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Joint of silicon nitride and molybdenum with vanadium foil, and its high-temperature strength

YOSHIRO ITO, KAZUMASA KITAMURA*, MASAYOSHI KANNO
Department of Mechanical Engineering, Nagaoka University of Technology, 1603-1, Kamitomioka, Nagaoka, Niigata, 940-21, Japan

Joints of silicon nitride and molybdenum with a vanadium interlayer were fabricated using a vacuum hot-pressing facility. The optimum joining conditions for producing a joint with the highest shear strength were found to be as follows: a temperature of 1328 K, a mechanical pressure of 20 MPa and a bonding time of 5.4 ks. The effect of test temperature on shear strength was also examined. The strength level was initially 118 MPa at room temperature and this level gradually decreased as the test temperature rose. At 973 K, the strength level was still 70 MPa. Observations of the interface by scanning electron microscopy (SEM) and electron probe X-ray microanalysis (EPMA) revealed that a layer of reaction product V_3Si formed at the silicon-nitride–vanadium interface.

1. Introduction

The successful joining of ceramics to metals is an important technique in the application of ceramics. In high-temperature environments, the joints of ceramics and metals would be able to take advantage of the heat resistivity of ceramics. Several techniques for joining ceramics to metals have already been developed. Solid-state diffusion bonding is one such joining technique which can provide sound joints at both ambient and elevated temperatures [1, 2]. This technique, however, requires both a high fabrication temperature and a high pressure, thereby restricting the choice of metals to those that are refractory. Thus, it remains a challenge to develop a ceramic–metal joint which can endure high temperatures and yet can still be fabricated under moderate conditions.

One of the basic problems in joining a metal to a ceramic is how to relax or decrease the residual thermal stress caused by the thermal-expansion mismatch between the metal and the ceramic. In many joining techniques, soft-metal intermediate layers are used to relax the residual thermal stress successfully [2–6]. Soft and reactive metals and their alloys, such as aluminium, silver and their alloys, have been used as brazes and fillers. Residual thermal stress is relaxed by plastic deformation of these metals. Unfortunately, these metals have low melting points and, consequently, their joints will fail at elevated temperatures.

To reduce the stress, metals with low thermal-expansion coefficients are used as interlayers to compensate for their thermal-expansion mismatch. Niobium and molybdenum are two such metals. They are refractory and generally require a high reaction temperature and pressure to bond with ceramics. These limitations make it difficult to apply this method to a wide variety of joining pairs. From a practical point of view, more moderate bonding conditions are preferred.

Another problem area concerns reactions at the interface between ceramics and metals. Important questions arise here about the type of reactions which occur, the reaction conditions, the reaction products and their properties, and, finally, the effect of minor compounds and/or elements, which may be sintering additives, surface oxides, etc.

The aims of our research, therefore, were two-fold: to make ceramic–metal joints displaying high strength (100 MPa) even at high temperatures (about 973 K) under moderate conditions (e.g. at temperatures below 1573 K and pressures below 100 MPa), and to study the chemistry at the interface.

In this study, we chose silicon nitride and molybdenum as the joining pair. Molybdenum has a thermal-expansion coefficient close to those of ceramics such as silicon nitride. To increase reactivity at the interface and to moderate bonding conditions, vanadium foil was used as an interlayer. Vanadium is reactive and has a high melting point.

2. Experimental procedure

Beta-silicon nitride, TSN03, purchased from the Toshiba Company was pressureless sintered, and it contained several compounds of aluminium, yttrium and titanium as sintering additives. It was in the form of a cylinder measuring 12.5 mm in diameter and 5 mm thick with flat sides, which were polished to a roughness of 3 μm. A molybdenum rod 10 mm in

*Present Address, NGK Insulators, Ltd., Mizuho, Nagoya, Japan

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diameter was cut into discs 5 mm thick, and then their surfaces were polished to the same roughness as the silicon nitride. The thickness of the vanadium foil was 25 μm. Both metals had a purity of 99.95%.

