Friction Bonding of Silicon Carbide to Oxygen-Free Copper with an Intermediate Layer of Reactive Metal*1

Akio Nishimoto1,2, Masaaki Ando2, Makoto Takahashi1, Masatoshi Aritoshi3 and Kenji Ikeuchi1

1Joining and Welding Research Institute, Osaka University, Ibaraki 567-0047, Japan
2Akita National College of Technology, Akita 011-0923, Japan
3Hyogo Prefectural Institute of Industrial Research, Kobe 654-0037, Japan

Intermediate layers of various metals ranging from reactive metals to noble metals have been applied to friction bonding of SiC (pressureless-sintered silicon carbide) to Cu (oxygen-free copper), and their influences on the bond strength and microstructures of the joint have been systematically investigated by means of TEM observations. When a thin foil of reactive metal, Al, Ti, Zr, or Nb, was applied as the intermediate layer, the bond strength of SiC to Cu was improved considerably. In contrast, when an intermediate layer of Fe, Ni, or Ag was applied, the SiC specimen separated from the Cu specimen immediately after the bonding operation without the application of external load, similar to the case of bonding without an intermediate layer. During friction bonding with an intermediate layer of reactive metal, the intermediate layer was mechanically mixed with Cu to form a very complicated microstructure extending over a region as wide as a few 100 μm. TEM observations have revealed that very thin reaction layers between the SiC and reactive metals were formed. When the Ti intermediate layer was applied, a TiC layer 10–30 nm thick was formed over almost the entire area along the interface, and between this layer and the SiC matrix a very thin layer of a Cu solid solution was detected. On the other side of the TiC layer, a Ti4Si3 layer ~100 nm thick was partially observed. When the Nb or Zr intermediate layer was applied, a very thin interfacial layer, in which Nb or Zr was significantly concentrated, was observed in addition to the reaction layers of Nb5Si3, NbC, and ZrC. These interfacial layers can be characterized by their much smaller thickness and finer grain size than those observed in diffusion-bonded and brazed joints. Apart from the layers mentioned above, amorphous silicon oxide layers were occasionally observed, suggesting that the reactive metal enhanced the removal of the oxide film on the SiC surface.

(Received June 23, 2000; Accepted November 1, 2000)

Keywords: silicon carbide, copper, reactive metal, friction bonding, reaction layer, ceramic/metal interface, transmission electron microscopy, bond strength

1. Introduction

Many investigations of the diffusion bonding and brazing of ceramics to metals have been reported.1–7 An important result obtained from these investigations is that the bond strength of the ceramics/metal joint is improved considerably by the application of an intermediate layer (or a filler) containing a reactive metal such as Ti, Nb, Zr, or Cr. This effect of the reactive metal has been attributed to the formation of an interfacial layer by the reaction between the reactive metal and ceramic. That is, the interfacial reaction layer has been considered to be a binder between the ceramic and metal.8 In fact, it has often been observed that the reaction layer has a preferred orientation relationship with the adjacent ceramic grains, and the misfit of the lattice spacing at the ceramic/reaction-layer interface is very small, when this relationship is satisfied.3,6,9,10

On the other hand, friction bonding has been widely applied to join dissimilar metals. A salient feature of friction bonding is that the formation of the observable intermetallic compound layer can be suppressed by choosing appropriate bonding parameters, even if intermetallic compounds are formed under equilibrium conditions. For this reason, friction bonding has been practically applied to a number of dissimilar-metals combinations that are difficult to join owing to the formation of brittle intermetallic compounds at the interface. It has been pointed out in several papers11–13 that in ceramic/metal bonding by diffusion bonding and brazing, an excessive thickness of the reaction layer has a detrimental effect on the joint strength, although an appropriate thickness contributes to the strengthening of the ceramics/metal interface. Thus, the thickness of the interfacial reaction layer has been taken to be a critical factor governing the bond strength of the ceramic/metal joint. Therefore, we have undertaken this investigation to study the effect of the reactive metal on the bond strength of the ceramic/metal joint produced by friction bonding, i.e., a joint in which the interfacial reaction layer is expected to be much thinner than those in the diffusion-bonded and brazed joints. For this purpose, an intermediate layer of various metallic foils, ranging from reactive metals to noble metals, have been applied to friction bonding of ceramics to metal, and their effects on the bond strength and microstructure of the ceramic/metal interface have been systematically investigated.

