57}\text{Cu}_{38}\text{Ti}_5$ brazing filler metal

A.-P. XIAN, Z.-Y. SI

Institute of Metal Research, Academia Sinica, 72 Wenhua Road, Shenyang 110015, People's Republic of China

Hot-pressed Si_3N_4 was joined using $\text{Ag}_{57}\text{Cu}_{38}\text{Ti}_5$ brazing filler metal at 1103 to 1253 K for 5 min in a vacuum. The interface reactions between Si_3N_4 and the brazing filler metal during brazing are reported. An important event is sufficient interface reaction, characterized by the formation of a layer of TiN with an appropriate thickness at the ceramic-filler interface. The joining strength of the butt joint depends on the interface reaction, and a maximum joining strength of 490 MPa measured by the four-point-bend method is achieved for the Si_3N_4 - Si_3N_4 joint brazed at 1153 K for 5 min. It is also discussed how to design the best brazing filler metal for joining ceramic to ceramic or ceramic to metal.

1. Introduction

Silicon nitride has recently attracted interest for structural components because of its superior physical, chemical and mechanical properties. The joining of the ceramic to ceramics or the ceramic to metals is of importance to practical application of the ceramic. Silicon nitride has been joined with oxide glass [1, 2] or with brazing filler metal which can wet the ceramic [3, 4]. The first method is based on the concept [1] that an oxide glass whose composition is similar to the additives in the ceramic can react with Si_3N_4 at the brazing temperature to form an oxynitride glass whose composition and properties are similar to those found at grain boundaries of the silicon nitride. One can therefore expect to obtain the best joint of Si_3N_4 - Si_3N_4 by this method. On the other hand, joining with a brazing filler metal is mainly used to join the ceramic to metals [4].

The process of brazing ceramics to metals is too complex to understand thoroughly because of the following reasons. First, the composition of the braze metal after brazing is too complex to make it clear, and it is also difficult to study unknown phases both in the braze metal and on the interfaces of ceramic-braze metal-joined metal after brazing, since elements in the ceramic and joined metals may diffuse into the brazing filler metal during brazing. Secondly, in most cases the joining strength depends on the level of the residual stress, and the latter depends on (i) the difference of the coefficients of thermal expansion between the ceramic and metal, (ii) the modulus of elasticity of the joined metal, and (iii) the brazing temperature. Therefore it is not easy to study the effect of the interface reactions on joining strength.

In this paper, hot-pressed Si_3N_4 was joined by $\text{Ag}_{57}\text{Cu}_{38}\text{Ti}_5$ brazing filler metal, without the effect of dilution of the braze metal by joined metals and that of residual stress on the joining strength. The effects of joining temperature on the interface reaction, and also

that of the interface reaction on joining strength were studied. It is also discussed how to design the best brazing filler metal for joining ceramic to ceramic or ceramic to metals.

2. Experimental procedure

2.1. Materials

The hot-pressed sintered Si_3N_4 used in this study was obtained from the Institute of Ceramics, Academia Sinica. The size of the Si_3N_4 bars was 3 mm × 3 mm × 20 mm and the bend strength of the bars was above 800 MPa. The faying face of the bars was mechanically polished with diamond paste. $\text{Ag}_{57}\text{Cu}_{38}\text{Ti}_5$ brazing filler metal was prepared by melting twice in a vacuum arc furnace; it was then rolled into 100 μm strip and cut into an appropriate size for brazing. Both the brazing filler metal and the ceramic were carefully cleaned with acetone before joining.

2.2. Joining experiments

The test sample for a butt joint, consisting of two bars of Si_3N_4 separated by a layer of the brazing filler metal, was fixed in an iron jig as illustrated in Fig. 1. The jig was rapidly heated in a cold-wall type vacuum brazing furnace to the brazing temperature and then held for 5 min. The heating rate below 600°C was 60°C min⁻¹, then about 20°C min⁻¹ to the brazing temperature. The cooling rate after brazing was 15°C min⁻¹ above 400°C, then about 1.5°C min⁻¹ to room temperature. The pressure of the furnace chamber was kept between 1×10^{-4} and 1×10^{-5} torr during the heating and cooling.