The joined sample was fabricated using a vacuum furnace equipped with a hand-made press system. A schematic drawing of the furnace is presented in Fig. 1. The rate of temperature change of the furnace was about $0.2\ \mathrm{K\,s^{-1}}$ during heating and $0.6\ \mathrm{K\,s^{-1}}$ during cooling down to 1173 K. This rate gradually slowed on further cooling, measuring $0.03\ \mathrm{K\,s^{-1}}$ between 873 K and room temperature. The pressure in the furnace was 0.9 to 12.0×10^{-3} Pa in all cases.

The bonding pressure was measured by a load cell. Pressure was applied when the temperature reached the designated value for bonding periods. A slight pressure of 2 MPa, resulting from the weight of the pressing rod and atmospheric pressure, was applied during the cooling period.

The shear strength of the joint was measured by an autograph (Shimazu Company, DSS500) equipped with a hand-made jig with a crosshead speed of $8.33 \times 10^{-5}\ \mathrm{m\,s^{-1}}$. A schematic drawing of the sample and the testing jig are shown in Fig 2.

The interfaces of the joints were observed by scanning electron microscopy (SEM) equipped for electrone probe X-ray microanalysis (EPMA), by transmission electron microscopy (TEM) and by X-ray diffraction.

3. Results

In the shear-strength tests, two types of load–displacement curves, which corresponded to the two different fracture positions, were observed. Examples of these curves are shown in Fig. 3. When the sample fractured only at the interface between the ceramic and the metal, the curve in Fig. 3a was obtained. The curve in Fig. 3b was obtained when additional fractures occurred in the ceramic at the loads corresponding to the small peaks on this curve. The final fracture occurred at the interface in both cases; the shear strength of the interface was determined from these curves.

The effect of bonding pressure on the shear strength of the joint at room temperature is shown in Fig. 4 for three different bonding times. In each sample, the bonding temperature was 1328 K. A short bonding period of 10 min resulted in weak joints even with a pressure of 25 MPa. Bonding times longer than 90 min yielded a maximum strength of about 120 MPa when sufficient pressure was applied. The pressure needed to obtain the maximum strength decreased as the bonding time lengthened.

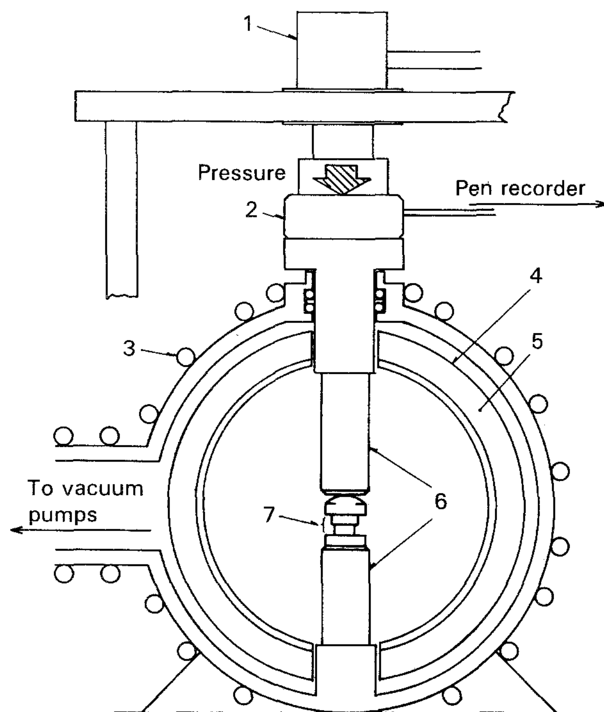

Figure 1 Schematic drawing of the furnace and hand-made press system. (1) oil cylinder, (2) load cell, (3) cooling water coil, (4) radiation shields, (5) molybdenum heating element, (6) pressing rods (SUS 304), and (7) the sample.