Little information has been reported on the application of the intermediate layer to friction bonding,14,15 since a variety of dissimilar-metals combinations can be friction-bonded successfully with a suitable choice of bonding parameters. However, in our opinion, more attention should be paid to the application of the intermediate layer to friction bonding, particularly when the dissimilar materials to be bonded have extremely different properties, such as metals and ceramics. In this respect, the identification of effective intermediate layers to facilitate ceramic/metal friction bonding is another objective of the present investigation.

*1 This Paper was Originally Published in Journal of the Japan Institute of Metals 65 (1999), 895–904.
*2 Graduate Student, Osaka University, Present address: Kansai University.
2. Experimental Details

The ceramic specimen to be bonded was a silicon carbide (SiC) produced through pressureless sintering at 2273 K with the aid of a few% Al₂O₃ and Er₂O₃. This SiC specimen had sufficient thermal-shock resistance and strength to withstand the very rapid thermal cycle and friction torque imposed during friction bonding. Oxygen-free copper (Cu) annealed for 3.6 ks at 773 K was employed as the metal specimen, since (1) the effect of the reactive-metal intermediate layer can be observed distinctively, and (2) Cu, having low flow stress, has been widely applied to the relaxation of the residual stress generated by the difference in thermal expansion between the metal and ceramic. The SiC and Cu specimens were rods of 16 mm diameter. The intermediate layers were foils of Al 10 μm, Ti 20 μm, Zr 20 μm, Nb 20–25 μm, Fe 30 μm, Ni 20 μm, and Ag 15 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 layers were degreased by washing in acetone just before bonding.

Friction bonding was carried out in a brake-type machine by pressing a Cu specimen to a rotated SiC specimen. The following friction-bonding conditions were employed: rotation speed \( N = 26.7–53.2 \, \text{s}^{-1} \), friction time \( t_f = 3–10 \, \text{s} \), friction pressure \( P_f = 20 \, \text{MPa} \), forge time \( t_g = 6 \, \text{s} \), forge pressure \( P_g = 30–70 \, \text{MPa} \). In order to avoid rapid oxidation of the intermediate layer during friction bonding, the bonding zone was sealed from the atmosphere by dousing with liquid nitrogen. After friction bonding, the joint was cooled slowly in a heat-insulating material.

The bond strength of the joint was estimated from the tensile strength. The tensile test was carried out using an Instron-type machine at a deformation rate of \( 1.7 \times 10^{-5} \, \text{mm/s} \). A device was developed which allows us to carry out the tensile test without further machining of the joint.

The microstructure of the joint has been observed with an optical microscope, SEM (scanning electron microscope), and TEM (transmission electron microscope). The thin foil specimen for TEM observation was prepared from a plate \( \sim 0.5 \, \text{mm} \) thick cut from a joint by grinding with a dimpler and subsequent Ar-atom milling. TEM observations were performed using a JEOL JEM-2010 operated at an acceleration voltage of 200 kV.

3. Experimental Results

The bond strength of the SiC specimen to the Cu specimen was influenced strongly by the intermediate layer of reactive metal, as shown in Fig. 1. When the Cu specimen was bonded directly to SiC, they were separated at the interface immediately after the bonding operation without the application of an external load. Similar results were obtained when the intermediate layers of Fe, Ni, and Ag were applied. In contrast, when an intermediate layer of a reactive metal, Al, Ti, Zr, or Nb, was applied, the upset deformation of the Cu specimen was markedly enhanced, and joints which could withstand the load imposed during the machining of the specimen for metallographic observation were obtained.