2.3. Mechanical tests and microscopy

The joining strength of the butt joint was determined by a four-point bend test (Fig. 2) with a crosshead speed of 0.2 mm min⁻¹ at room temperature.

The distribution of the elements in the unbroken joint was examined by scanning electron microscopy

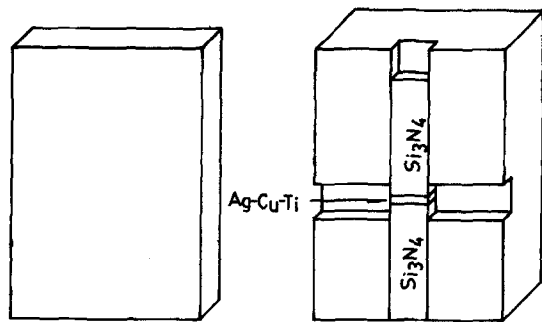


Figure 1 Iron jig used in joining two Si_3N_4 bars.

with an energy-dispersive X-ray system. The fracture surface was examined by a D/Max-rA X-ray diffractometer to identify the phases in the joints.

3. Results and discussion

3.1. Interface reactions between Si_3N_4 and brazing filler metal

Fig. 3 shows the microstructure of a joint brazed at 1203 K for 5 min; the thickness of the brazing seam is about $75\ \mu\text{m}$. Fig. 4 shows the element area distribution images of titanium, silicon, copper and silver and Fig. 5 shows element spot analyses of the braze metal of the joint. Obviously the active element titanium in the brazing filler metal was strongly segregated at the ceramic–filler interface, and a small amount of silicon was also present near the interface after brazing, while a uniform distribution of silver and copper in the brazing seam was observed.

The joints can be divided into three layers from Fig. 4, i.e. ceramic, interlayer and brazing filler metal. The interlayer is about 4 to $8\ \mu\text{m}$ thick for the joint brazed at 1203 K for 5 min, and its main component is titanium which reacts with Si_3N_4 to form titanium nitride and titanium silicide, depending on the brazing temperature and time.

Further, Fig. 6 shows the X-ray diffraction patterns of the fracture surfaces of samples brazed at various temperatures. In all joints, silver and copper in the braze metal were present in the form of a monophase of fcc structure; no silver–titanium or copper–titanium compounds were observed. The structure of the interlayer depends on the temperature of the interface reaction between brazing filler metal and silicon nitride. The interlayer is composed of Ti_5Si_3 and hcp titanium when brazed at 1103 K for 5 min; TiN , Ti_5Si_3 and hcp titanium when brazed at 1153 K for 5 min; and TiN when brazed at 1253 K for 5 min, as shown in Fig. 7.

From the above-mentioned results, the active element titanium in the brazing filler metal is almost completely enriched at the ceramic–metal interface and it will further react with the ceramic surface,

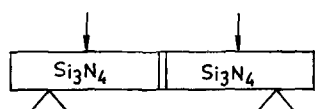


Figure 2 Four-point bend test for measuring the joining strength of the Si_3N_4 – Si_3N_4 joint.