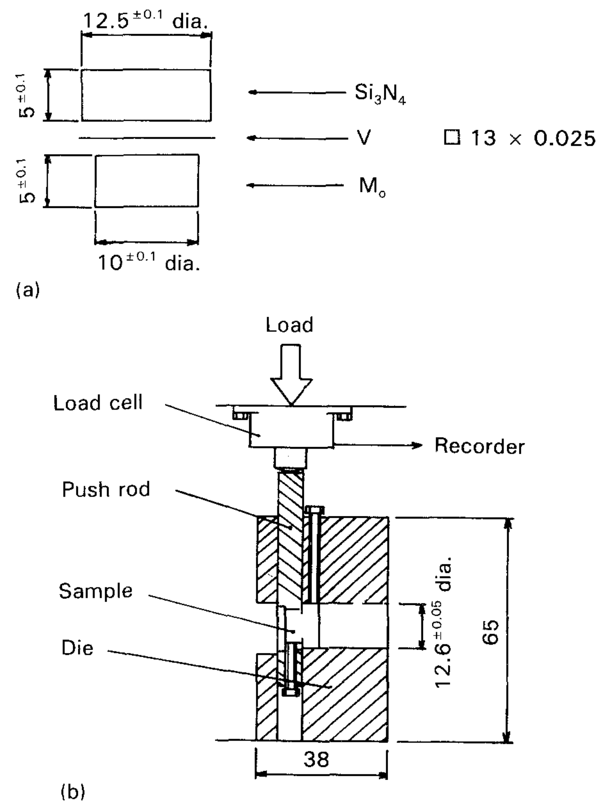

Figure 2 Schematic drawing of (a) the sample and (b) the jig.

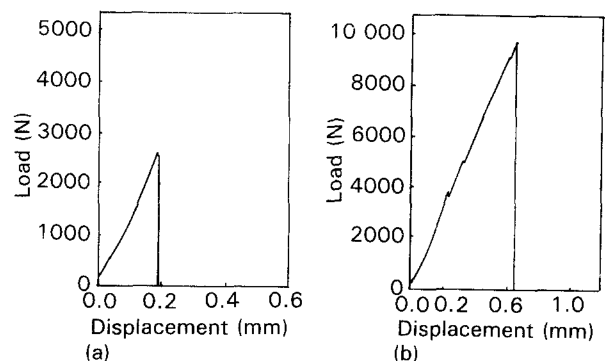

Figure 3 Examples of load–displacement curves: (a) the sample only fractured at the interface. (b) additional fractures occurred in the ceramic.

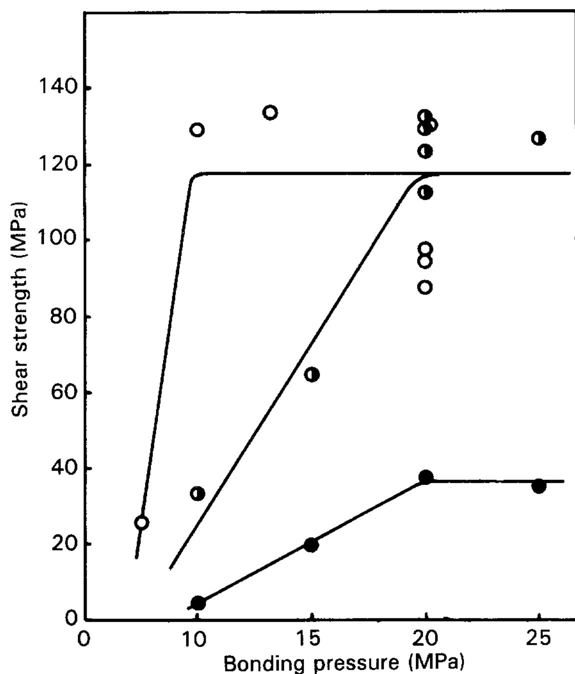

Figure 4 Effect of bonding pressure on the shear strength of the joint at room temperature for three different bonding times: (●) 10 min, (◑) 90 min, and (○) 160 min. The bonding temperature was 1328 K.

