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Joining of silicon nitride to silicon nitride and to Invar alloy using an aluminium interlayer

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Si_3N_4 has been bonded to Si_3N_4 and to the Invar alloy using an aluminium interlayer at temperatures above the melting point of aluminium. Reaction was hardly observed at the interface between Si_3N_4 and aluminium up to 1223 K. The highest strength of the Si_3N_4–Al–Si_3N_4 joints was beyond 500 MPa. In the Si_3N_4–Al–Invar joint, two main intermetallic compound layers were formed at the Al–Invar interface. The strength of the joints was between 150 and 200 MPa. It is expected that the aluminium layer and the reaction layer with the fine cracks growing perpendicular to the interface play an important role to compensate for the thermal expansion mismatch.

1. Introduction

To give the reliabilities for ceramics as structural materials and to make up for their low workability, it is necessary to establish the joining techniques of ceramics/ceramics and ceramics/metals. There are many factors affecting the properties of joints. When a joint has a ceramic–metal interface, the reactivity and the thermal expansion mismatch between a ceramic and a metal will play an important role in determining the strength of a joint.

Silicon nitride is one of the most interesting ceramics for engineering use. It has excellent strength, high resistance to wear and corrosion, etc. at elevated temperature conditions. But silicon nitride is difficult to join with metals because of its small thermal expansion. The mean thermal expansion coefficient of silicon nitride from room temperature to 1273 K is about $3.0 \times 10^{-6} K^{-1}$, while that of tungsten, which has the smallest thermal expansion coefficient of all metals, is about $4.5 \times 10^{-6} K^{-1}$. Since this difference causes the failure of the joint when they are bonded directly at elevated temperature, it is necessary to introduce some appropriate interlayer for joining silicon nitride to metals.

Recently, the present authors have developed a new bonding technique for this purpose [1]. The selected interlayer consisted of a laminate of aluminium and the Invar alloy. Although aluminium has an upper limit temperature of about 573 K for higher temperature application, it has good effects on the thermal expansion mismatch as a soft metal layer [2]. It is well known that aluminium does not wet silicon nitride but can bond well to silicon nitride [1]. The purpose of the present study is to survey the bonding conditions of silicon nitride with an aluminium layer, and of the silicon nitride–aluminium–Invar alloy.

2. Experimental procedure

2.1. Materials

The silicon nitride used in this study was pressureless-sintered material, SN601 manufactured by Narumi Ceramic Co. Ltd, Aichi, Japan. They were discs of 7 mm in diameter and 1 mm in height, rods of 7 mm in diameter and 7 mm in height, and discs of 13 mm in diameter and 10 mm in height. The 1 mm high discs were used for the joint constructed as Invar–aluminium–silicon nitride–aluminium–Invar. The effect of bonding temperature was examined using the rods of 7 mm diameter and 7 mm height. The discs of 7 mm height and 13 mm diameter were used for the examination of the effect of bonding pressure for the silicon nitride–aluminium–silicon nitride joints. The surface to be bonded was polished mechanically to optical flatness.

The Invar alloy used in this study was "Super Invar Alloy", Fe–32 wt % Ni–5 wt % Co. The rods of 7 mm diameter and 7 mm height were used. One surface of the rod was polished mechanically to optical flatness. The aluminium was in the form of a 0.5 mm thick sheet. Its purity was 99.9 wt %. Discs of 7 mm in diameter were cut from the sheet. All materials were cleaned in acetone before bonding.

2.2. Bonding

Bonding experiments were performed at the temperatures of 973 to 1223 K, beyond the melting temperature of aluminium, and the pressures of 0 to 0.15 MPa for 2 to 30 min. The bonding jig is illustrated in Fig. 1. The jig was placed in a furnace under a stream of argon, nitrogen and air. After bonding, specimens were furnace-cooled.

2.3. Evaluation

Microstructural observations were conducted by

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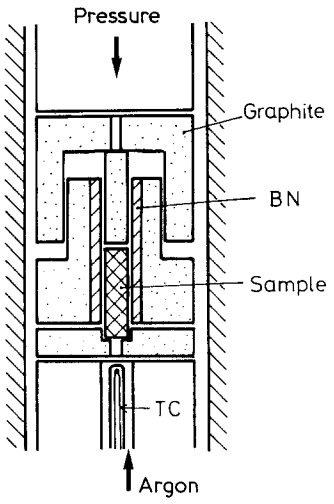

Figure 1 Schematic diagram of the present bonding assembly. BN = boron nitride, TC = thermocouple.