Results of the tensile test of joints bonded with the Ti and Nb intermediate layers are summarized in Table 1. Joints bonded with the intermediate layer of Ti or Nb were fractured in SiC in the tensile test, although the fracture strength was much lower than that of the SiC base material. The fracture strength of these joints were also significantly lower than those observed in diffusion-bonded and brazed joints.\(^7\)\(^,\)\(^1\)\(^,\)\(^2\)\(^,\)\(^3\) Cracks formed during the tensile test of these joints propagated along a path characteristic of fracture under the influence of residual stresses caused by the difference in thermal expansions between ceramic and metal.\(^1\) This suggests that the residual thermal stress significantly reduced the strength of the SiC/Cu joint produced by the friction bonding with the Ti or Nb intermediate layer. When the intermediate layer of Fe or Ni was applied, as shown in Table 1, the degree of upset deformation of the Cu specimen increased with the rotation speed and friction time to almost the same levels as those observed in joints bonded with the Ti and Nb intermediate layers. Even in these cases, however, joints were fractured at the interface at very low stress levels. These results suggest that the marked improvement in the bond strength of the SiC/Cu
joint with the intermediate layer of reactive metal cannot be attributed simply to the difference in the degree of upset deformation of the Cu specimen.

When the intermediate layer of reactive metal was applied, a region presenting a complicated microstructure was observed, in which the intermediate layer was mixed with Cu, as shown in Fig. 2. The width of this mixed region was generally much greater than the thickness of the intermediate layer (more than 200 µm for the intermediate layers of Al, Ti, and Nb). In the ceramic adjacent to the interface, microcracks

<table>
<thead>
<tr>
<th>Intermediate layer</th>
<th>Thickness (µm)</th>
<th>Weld. param.</th>
<th>Axial displacement (mm)</th>
<th>Strength (MPa)</th>
<th>Fracture location</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>20</td>
<td>I</td>
<td>1.1</td>
<td>4.0</td>
<td>SiC</td>
</tr>
<tr>
<td>Ti</td>
<td>20</td>
<td>III</td>
<td>1.7</td>
<td>15.4</td>
<td>SiC</td>
</tr>
<tr>
<td>Ti</td>
<td>20</td>
<td>IV</td>
<td>0.4</td>
<td>4.1</td>
<td>SiC</td>
</tr>
<tr>
<td>Ti</td>
<td>20</td>
<td>V</td>
<td>1.8</td>
<td>11.8</td>
<td>SiC</td>
</tr>
<tr>
<td>Nb</td>
<td>25</td>
<td>I</td>
<td>3.4</td>
<td>41.0</td>
<td>SiC</td>
</tr>
<tr>
<td>Nb</td>
<td>20</td>
<td>III</td>
<td>2.0</td>
<td>19.1</td>
<td>SiC</td>
</tr>
<tr>
<td>Nb</td>
<td>20</td>
<td>III</td>
<td>8.2</td>
<td>34.5</td>
<td>SiC</td>
</tr>
<tr>
<td>Nb</td>
<td>20</td>
<td>IV</td>
<td>15.2</td>
<td>47.8</td>
<td>SiC</td>
</tr>
<tr>
<td>Nb</td>
<td>20</td>
<td>IV</td>
<td>8.1</td>
<td>32.0</td>
<td>SiC</td>
</tr>
<tr>
<td>Nb</td>
<td>20</td>
<td>V</td>
<td>6.2</td>
<td>22.0</td>
<td>SiC</td>
</tr>
<tr>
<td>Fe</td>
<td>30</td>
<td>I</td>
<td>0.8</td>
<td>Not bonded</td>
<td>Interface</td>
</tr>
<tr>
<td>Fe</td>
<td>30</td>
<td>II</td>
<td>4.3</td>
<td>A</td>
<td>Interface</td>
</tr>
<tr>
<td>Ni</td>
<td>20</td>
<td>I</td>
<td>0.7</td>
<td>Not bonded</td>
<td>Interface</td>
</tr>
<tr>
<td>Ni</td>
<td>20</td>
<td>II</td>
<td>1.7</td>
<td>Not bonded</td>
<td>Interface</td>
</tr>
<tr>
<td>Cu (direct bonding)</td>
<td>I</td>
<td>0.7</td>
<td>Not bonded</td>
<td>Not bonded</td>
<td>Interface</td>
</tr>
<tr>
<td>Ag</td>
<td>10</td>
<td>I</td>
<td>0.7</td>
<td>Not bonded</td>
<td>Interface</td>
</tr>
</tbody>
</table>