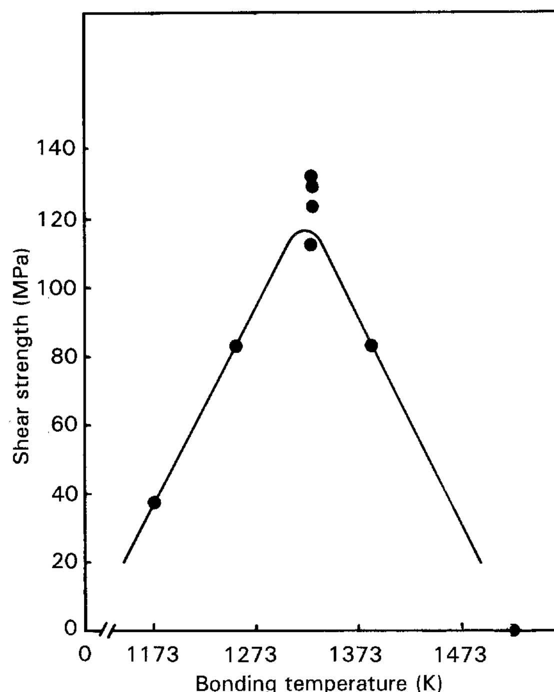

Figure 6 The influence of bonding temperature on the shear strength of the joint measured at room temperature, for a bonding time of 90 min and a bonding pressure of 20 MPa.

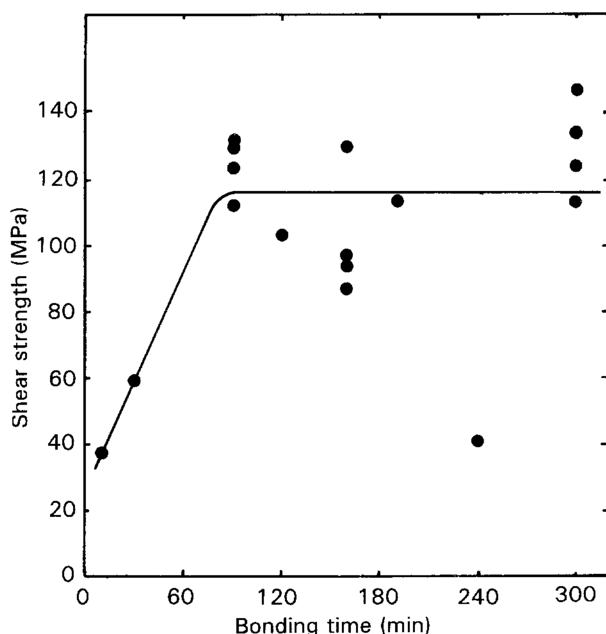

Figure 5 The influence of bonding time. The temperature and pressure were 1328 K and 20 MPa, respectively.

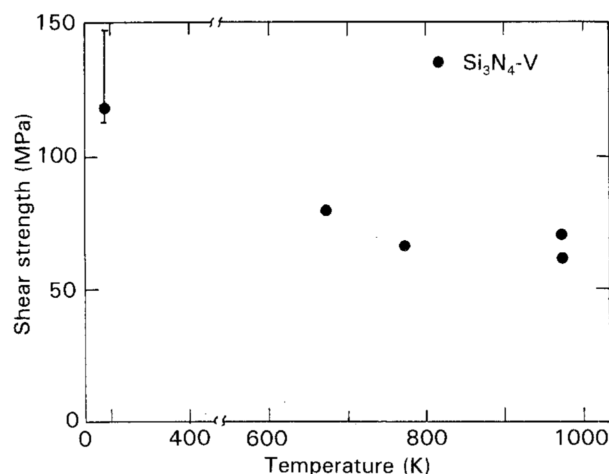

Figure 7 Shear-strength levels of the joints measured at elevated temperatures. The joints were fabricated under the optimum conditions.