SEM and EPMA. Reaction products were examined by the X-ray diffraction method. The strength of the joints was evaluated by a three point bend test for the silicon nitride–aluminium–silicon nitride joints and by a four point bend test for the silicon nitride–aluminium–Invar alloy joints. The span was 10 mm for the three point bend test. For the four point bend test, the upper span was 5 mm and the lower was 12 mm. The dimensions of the test specimens were $2 \times 2 \times 15\,mm^3$. These specimens were cut from the joints.

3. Results

3.1. Silicon nitride–aluminium–silicon nitride

3.1.1. Effects of bonding temperature

Fig. 2 shows the effect of bonding temperature on the strength of the joints. All specimens failed almost within the aluminium layer. Note that the strength of the sample was relatively high, 400 to 500 MPa, when the joints were bonded above 1000 K. It is quite

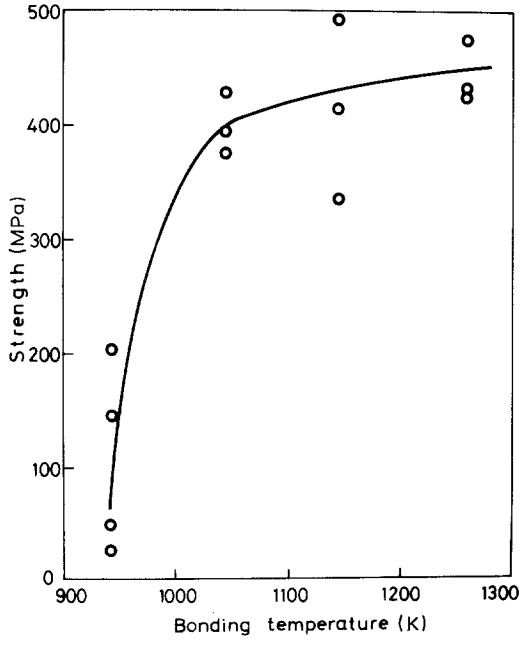

Figure 2 Strengths of the silicon nitride–aluminium–silicon nitride joints bonded for 10 min at various temperatures.

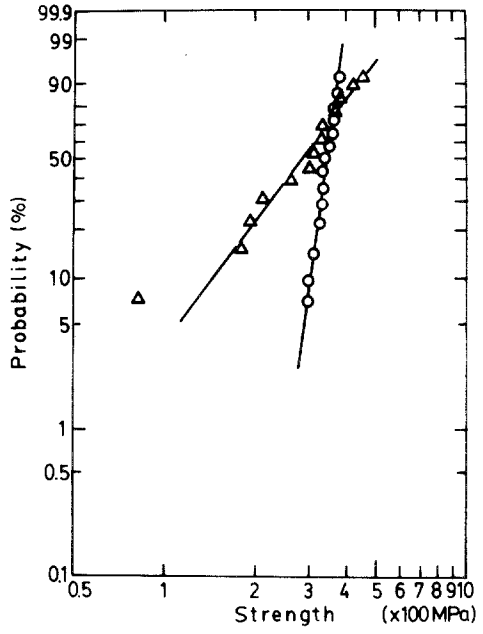

Figure 3 Weibull plots of the strengths of the silicon nitride joints bonded at 1073 K for 10 min using aluminium. ○, bonded at 0.05 MPa, $M = 14.8$; △, bonded at 0 MPa, $M = 2.8$.

curious that the strength of 500 MPa is beyond the strength of aluminium. It is considered that the high strength of the present joint is due to the very thin aluminium layer of about 10 to 20 μm. No reaction was observed between silicon nitride and aluminium in the present experimental temperature conditions by means of SEM, EPMA and X-ray diffraction analysis.

3.1.2. Effects of applied pressure

Fig. 3 shows Weibull plots of the strength of the joints bonded under two different pressure conditions of 0 and 0.05 MPa. As seen in this figure, the strength distribution of the samples bonded under 0 MPa was very wide and the Weibull slope was 2.8, while that of the joints bonded at 0.05 MPa was 14.8. In the case of the pressureless bonding experiments, there were many pores and the thickness of the aluminium layer was not uniform. On the other hand, under conditions of 0.05 MPa intimate contact was produced at the interface with the 10 to 20 μm aluminium layer. It seems that this microstructural difference influenced the strength.

