Interfacial Reaction Layers in SiC/Cu Joint Friction-Bonded with Nb Intermediate Layer[†]

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The influences of the interfacial reaction on the microstructure and bond strength of the SiC/Cu joint friction-bonded with a Nb intermediate layer have been investigated mainly by TEM observations. It has been found that the reaction at the joint interface proceeded during the heat treatment even at temperatures below 800 K to form reaction layers ~100 nm thick, which caused serious degradation of the joint strength. An attempt is made to thermodynamically explain the evolution of the interfacial microstructure caused by the reaction during the heat treatment.

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I. Introduction

In a previous paper⁽¹⁾, we reported that the strength of the friction-bonded joint of silicon carbide (SiC) to oxygen-free copper (Cu) could be improved drastically by the application of a Nb intermediate layer, and that reaction layers much thinner than those observed in brazed and diffusion-bonded joints were formed at the joint interface. It has been pointed out in several papers⁽²⁾⁻⁽⁴⁾ that for ceramic/metal bonding by brazing and diffusion bonding, an excessive thickness of the reaction layer has a detrimental effect on the joint strength, although a proper thickness contributes to strengthening of the ceramic/metal interface. The present study, therefore, is aimed at investigating the influence of high temperature heat treatment on the microstructure and bond strength of the SiC/Cu joint, since the interfacial reaction occurring at high temperatures in many cases leads to excessive growth of the reaction layer, which limits the application temperature of the ceramic/metal joint.

II. Experimental Details

The ceramics specimen to be bonded was a silicon carbide (SiC) produced through pressureless sintering with the aid of Al₂O₃ and Er₂O₃ (~a few%). The metal specimen was oxygen-free copper (Cu) with ~5 ppm O annealed for 3.6 ks at 773 K. The specimens were rods of 16 mm diameter. The intermediate layer was a foil of

commercially pure niobium (Nb) 20 µm thick. The surfaces of the Cu and SiC specimens were finished to JIS 3S by turning in a lathe and by grinding, respectively. The surfaces of the specimens and intermediate layer were degreased by washing in acetone just before bonding. Friction bonding was carried out with a brake-type machine by pressing a Cu specimen to a rotated SiC specimen. Friction-bonding parameters were as follows: rotation speed $N=26.7-53.2\text{ s}^{-1}$, friction time $t_1=3-6\text{ s}$, friction pressure $P_1=20\text{ MPa}$, forge time $t_2=6\text{ s}$, forge pressure $P_2=30-70\text{ MPa}$. In order to avoid significant oxidation of the intermediate layer during friction bonding, the bonding zone was sealed from the atmosphere by dausing with liquid nitrogen. The bond strength of the joint was estimated from the tensile strength at room temperature. Heat treatments of the joints were carried out at 773-1073 K in a vacuum furnace of $\sim 10^{-2}\text{ Pa}$. TEM observations were performed using a JEOL JEM-2010 operated at 200 kV.

III. Experimental Results

At the interface of a SiC/Cu joint friction-bonded with the Nb intermediate layer, three types of microstructures characterized by different interfacial layers were observed, as shown in Fig. 1⁽¹⁾. The most dominant reaction layer, shown in Fig. 1(a), was identified as Nb₅Si₃ based on SAD patterns and EDX analysis⁽¹⁾. In the region where the interface was curved toward the SiC side, a reaction layer consisting of NbC was observed, as shown in Fig. 1(b)⁽¹⁾. The microstructure observed over the second-widest areas was a Nb-rich layer as thin as a few nm, and in those areas, no obvious reaction layer could be detected, as shown in Fig. 1(c)⁽¹⁾.

When the SiC/Cu joint friction-bonded with the Nb

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Fig. 1 TEM micrographs of a SiC/Cu joint interface bonded with a Nb intermediate layer: (a) Nb₅Si₃ layer, (b) NbC layer, and (c) Nb-rich layer.

Table 1 Strength of SiC/Cu joints friction-bonded with a Nb intermediate layer.