Fig. 5 shows a more detailed study of the influence of bonding time. The temperature and pressure were 1328 K and 20 MPa, respectively. The interface strength increased as the bonding time lengthened and reached its maximum at 90 min. Longer holding periods gave no further increase in strength.

The influence of fabricating temperature is presented in Fig. 6. The pressure was 20 MPa and the holding time was 90 min. The strength increased with increasing temperature in the region between 1173 and 1328 K. At higher temperatures, it decreased with increases in temperature, and finally no bonding occurred at 1523 K. The strongest joints were obtained at 1328 K and their average interface strength was 120 MPa, with the maximum and the minimum values being 147.3 and 112.5 MPa, respectively.

The optimum fabricating conditions thus determined are: temperature, 1328 K; pressure, 20 MPa; and bonding time, 90 min. This pressure and time are the minimum necessary to attain high shear strength.

Fracturing in the ceramic occurred at small peaks in the load–displacement curves shown in Fig. 3b. The first small peak appeared at almost equal loads and some cracks were observed in the ceramic. The crack started at the upper edge of the metal disc, which was smaller than the ceramic disc, and extended into the ceramic. This type of failure was evidently caused by residual thermal stress concentrated on the boundary of the metal disc.

Shear-strength levels measured at elevated temperatures are shown in Fig. 7. Test jigs used in high-temperature measurements were different from those

used at room temperature. The clearance between the holding and the pushing jigs was larger than that of the room-temperature jigs to allow for thermal expansion at high test temperatures. Therefore, a fracture occurred in silicon nitride (Si_3N_4) and determination of the interface strength was difficult with these jigs being at such low temperatures. At high temperatures, the joint fractured at the interface and no crack appeared at low load. The shear strength of the interface was 79.9 MPa at 673 K and 70 MPa at 973 K. The strength value seemed to diminish slightly as the test temperature increased.

A SEM photograph of the join is shown in Fig. 8. The interface between the molybdenum and vanadium was a smooth and clear single boundary without any cracks or voids. Between vanadium (V) and Si_3N_4, a new layer about 2 μm thick was formed. Both boundaries of the layer were smooth and free of voids or cracks.

The distribution of several elements across the V–Si_3N_4 interface, as measured by EPMA, is shown in Fig. 9. The distribution profiles of vanadium and silicon (Si) showed plateaus which were clearly coincident in the intermediate layer. The profiles of the other elements did not show such plateaus. A similar measurement across the molybdenum–vanadium interface revealed that both elements smoothly penetrated into each other without any peaks or plateaus.

An XRD measurement of the fractured surface showed peaks originated from V_3Si in addition to V or Si_3N_4. The peaks of V were absent in the diffraction pattern from the ceramic side and vice versa, but the peaks from V_3Si were observed on both sides. Thus, it is evident that the joint fractured in the V_3Si layer located between V and Si_3N_4. The X-ray patterns from the pairs treated at 1523 K showed additional peaks of V_5Si_3.

In TEM observations of the V–Si_3N_4 interface, no void was observed at this interface. Diffraction patterns indicated the presence of V_3Si in the interlayer. At a certain part of the interface, a pattern of a vanadium oxide (V_2O_3) was obtained.

4. Discussion

Vanadium formed a strong interlayer of V_3Si by reacting with the silicon nitride used. Interfaces between the interlayer and Si_3N_4 or V were very smooth and, compared with other systems such as Si_3N_4–nickel [6], were free of voids. The interlayer had a high mechanical strength up to 1000 K, and this layer determined the interface strength. The mechanical properties of V_3Si have not been studied fully as far as we know and only the yield strength and hardness have been reported [7, 8]. V_3Si has a high yield strength up to about 1500 K; this is in agreement with our results.