3.1.3. Effects of atmosphere

Fig. 4 shows the effect of atmosphere on the strength. Two atmospheres, air and nitrogen, were selected along with argon. The argon atmosphere made the strongest joint and the air made the weakest. Fig. 5 shows three kinds of fracture surfaces corresponding to the three atmospheres. The argon and nitrogen produced a similar fracture mode which consisted of ductile fracture of the aluminium layer and of the brittle fracture in the silicon nitride side near the bond face. X-ray diffraction analysis of these fracture surfaces could not detect any phase except for silicon nitride and aluminium. On the other hand, the air atmosphere produced the flat fracture surface which was the interface between the aluminium layer and silicon nitride. Although X-ray diffraction analysis

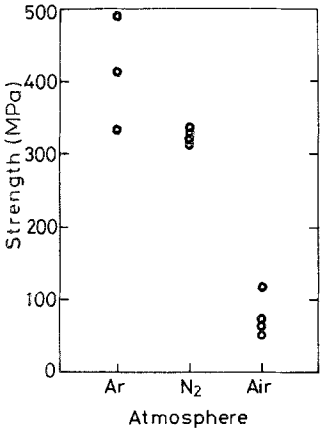

Figure 4 Effects of bonding atmosphere on the strength of the silicon nitride joints using aluminium.

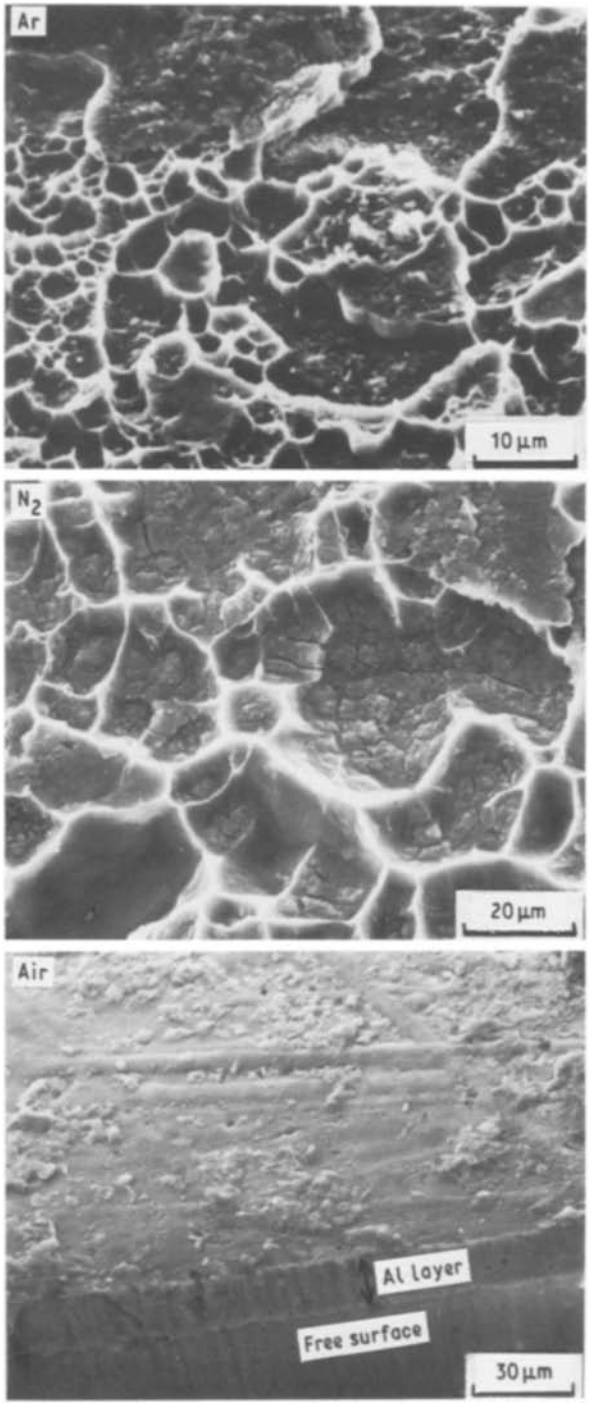

Figure 5 Three types of fracture surfaces bonded in argon flow, in nitrogen flow and in air.

could not also detect the formation of any aluminium oxide, the oxidation of aluminium in air seems to prevent the bonding at the silicon nitride–aluminium interface.