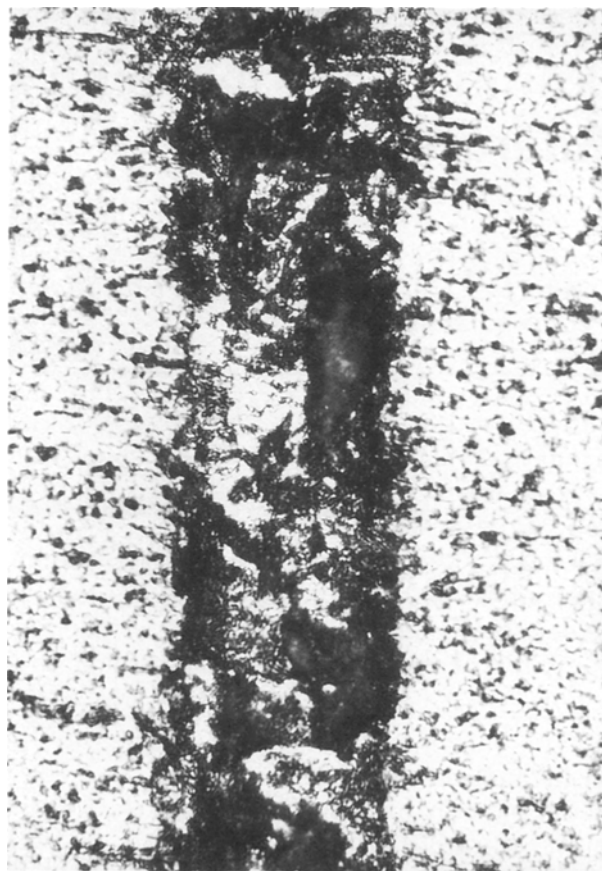


Figure 3 Microstructure of Si_3N_4 – Si_3N_4 joint brazed at 1203 K for 5 min with $\text{Ag}_{57}\text{Cu}_{38}\text{Ti}_5$ brazing filler metal (400 \times).

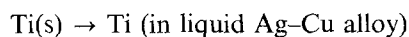
which results in the wetting of the ceramic surface by the brazing filler metal. The reduction reaction of silicon nitride by titanium enriched on the interface can be considered as two steps. First, titanium reacts with Si_3N_4 to form TiN and free silicon:



then silicon atoms freed by Reaction 1 will react with titanium metal to form titanium silicide if the amount of titanium atoms is enough:



Thermodynamic calculation [3] for Reactions 1 and 2 shows that both reactions may occur; however, since there is a lack of thermodynamic data for the solution reaction



a detailed calculation for Reactions 1 and 2 during brazing cannot be made now.

On the other hand, whether titanium silicide or titanium nitride compound is first formed during brazing depends on the kinetics of reaction. It is notable that Reaction 2 can independently take place at first in the presence of free silicon in the ceramic, even though the reaction time and temperature are insufficient, since this reaction does not involve the decomposition of stable Si_3N_4 . Once a layer of continuous and compact Ti_5Si_3 film is formed at the interface, this being a very stable compound with a melting point at 2403 K [5], it will become a diffusion barrier