Fig. 3 SEM micrograph of a SiC/Cu joint bonded with the Nb intermediate layer and EDX line analyses along line A'-A'.

Fig. 2 Microstructures of SiC/Cu joints friction-bonded with intermediate layers of Al (a), Ti (b), and Nb (c).
were observed, as shown in Figs. 2(b) and 2(c). These cracks were probably caused by residual thermal stress or friction torque during friction bonding.

The reactive metals of Ti, Nb, and Zr form stable silicides and carbides according to the phase diagrams. As shown in Fig. 2, however, no reaction layer could be detected at the friction-bonded interface with an optical microscope. Therefore, the microstructure of the joint was observed at higher magnifications. A SEM micrograph of a joint bonded with the Nb intermediate layer is shown in Fig. 3 along with the distribution profiles of Nb, Si, and Cu contents obtained by EDX analyses. It can be seen that intimate contact between the SiC and Cu surfaces was achieved even at positions where the SiC surface became highly uneven. In the region where the Nb intermediate layer was mixed with Cu, many particles a few \( \mu \text{m} \) in diameter were observed. These particles, rich in Si as can be seen from Fig. 3, can be regarded as SiC particles. Thus the SiC particles as well as the intermediate layer were involved in the mixed region. Such a complicated microstructure is unlikely to be formed over a region more than 100 \( \mu \text{m} \) wide by the diffusion mechanism, since the whole friction bonding process is completed within 10–20 s. Therefore, it can be considered that this microstructure is formed by mechanical mixing of the intermediate layer and SiC particles with Cu during the friction stage. In spite of such a vigorous mixing effect, no interfacial reaction layer was observed with an optical microscope or SEM, as can be concluded from Figs. 2 and 3. Similar microstructures were also observed with a SEM for joints bonded with the intermediate layer of Ti or Zr.

TEM observations revealed that reaction layers much thinner than those observed in diffusion-bonded and brazed joints were formed at the friction-bonded interface, when the Ti, Nb, and Zr intermediate layers were applied. A TEM microstructure of a joint bonded with the Ti intermediate layer is shown in Fig. 4(a). Two interfacial layers were observed between the SiC matrix and Cu–Ti mixed region. These were identified as Cu and TiC layers based on NBD (nanobeam diffraction) patterns, as shown in Figs. 4(b) and 4(c). EDX spectra from these two layers (see Fig. 5) indicate that the layer adjacent to SiC is composed of a Cu solid solution containing Si and Ti, and the other is composed of TiC. These double layers consisting of TiC and Cu solid solution were observed over almost the entire area of the interface. In addition to these layers, a \( \text{Ti}_5\text{Si}_3 \) layer was partially formed on the Cu side of the TiC layer, as shown in Fig. 6. This \( \text{Ti}_5\text{Si}_3 \) layer was identified based on a SAD (selected-area diffraction) pattern (see Fig. 6(b)) and EDX analyses. Thus, the microstructure of the joint bonded with the Ti intermediate layer consisted of the Cu layer, TiC.

![TEM micrographs of a SiC/Cu joint interface bonded with the Ti intermediate layer: (a) bright-field image, (b) NBD pattern from [011] pole of TiC and Cu layers, and (c) key diagram of Fig. 4(b).](image-url)
layer, Ti$_5$Si$_3$ layer, and Cu–Ti mixed region. The thickness of the Cu, TiC, and Ti$_5$Si$_3$ layers, not more than 200 nm in total, was much smaller than those observed in the diffusion-bonded and brazed joints.