Taking the industrial cost into account, the preferred order would be air, nitrogen and then argon. However, the argon atmosphere was effective for the production of high strength joints.

3.2. Silicon nitride–aluminium–Invar alloy

3.2.1. Interfacial microstructure

The transverse cross sections of the joints are shown in Fig. 6. Between silicon nitride and aluminium, no reaction zone was detected at bonding temperature conditions up to 1223 K. On the other hand, an apparent reaction zone was observed between aluminium and the Invar alloy. There were two distinct layers in the reaction layer.

Fig. 7 shows the results of the line analysis by EPMA. The narrow layer on the aluminium side is considered to be M_2Al_9 (Co_2Al_9 type structure with monoclinic symmetry) and the thicker layer on the Invar alloy side is MAl_3 ($NiAl_3$ type structure with orthorhombic symmetry). The amount of cobalt and nickel elements of the former product was more than those of the latter. When the sample was bonded at 1223 K, no aluminium layer remained at the silicon nitride–reaction layer interface. Two additional layers

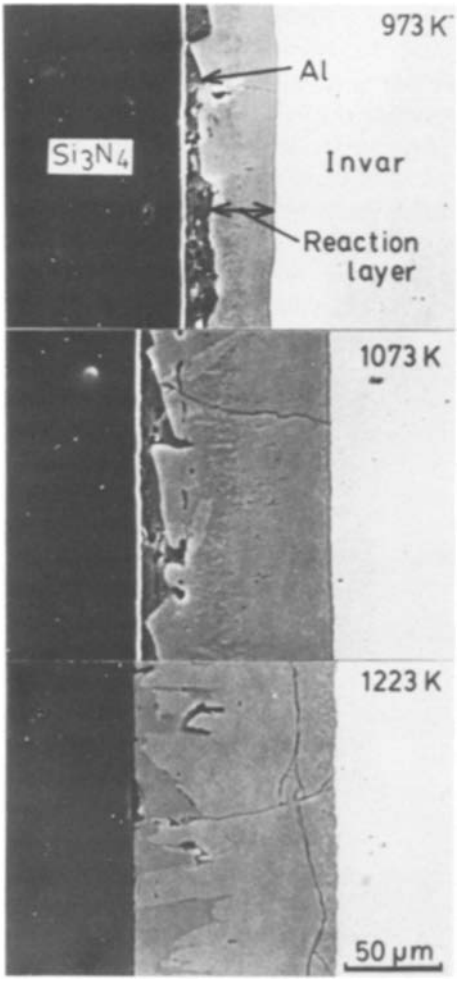

Figure 6 Interfacial structures of the silicon nitride–aluminium–Invar alloy bonded at various temperatures for 7 min (SEM).

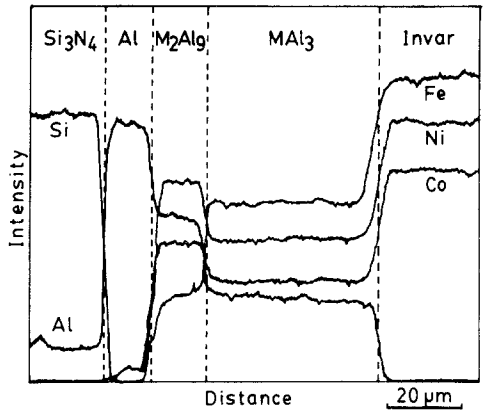

Figure 7 Electron probe trace of the silicon nitride–aluminium–Invar alloy joint bonded at 1073 K for 7 min.

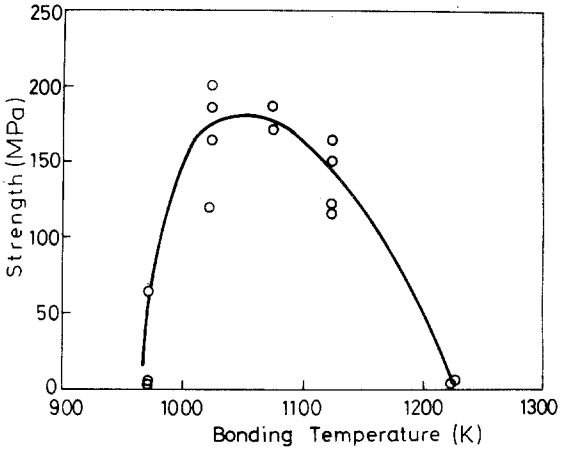

Figure 9 Strength of the joints bonded for 7 min at various temperatures.

were recognized at the MAl_3–Invar interface in all temperature ranges (Fig. 8). However, these phases could not be identified because they were very thin.