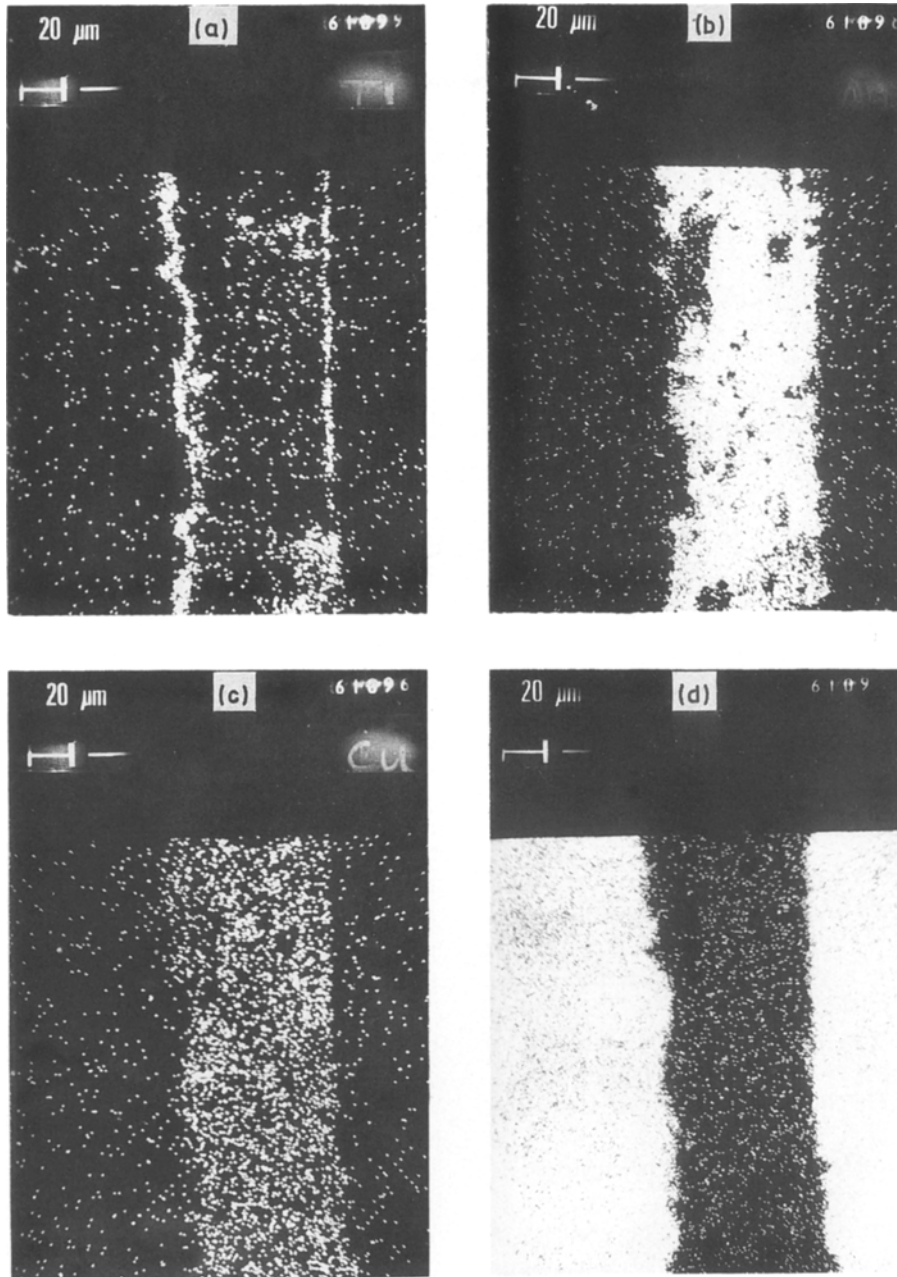
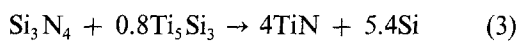


Figure 4 Element area distribution images of the brazing seam in Si_3N_4 - Si_3N_4 joint using $\text{Ag}_{57}\text{Cu}_{38}\text{Ti}_5$ brazing filler metal at 1203 K for 5 min: (a) titanium, (b) silver, (c) copper, (d) silicon.

for titanium atoms. The reaction



will then not easily take place until a higher temperature, since it involves decomposition of both Si_3N_4 and Ti_5Si_3 . Therefore the effect of free silicon in silicon nitride or silicon carbide ceramic on joining is a noteworthy topic.

In the case of limited addition of titanium, the interface reaction will gradually stop during brazing because of a lack of the reactive element titanium in the brazing filler metal. In contrast with the case of a high titanium content in the brazing filler metal [3], it is expected that the reaction between Si_3N_4 and brazing filler metal with a low titanium content will not be sensitive to brazing temperature and time within a broad range.