Tensile strength (MPa)	Fracture location	Heat treatment
47.8	SiC	as bonded
32.0	SiC	as bonded
0.5	Interface	1073 K–18.0 ks
5.2	Interface	1073 K–18.0 ks
43.0	SiC	773 K–3.6 ks
8.4	Interface	773 K–3.6 ks

SiC in Cu. In fact, ~7 at% Si was detected in the Cu layer by EDX analyses. Therefore, the graphite layer can be considered to be formed by precipitation from the Cu layer saturated with C, since the solubility limit of C in Cu is very low⁽⁵⁾. The SAD pattern shown in Fig. 2(b) indicates that the Cu layer had an orientational relationship with the SiC grain described by

$$(0001)_{\text{SiC}} // (1\bar{1}1)_{\text{Cu}}, [\bar{1}210]_{\text{SiC}} // [110]_{\text{Cu}}. \quad (1)$$

The misfit parameter between SiC and Cu lattices was estimated to be 18% when this relationship was satisfied. The graphite layer exhibited no preferred orientation, as can be seen from the SAD pattern in Fig. 2(b). In the area shown in Fig. 2(a), no reaction products other than the Cu, graphite, and Nb-rich layers could be observed.

In the region shown in Fig. 3, on the other hand, the Cu or graphite layer could not be detected after the heat treatment at 773 K. The reaction layer observed in this field consisted of Nb₅Si₃ (Cr₅B₃-type tetragonal) and NbC, as can be seen from the SAD pattern (see Fig. 3(c)) and dark field image (Fig. 3(b)). Since this layer consisted mainly of Nb₅Si₃ and the NbC layer did not coexist with the Nb₅Si₃ layer in the as-bonded state, it can be considered that NbC observed in Fig. 3 was formed during the heat treatment through the reaction between SiC and Nb₅Si₃. The absence of detectable Cu and graphite layers in this area suggests that the Nb₅Si₃ layer retards the formation of these layers.

When the joint was subjected to the heat treatment at 1073 K, Cu and graphite layers similar to those shown in Fig. 2 were observed in areas where only the Nb-rich layer had been formed in the as-bonded state. These layers, particularly the graphite layer, grew during the heat treatment at 1073 K, as compared with those observed after the heat treatment at 773 K.

In the region shown in Fig. 4, the NbC layer was observed after the heat treatment at 1073 K. Between this NbC layer and the SiC matrix, a Cu layer ~50 nm thick was formed, while no graphite layer could be detected. The Cu layer observed in this region was considerably thinner than those observed in regions where the Nb-rich layer was formed. The Cu layer observed in this region also had the orientational relationship (1) with the SiC grain (see Fig. 4(b)).

Fig. 2 TEM micrographs of a SiC/Cu joint interface bonded with the Nb intermediate layer and heat-treated for 3.6 ks at 773 K: (a) bright field image and (b) SAD pattern from the graphite layer, Cu layer, and adjacent SiC matrix, where pole figures of [110] Cu and [1210] SiC can be observed.

intermediate layer was subjected to heat treatments at 773 and 1073 K, the tensile strength of the joint interface was seriously impaired, as shown in Table 1. However, no significant change in the interfacial microstructure could be observed by optical or scanning electron microscopy.

TEM microstructures of the joint interface subjected to the heat treatment at 773 K are shown in Figs. 2 and 3. In the region where the Nb-rich layer was formed before the heat treatment, two layers of ~100 nm thickness were observed, as shown in Fig. 2(a). They were identified as Cu and graphite layers based on SAD patterns shown in Fig. 2(b), and dark field images. Since these layers were formed on the SiC side of the Nb-rich layer, it can be considered that they grew by the dissolution of

Fig. 3 TEM micrographs of a SiC/Cu joint interface bonded with the Nb intermediate layer and heat-treated for 3.6 ks at 773 K: (a) bright field image, (b) dark field image of NbC, and (c) SAD pattern from the Nb_5Si_3 and NbC layer.

Fig. 4 TEM micrographs of a SiC/Cu joint interface bonded with the Nb intermediate layer and heat-treated for 1.8 ks at 1073 K: (a) bright field image and (b) SAD pattern from the Cu layer and adjacent SiC matrix, where pole figures of $[110]$ Cu and $[\bar{1}210]$ SiC can be observed.

Fig. 5 TEM micrograph of a SiC/Cu joint interface bonded with the Nb intermediate layer and heat-treated for 1.8 ks at 1073 K.