Furthermore, several cracks growing perpendicularly to the bonded interface were observed for the joints bonded below 1100 K. Above a bonding temperature of 1100 K, cracks growing parallel to the interface were also present.

3.2.2. Bonding strength

Fig. 9 shows the bonding temperature dependence of the strength of the joints. As seen in this figure, it is possible to achieve a strength higher than 100 MPa at the bonding temperature range between 1000 and 1150 K. In this temperature range, the fracture occurred partially within the aluminium layer and partially within the reaction layer, as shown in Fig. 10. On the fracture surface through the reaction layer, the network of cracks growing perpendicular to the interface was observed. Below the bonding temperature of 1000 K, the joints failed at the silicon nitride–aluminium interface.

The effect of bonding time on strength is shown in Fig. 11. The highest strength was achieved within 10 min. Beyond 10 min, the strength decreased gradually as the reaction layer between aluminium and Invar alloy grew.

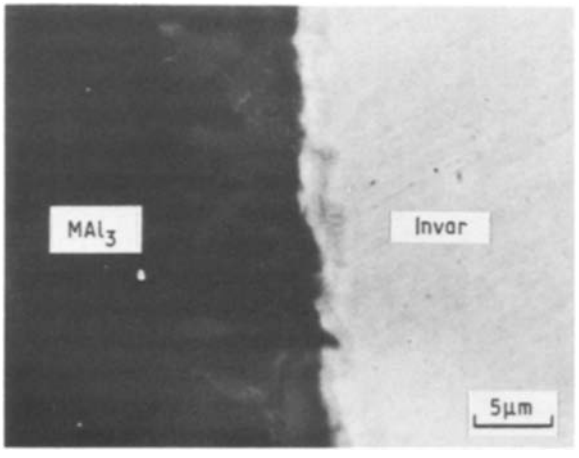

Figure 8 Thin reaction layers at the MAl_3–Invar interface. Bonded at 1223 K for 7 min in argon gas flow.

4. Discussion

4.1. Bonding of silicon nitride using aluminium

In recent years, several bonding processes of silicon nitride have been developed, that is, hot-pressing, hot isostatic pressing (HIP) and brazing. In the former two methods, the magnitude of pressure of 10 to 100 MPa was applied for bonding reaction. The applied pressure acted as a force to achieve close contact at the interface. For direct bonding, the application of high pressure at high temperature conditions was required. Two of the present authors (M. S. and M. K.) have investigated the direct bonding of silicon nitride with or without additives under a pressure of 3.0 GPa at 2073 K [3]. Without additives, no sign of interface of the joint was recognized. When Y_2O_3 was used as an additive, however, a Y_2O_3-enriched layer was formed at the interface. These results indicated that the application of an ultra-high pressure for bonding reaction would enable us to achieve a complete joint. Kanzaki *et al.* have examined the hot-pressing technique for the bonding of the silicon nitride containing Al_2O_3 and MgO as additives [4]. They reported that the bending strength of joints bonded at 20 MPa and 1873 K was 540 MPa, which was equal to the strength of the original body. But the strength of the joint bonded without pressure was 360 MPa. Thus, the high pressure bonding method can produce high strength joints.

However, it is necessary to develop a low pressure bonding process, which offers the advantages of less fixtures and of lower costs. Becher *et al.* examined the bonding process of the hot-pressed silicon nitride using ZrO_2 as a filler [5]. ZrO_2 powder was used to make an interlayer between the bonding bodies and was densified during bonding reaction. The bonding was carried out at 1773 K for 60 min under a pressure below 1.5 MPa. The bending strength of the joint was 175 MPa. Siebels also investigated the brazing methods using several metals [6]. He pointed out that the important processing parameters were the vapour pressures and the evaporation rates of the brazing element used. Furthermore, it must be noticed that reactive gas, N_2, will prevent silicon nitride and aluminium from contacting as a result of pore formation in brazing methods.