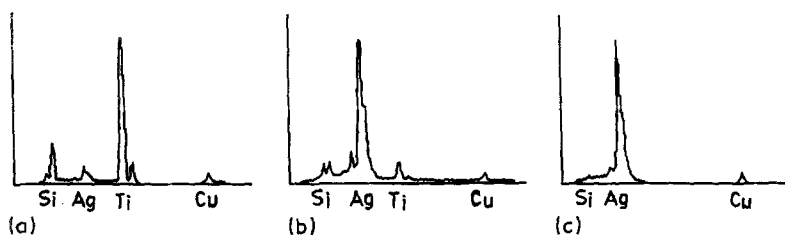
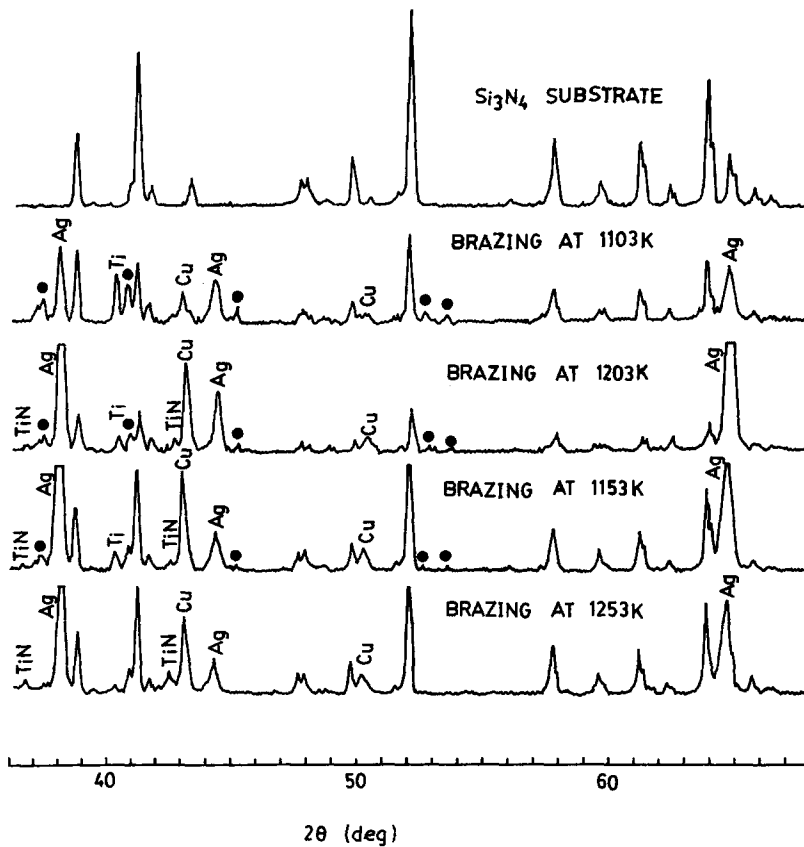


Figure 5 Element spot analyses of the brazing seam of Si_3N_4 - Si_3N_4 joint using $\text{Ag}_{57}\text{Cu}_{38}\text{Ti}_5$ brazing filler metal at 1203 K for 5 min: (a) at interface, (b) near interface, (c) in the middle of the brazing seam.

Figure 6 X-ray diffraction patterns of fracture surfaces of Si_3N_4 - Si_3N_4 joints using $\text{Ag}_{57}\text{Cu}_{38}\text{Ti}_5$ brazing filler metal at 1103 to 1253 K for 5 min. Unmarked peaks belong to the Si_3N_4 substrate; (●) Ti_5Si_3 .



Though TiN is not observed at the ceramic-filler interface of the joint brazed at lower temperature and shorter time in this study, this does not confirm that no titanium nitride is present at the interface, if the layer of titanium nitride is too thin to be observed by diffraction. However, it is certain that the film of titanium nitride does not grow obviously during brazing at a temperature below 1153 K, even if it is present.

3.2. Effect of interface reaction on joining strength

Fig. 8 shows the brazing temperature dependence of the joining strength of Si_3N_4 - Si_3N_4 joints using $\text{Ag}_{57}\text{Cu}_{38}\text{Ti}_5$ brazing filler metal. The maximum joining strength was 490 MPa for the joint brazed at 1153 K for 5 min.