The load–displacement curves obtained suggested that the level of residual thermal stress in the ceramic

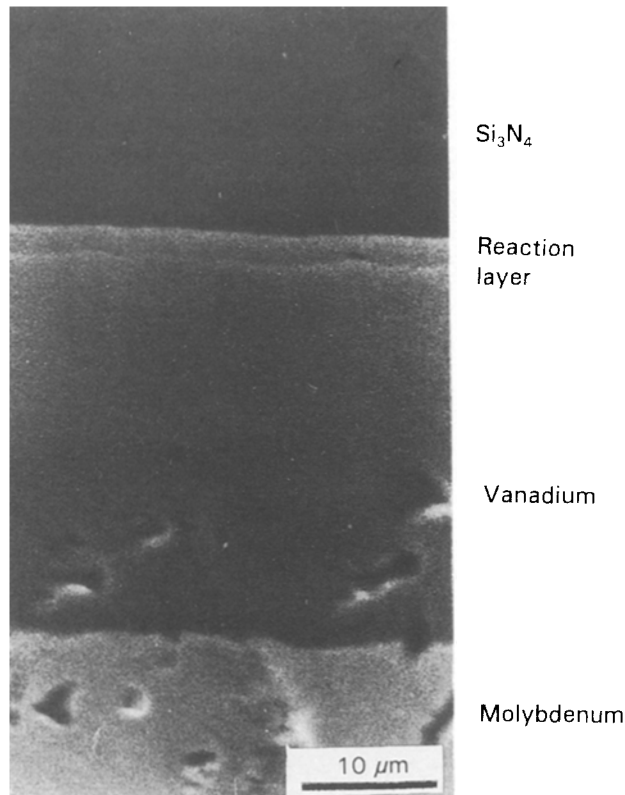

Figure 8 SEM photograph of the interfaces.

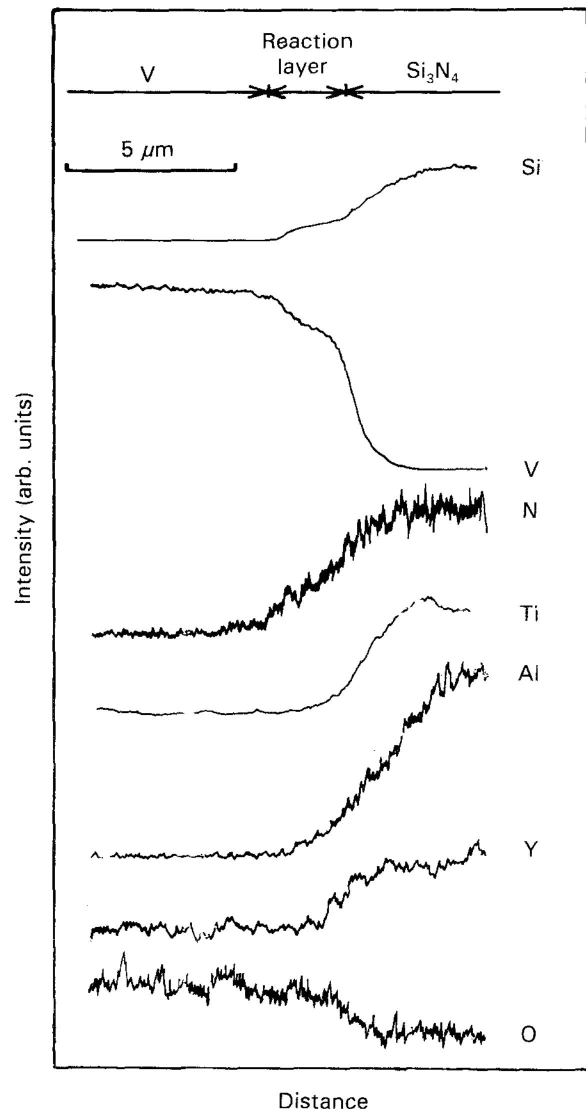

Figure 9 Distribution of several elements across the V–Si_3N_4 interface measured by EPMA.

was still high enough to start cracks at a rather low load. The crack started at the edge of the molybdenum disc and ran into the silicon nitride. It thus appears that vanadium, and not molybdenum, determined the stress. To increase the strength of the joint, the thickness of the foil should be decreased.