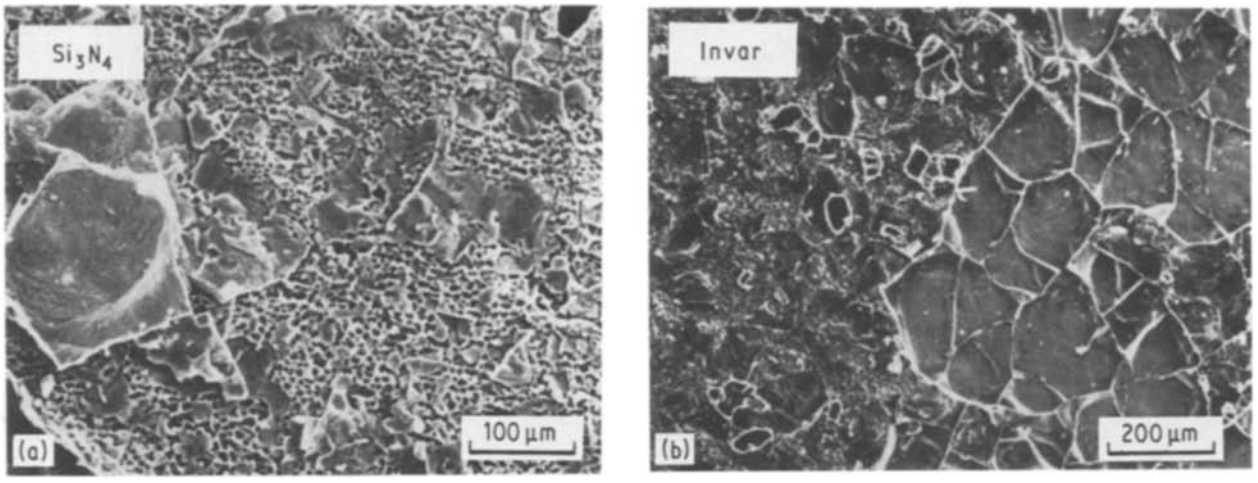

Figure 10 Fracture surfaces of the silicon nitride–aluminium–Invar alloy bonded at 1073 K for 7 min (SEM). (a) Silicon nitride side, (b) Invar side.

In the present study, aluminium was used as a brazing material. The main advantage of the present method was to reduce the bonding temperature, bonding pressure and bonding time, to reduce the cost of the bonding process. In addition to the object mentioned above, it is expected that the obtained joints have not only high strength but also high reliability. The present process will be adopted as one of the simplest methods to bond two parts of silicon nitride.

There was little reaction between silicon nitride and aluminium up to 1223 K in the present experimental results. Many works have been carried out to clarify the reaction between silicon nitride and aluminium [7, 8], but almost all of these have not detected any reaction up to 1273 K. Only one report on the reaction at 833 K in aluminium-coated silicon nitride whisker has been reported by Andrews [8]. Siebels reported that reactions between the reaction sintered silicon nitride and aluminium and between the hot-pressed silicon nitride and aluminium occurred at 1573 K in vacuum. The present results also indicate that, below 1223 K, if any reaction can be brought about it will be restricted to a narrow region near the interface. Recent TEM studies of the silicon nitride–aluminium interface indicated the formation of some reaction layer which has not yet been described [9, 10]. The reaction at 1073 K for 10 min produced a 100 nm thick reaction layer [10]. Thermodynamically, the formation of aluminium nitride or aluminium oxide is possible in this temperature range [11].

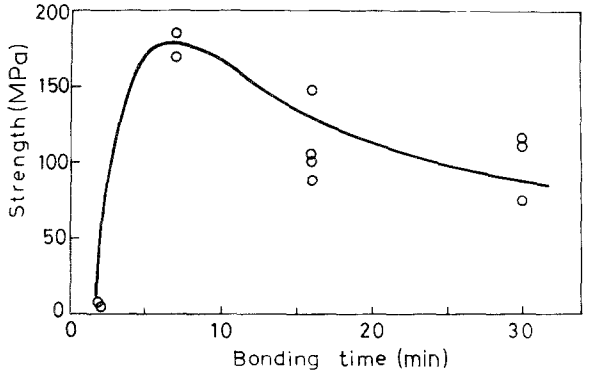

Figure 11 Strengths of the joints bonded for various times at 1073 K.