It is observed that cracking of all joints originated at the underlying layer of Si_3N_4 ceramic just near the ceramic-filler interface; cracks propagated along the ceramic-filler interface when brazed at 1253 K, and along the braze metal when brazed at other temperatures. On fracture, a little grey-coloured Si_3N_4 is seen stuck to the braze metal surface in the crack initiation zone (Fig. 9).

In a layered ceramic-interlayer-braze metal structure, fracture will occur at the weakest chain which

limited the joining strength. In this study, all cracks initiate in the Si_3N_4 -interlayer region; therefore the joining strength depends on the interlayer, which in turn depends on the interface reaction.

The joining strength of the Si_3N_4 - Si_3N_4 joint could be improved by brazing above 1153 K; Figs 6 and 8 reveal that the improvement of joining strength is due to formation of TiN. Moreover, the strength of the braze metal could be also improved by brazing at 1253 K because of diffusion of silicon freed by Reaction 1 into the braze metal, which results in the crack propagating along the ceramic-filler interface of the joint when brazing at 1253 K, but along the braze metal when brazing at lower temperatures. In order to obtain a high joining strength it is important that there should be no brittle phases such as silver-titanium, copper-titanium, silver-silicon or copper-silicon present in the braze metal after brazing. Therefore, the amount of active element titanium in the brazing filler metal must be limited, which results in the limitation both of the interface reaction between ceramic and brazing filler metal and of the formation of the above-mentioned metal compounds.

The joining strength of metal-ceramic is related to the wetting of the ceramic by the melted metal, the latter depending on the work of adhesion which can be

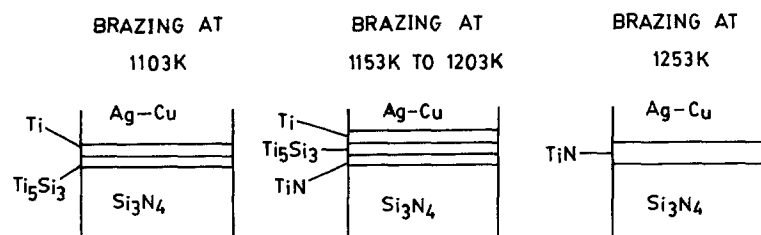


Figure 7 Schematic illustration of layer interface structure in Si_3N_4 - Si_3N_4 joints using $\text{Ag}_{57}\text{Cu}_{38}\text{Ti}_5$ brazing filler metal at various temperatures.

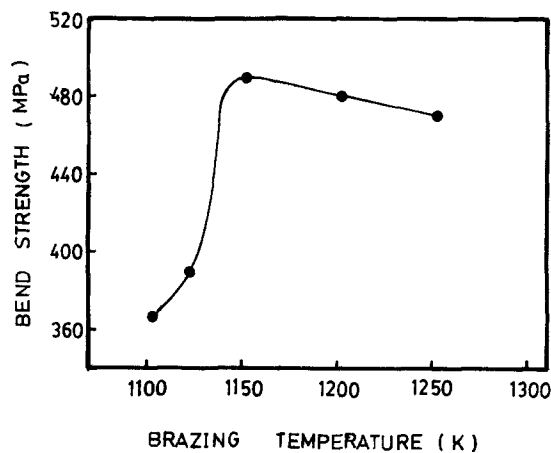


Figure 8 Change in bend strength of Si_3N_4 - Si_3N_4 joint using $\text{Ag}_{57}\text{Cu}_{38}\text{Ti}_5$ brazing filler metal with brazing temperature at brazing time of 5 min.

estimated [6] from the equation

$$W_a = -\alpha\Delta G^0 + \beta$$

where ΔG^0 is the standard free energy of the reaction between brazing filler metal and ceramic; α and β are constants which depend on the ceramic. From this relationship, the more ΔG^0 determined by different reactions is, the more the work of adhesion is, therefore the higher the joining strength of the joint will be. Moreover, from Askay *et al.* [7], the effective free energy of the interface reaction is also dependent on the thickness of the reaction layer; the thicker the reaction layer is, the more the effective free energy is and the higher the joining strength will be. Hence the joining strength will increase with the thickness of TiN.