In the microstructure shown in **Fig. 5**, the Nb_5Si_3 layer was observed after the heat treatment at 1073 K. SAD patterns and dark field images of this field indicated that this Nb_5Si_3 layer contained considerable amounts of NbC. Between this layer and the SiC matrix, a Cu layer with small graphite particles was also observed, as shown in Fig. 5. This Cu layer also had orientational relationship (1) with the SiC grain. Thus, in the regions where the reaction layers consisting of Nb_5Si_3 and NbC were observed, the Cu layer formed during the heat treatment was considerably thinner than those observed in the absence of these reaction layers, suggesting that they acted as a diffusion barrier to reduce the Cu flow toward the

SiC side. In this field, significant development of the graphite layer was also suppressed, as shown in Figs. 3–5. This effect can be explained by considering the interaction of C with NbC and Nb_5Si_3 , as described in the following section. During the heat treatment at 1073 K, grains in the Nb_5Si_3 layer grew slightly as compared with those observed in the as-bonded joint, although the grain size did not exceed 100 nm.

IV. Discussion

As shown in Fig. 2, a Cu layer accompanied by a graphite layer formed during heat treatments at 773 and 1073 K in the region where no obvious reaction layer was formed, except for a Nb-rich layer in the as-bonded state. These Cu and graphite layers can be considered to have developed from the original joint interface toward the SiC matrix, since they were on the SiC side of the Nb-rich layer. With respect to the above, Suganuma and Nogi⁽⁶⁾ observed, in the reactive wetting experiment of molten Cu on single-crystal SiC, that the SiC is dissolved into the liquid Cu at 1373 K, and after the solidification of the Cu, a Cu–Si alloy layer, followed by a very thick graphite-precipitated zone, is formed at the interface. The Cu–Si alloy layer had the same orientational relationship as the Cu layer observed in the present investigation. They reported that this graphite-precipitated zone is very weak and fracture occurs in this zone at very low stresses. Similarly, the formation of the graphite layer shown in Fig. 2 can be regarded as a cause of the serious degradation of the joint strength observed after the heat treatment, since no substantial growth of the other reaction layers was observed after the heat treatment.

Although SiC is a very stable compound, the dissolution of SiC into Cu solution, which results in the formation of graphite precipitates, is thermodynamically permissible because of the very low activity coefficient of Si in the Cu solution⁽⁶⁾. The activities of Si in equilibrium with SiC and graphite were calculated to be 2.35×10^{-3} at 1073 K from the reported value of the standard free energy of formation of SiC⁽⁷⁾. According to the regular solution approximation, the activity coefficient of Si in Cu decreases exponentially with decreasing temperature⁽⁶⁾⁽⁸⁾, and the activity coefficient at the solidus con-

tent γ_{sol} is generally given by

$$\gamma_{\text{sol}} = (x_{\text{liq}}/x_{\text{sol}})\gamma_{\text{liq}}, \quad (2)$$

where x_{liq} is the liquidus content, x_{sol} the solidus content, and γ_{liq} the activity coefficient at the liquidus content. On this basis, the activity of Si in the Cu layer (~ 7 at% Si) at 1073 K is estimated to be 1.30×10^{-4} using the extrapolated value of $(x_{\text{liq}}/x_{\text{sol}})^{(9)}$. Thus, the activity of Si in the Cu layer is well below that of Si equilibrated with SiC and graphite. Although this estimation is based on the activity coefficient of Si at much higher temperatures, it strongly supports the conclusion that the dissolution of SiC into the Cu solid solution is thermodynamically explainable. In a similar way, it can be shown that the SiC can be dissolved into the Cu solid solution at 773 K.

As mentioned in the preceding section, Figs. 3–5 indicate that the NbC and Nb₅Si₃ layers retard the growth of the Cu layer during the heat treatments at 773 and 1073 K. The NbC and Nb₅Si₃ layers probably act as barriers that reduce the diffusion flow that supplies Cu to the reaction front of the SiC. In the region where the NbC and Nb₅Si₃ layers were observed, substantial growth of the graphite layer during the heat treatment was also suppressed, as shown in Figs. 3–5. According to the phase diagram of the Nb–C system⁽¹⁰⁾, NbC has a wide homogeneity range; *i.e.*, it can dissolve C to the upper limit of the homogeneity range. Therefore, the formation of the graphite layer will be suppressed in the neighborhood of the NbC layer, until it is saturated with C. This effect, in addition to the reduction in the diffusion flow, will probably explain why the NbC layer suppresses the development of the graphite layer.