At the optimum fabrication temperature, 1328 K, only the V_3Si interlayer was formed, and increases in the bonding time resulted in increases in the thickness of this layer. At 1523 K, another silicide, V_5Si_3, was found in addition to V_3Si.

Phase diagrams and reactions of V–Si and V–Si_3N_4 systems have been reported [9–13]. Typical metal silicides formed with metal–Si reactions in the phase which is richest in Si (the VSi_2) in the V–Si case. The VSi_2 was formed from the direct reaction of the thin vanadium layer with silicon at temperatures above 873 K. The reaction of the vanadium layer with the oxidized silicon surface, however, resulted in the formation of V_3Si at the interface and of V_5Si_3 at the outer side of the layer. In the latter case, Tu *et al.* concluded that the reaction occurred between SiO_2 and vanadium [11, 12]. Schutz and Testardi [13] reported that either V_3Si or VSi_2 grew at a vanadium–silicon interface at about 1000 K and that they were never observed together. They suggested that varying the oxygen content could switch the growing phase: when the oxygen content in silicon was very low VSi_2 was formed; when it was slightly higher V_3Si was formed.

In our case, however, we could not find any SiO_2 phase in the ceramic. It is probable that SiO_2 existed in a very-thin surface layer and/or grain boundary. The thickness of V_3Si, however, did increase with the bonding time and the total amount of the V_3Si was much greater than expected from the probable SiO_2 layer and/or boundary. The vanadium should react with the silicon originating from Si_3N_4 to form silicides. Even though VSi_2 formed at the V–Si interface at lower temperatures than the optimum bonding temperature, we never observed the VSi_2 phase at the V–Si_3N_4 interface.

We conclude that the formation of a vanadium rich silicide at the V–Si_3N_4 interface was probably due to a kinetic effect: the supply of Si was controlled by both the diffusion of Si through the V_3Si layer and the dissociation of Si_3N_4. The appearance of V_5Si_3, a richer Si phase, at higher temperatures would support this explanation, because both the diffusion and the dissociation rates increased with the temperature. More detailed discussion, however, is difficult because we know little about the diffusion characteristics of silicon and/or vanadium through the V_3Si layer.

If the vanadium silicides were formed from reaction of the silicon originating from Si_3N_4, vanadium nitride should also be formed. Schuster and Nowotny reported that at 1273 K a ternary phase $V_5Si_3N_{1-x}$ was in equilibrium with Si_3N_4, V_9N_4, V_3Si, V_5Si_3, V_6Si_5 and VSi_2 [10]. In our XRD measurements and TEM observations, however, we found only V_3Si and no vanadium nitride in the system. It is likely that most of the nitrogen was solved in the metal and/or ceramic phase. It seems probable that part of the nitrogen escaped out to vacuum as N_2.

5. Conclusion

Joints of silicon nitride and molybdenum with a vanadium interlayer were fabricated using a vacuum hot-pressing facility. The strength was 118 MPa at room temperature and gradually decreased with increases in temperature, reaching 70 MPa at 973 K. The optimum joining conditions for producing a joint with the highest shear strength were as follows: a temperature of 1328 K, a pressure of 20 MPa and a bonding time of 5.4 ks. Observations of the interfaces by SEM and EPMA revealed that a reaction layer of V_3Si was formed at the silicon-nitride–vanadium interface and that the interface was smooth and had no voids.

Solid-state diffusion bonding using an interlayer of a refractory and a reactive metal should create a joint which is strong at elevated temperatures.

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