On the other hand, the joining strength also has something to do with the layer interface structure which might affect the stress distribution in the joint. The best structure is a multilayer Si_3N_4 -TiN-Ti₅Si₃-Ti-brazing filler metal structure; the next best is Si_3N_4 -TiN-brazing filler metal, and the worst is Si_3N_4 -Ti₅Si₃-Ti-brazing filler metal.

4. Conclusions

Hot-pressed Si_3N_4 was joined using $\text{Ag}_{57}\text{Cu}_{38}\text{Ti}_5$ brazing filler metal in a vacuum. The maximum bend strength of the joint measured by the four-point bend method was 490 MPa when brazing at 1153 K for 5 min. It is important that there is sufficient reaction during brazing between the ceramic and the active element in the brazing filler metal, characterized by forming TiN with an appropriate thickness. On the other hand, insufficient interface reaction will decrease the joining strength.

This work shows that one can expect to obtain a high joining strength using Ag-Cu brazing filler metal with a small quantity of titanium as an active element, without forming a brittle dispersed phase such as silver-titanium or copper-titanium compound after

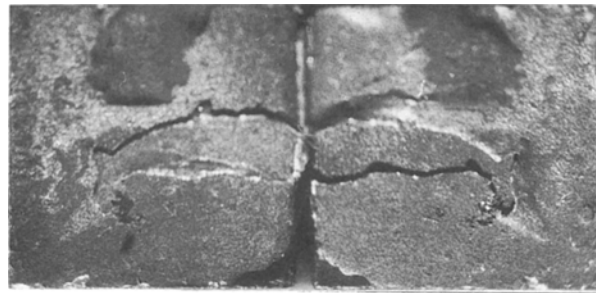


Figure 9 Fracture surface at low magnification showing origin of fracture at underlying layer of Si_3N_4 and subsequent fracture path through braze metal (brazing at 1103 K for 5 min).

brazing. From the above results, in order to obtain a high joining strength, the following points are suggested when one designs a brazing filler metal for joining ceramic to ceramic or ceramic to metal:

1. The selected active element should have a high free energy of reaction with the ceramic, and strong segregation on the ceramic-metal interface.
2. The lower limit of active element content in the brazing filler metal should ensure a good wetting of ceramic by the brazing filler metal, while the upper limit should be such that there is no brittle dispersed phase in the brazing filler metal.
3. The brazing temperature and time should be sufficient to ensure interface reaction of the brazing filler metal with ceramic.

Of course, in order to obtain the best joining of ceramic-ceramic or ceramic-metals, it is also necessary to reduce the thermal stress resulting from the mismatch of the coefficients of thermal expansion between the two joined materials.

Acknowledgements

This research was supported by the National Science Foundation of China. Hot-pressed Si_3N_4 ceramic was supplied by the Shanghai Institute of Ceramics, Academia Sinica. The authors would like to thank Professor B. N. Chian for valuable discussions.

References

1. S. M. JOHNSON and D. J. ROWCLITTE, *J. Amer. Soc.* **68** (1985) 468.
2. N. IWAMOTO, N. UMESAKI and Y. HAIBARA, *Trans. JWRI* **15**(2) (1986) 265.
3. M. NAKA, T. TANAKA and O. IKUO, *ibid.* **16**(1) (1987) 83.
4. M. NAKA, T. TANAKA and I. OKAMOTO, *ibid.* **14**(2) (1985) 285.
5. M. HANSEN, H. KESSLER and D. McPHERSON, *Trans. Amer. Soc. Met.* **44** (1952) 518.
6. J. E. McDONALD and J. G. EBERHART, *Trans. Metall. Soc. AIME* **233** (1965) 512.
7. I. A. ASKAY, C. E. HOGE and J. A. PASK, *J. Phys. Chem.* **78** (1974) 1178.

Received 5 April
and accepted 14 September 1989