4.2. Bonding silicon nitride to Invar alloy using aluminium

Although the technique of bonding ceramics to metals is important for using ceramics as practical materials, it is difficult to make a tight bonding due to the thermal expansion mismatch between ceramics and metals. Several methods have been developed to overcome this problem in the bonding of oxide ceramics to metals. Nicholas *et al.* [2] investigated the soft metal inserting method, in which aluminium was used as an interlayer in bonding alumina to steel. The elastic and plastic deformation of the aluminium layer relieves the residual stress caused by thermal expansion mismatch. Relatively high tensile strength of 70 MPa for the joint was achieved. Recently, the present authors have developed a new concept of interlayers to bond ceramics to metals on the basis of the thermal expansion coefficients of bonded materials [1, 12]. Joint constructions are divided into three types as follows:

Type 1,
ceramic–metal interlayer–metal
$\alpha_C \approx \alpha_{MI} < \alpha_M$

Type 2,
ceramic–metal interlayer 1-metal interlayer 2–metal
$\alpha_C \approx \alpha_{MI1} > \alpha_{MI2} < \alpha_M$

Type 3,
ceramic–soft metal–metal interlayer–metal
$\alpha_C \approx \alpha_{MI} < \alpha_M$

The present work is concerned with Type 3, which is a thermal expansion coefficient.

The main advantage in using aluminium as an interlayer for joining silicon nitride and Invar alloy is that it compensates the thermal expansion mismatch.

The aluminium layer plays the important role as a soft metal layer in the temperature range above 473 to 573 K where the difference in thermal expansion between silicon nitride and Invar alloy is quite large. In this temperature range during the cooling process the fine cracks grow perpendicular to the interface within the reaction layer, which was monitored by means of acoustic emission from the joint on cooling [13]. This crack formation will help the aluminium layer in relieving the internal stress. The fine crack

network made the joints stable even if the aluminium layer was as thin as shown in Fig. 6.

Although the high bonding temperature and the longer bonding time produced a tight bonding between silicon nitride and aluminium, the growth of the reaction layer and the shrinkage of the aluminium layer weakened the strength of the joints. Therefore, the bonding temperature conditions of 1000 to 1100 K and the bonding time of 5 to 10 min were the best conditions for bonding in the present system.

5. Conclusion

A process of bonding silicon nitride to silicon nitride and to Invar alloy using an aluminium layer has been investigated. It was revealed that aluminium was a good interlayer for bonding in both combinations. In the silicon nitride–Al–Invar alloy system, the aluminium layer and the reaction layer with the network of the fine cracks growing perpendicular to the interface compensated the thermal expansion mismatch. Since the present bonding process was very simple and did not require high bonding temperature, high bonding pressure or a long bonding time, it is concluded that the present bonding method was a good candidate as a practical bonding process. Precise evaluation of the reaction at the silicon nitride–aluminium interface will be reported in near future.

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References

1. K. SUGANUMA, T. OKAMOTO, M. KOIZUMI and M. SHIMADA, *J. Mater. Sci. Lett.* **4** (1985) 648.
2. M. G. NICHOLAS and R. M. CRISPIN, *J. Mater. Sci.* **17** (1982) 3347.
3. T. KABA, M. SHIMADA and M. KOIZUMI, *Comm. Amer. Ceram. Soc.* **66** (1983) 135.
4. H. KANZAKI and H. TABATA, *Yogyo-Kyokai-Shi* **91** (1983) 520.
5. P. F. BEHCER and S. A. HALEN, *Amer. Ceram. Soc. Bull.* **58** (1979) 582.
6. J. E. SIEBELS, in "Progress in Nitrogen Ceramics", edited by F. L. Riley (Martinus Nijhoff, Netherlands, 1983) pp. 455–63.
7. T. HIRAI and T. MATSUDA, *Kouon Gakkaishi* **3** (1977) 146.
8. E. H. ANDREWS, *J. Mater. Sci.* **1** (1966) 377.
9. M. NAKA, private communication, 1986.
10. K. SUGANUMA, unpublished work, 1986.
11. K. SUGANUMA, T. OKAMOTO, M. KOIZUMI and M. SHIMADA, *Adv. Ceram. Mater.* **1** (1986) 356.
12. K. SUGANUMA, T. OKAMOTO, M. KOIZUMI and M. SHIMADA, *Comm. Amer. Ceram. Soc.* **67** (1984) 256.
13. K. SUGANUMA, T. OKAMOTO, M. KOIZUMI and M. SHIMADA, *Amer. Ceram. Soc. Bull.* **65** (1986) 1060.

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