On the other hand, the influence of the Nb₅Si₃ layer on the development of the graphite layer can be explained by considering the following reaction:

The free energy change by this reaction ΔG is given by

$$\Delta G = \Delta G_{\text{NbC}}^{\circ} - \Delta G_{\text{SiC}}^{\circ} - (1/5)\Delta G_{\text{Nb}_5\text{Si}_3}^{\circ} - (8/5)RT \ln a_{\text{Si}}. \quad (4)$$

Although ΔG is a positive value when $a_{\text{Si}} = 1$, this reaction is thermodynamically permissible when $a_{\text{Si}} < 0.408$ at 1073 K. The activity of Si in the Cu layer adjacent to the Nb₅Si₃ layer has been estimated to be 1.30×10^{-4} , as described above in the discussion on the dissolution of SiC into the Cu solid solution. This result suggests that reaction (3) can proceed during heat treatment. In fact, it was observed that NbC was formed in the Nb₅Si₃ layer after the heat treatment (see Figs. 3 and 5), although it did not coexist in the as-bonded state. As long as this reaction proceeds, the significant development of the

graphite layer in the neighborhood of the Nb₅Si₃ layer will be suppressed.

These results suggest that the development of the graphite layer during the heat treatment at 773–1073 K can be controlled by the NbC and Nb₅Si₃ layers.

V. Summary

In order to discuss the influence of the interfacial reaction on the bond strength of the SiC/Cu joint friction-bonded with a Nb intermediate layer, the microstructure of the joint subjected to heat treatment has been investigated mainly by TEM observations, and its relationship to the tensile strength was elucidated. Three types of microstructures characterized by a Nb₅Si₃, NbC, or Nb-rich layer were observed at the joint interface in the as-bonded state. The heat treatment for 3.6–18.0 ks at 773–1073 K brought about serious degradation of the joint strength. After the heat treatment, a Cu layer followed by a thick graphite layer was observed to be in contact with the SiC matrix, in the region where no reaction layer other than the Nb-rich layer was formed in the as-bonded state. The formation of this graphite layer is the prime cause of the serious degradation of the joint strength. In the region where the Nb₅Si₃ and NbC layers were formed, the development of the graphite layer in particular was retarded as compared with those observed in the absence of the Nb₅Si₃ and NbC layers. Thermodynamical explanations have been given for the formation of the Cu and graphite layers, and the effects of the Nb₅Si₃ and NbC layers.

REFERENCES

- (1) A. Nishimoto, M. Ando, M. Takahashi, M. Aritoshi and K. Ikeuchi: *J. Japan Inst. Metals*, **63** (1999), 895–904.
- (2) S. Morozumi: *Bull. Japan Inst. Metals*, **29** (1990), 880–881.
- (3) Y. Nakao, K. Nishimoto and K. Saida: *Trans. JWS.*, **21** (1990), 135–143.
- (4) M. Naka and J. Feng: *J. Japan Inst. Metals*, **59** (1995), 79–83.
- (5) T. B. Massalski, J. L. Murray, L. H. Bennett and H. Baker: *Binary Alloy Phase Diagrams*, ASM, Metals Park, Ohio, **1** (1986), pp. 559.
- (6) K. Suganuma and K. Nogi: *J. Japan Inst. Metals*, **59** (1995), 1292–1298.
- (7) D. D. Wagman: *The NBS tables of chemical thermodynamic properties*, ACM, New York, (1982), pp. 24.
- (8) P. J. Bowles, H. F. Ramstad and F. D. Richardson: *J. I. S. I.*, **202** (1964), 113–121.
- (9) T. B. Massalski, J. L. Murray, L. H. Bennett and H. Baker: *Binary Alloy Phase Diagrams*, ASM, Metals Park, Ohio, **1** (1986), pp. 961.
- (10) T. B. Massalski, J. L. Murray, L. H. Bennett and H. Baker: *Binary Alloy Phase Diagrams*, ASM, Metals Park, Ohio, **1** (1986), pp. 577.