In the joint bonded with the Nb intermediate layer, three types of interfacial microstructures were observed, as shown in Figs. 7, 8 and 9. The reaction layers shown in Figs. 7 and 8 were identified as Nb$_5$Si$_3$ and NbC, respectively. SAD patterns from these layers and dark-field images (see Figs. 7(b)–(c) and 8(b)–(c)) indicate that they consisted of very fine grains (50 nm or less in size) without any preferred orientation relationship with the SiC grain. In the area shown in Fig. 9, no obvious reaction layer could be detected by the NBD technique, but very narrow Nb-rich layers (less than 10 nm thick) were found, as can be inferred from EDX spectra shown in Fig. 10. The Nb$_5$Si$_3$ and Nb-rich layers were dominant microstructures in this joint, while the NbC layer was observed at positions where the interface was curved toward the SiC side. In this joint, no double layer consisting of a Cu solid

![Fig. 5 EDX spectra from spots represented by the corresponding letters in Fig. 4(a).](image)

![Fig. 6 TEM micrographs of a SiC/Cu joint interface bonded with the Ti intermediate layer: (a) bright-field image and (b) SAD pattern from [031] pole of Ti$_5$Si$_3$.](image)

![Fig. 7 TEM micrographs of a SiC/Cu joint interface bonded with the Nb intermediate layer: (a) bright-field image, (b) dark-field image, and (c) SAD pattern from the Nb$_5$Si$_3$ layer.](image)
solution and Nb carbide was observed, in contrast to the joint bonded with the Ti intermediate layer.

In the joint bonded with the Zr intermediate layer, as shown in Fig. 11, a layer a few nm thick was observed over almost the entire area of the interface. The EDX spectrum from this layer (see Fig. 12) suggests that this layer is rich in Zr, similar to the Nb-rich layer shown in Fig. 9. At positions where the interface was curved toward the SiC side, a layer about 50 nm thick was partially formed, as shown in Fig. 13(a), which was identified as a ZrC layer based on the SAD pattern shown in Fig. 13(b).

Apart from the interfacial layers described above, amorphous Si oxide was occasionally observed at the joint interface and in the adjacent Cu/intermediate-layer mixed region, as shown in Fig. 14, when the intermediate layer of reactive metal was applied. That is, the area showing light contrast in Fig. 14 was identified as amorphous Si oxide, based on the SAD pattern and EDX spectrum. Amorphous Si oxide was similarly observed in joints bonded with the Ti and Nb intermediate layers. These amorphous oxides probably originate from the oxide film on the SiC surface. Therefore, it may be considered that the intermediate layer of reactive metal en-
hances the removal of the oxide film from the SiC surface, since the oxide film must have covered the entire SiC surface before friction bonding.

4. Discussion

4.1 Improvement in bond strength with intermediate layer of reactive metal

As can be seen in Fig. 1, the application of the intermediate layer of reactive metal markedly increased the bond strength and the degree of upset deformation of the Cu specimen in friction bonding of SiC to Cu. On the other hand, the intermediate layer of Fe, Ni, or Ag had almost no influence on the bond strength or upset deformation even under the same bonding conditions. When the rotation speed and friction time were increased in friction bonding with the intermediate layer of Fe or Ni, the Cu specimen could undergo upset deformation to almost the same degree as that observed in the joint bonded with a reactive-metal intermediate layer, as shown in Table 1. However, the bond strength was only slightly improved by increasing the rotation speed and friction time for joints bonded with the Fe and Ni intermediate layers, even when the degree of upset deformation was increased to almost the same levels as those of the joint bonded with an intermediate layer of reactive metal; i.e., the joint bonded with the Fe intermediate layer was fractured at the interface during machining of the specimen for metallographic observation, and
no bonded joint could be obtained when the Ni intermediate layer was applied. It is generally accepted that the increase of the rotation speed and friction time raises the temperature at the friction interface. These results suggest that the rise in the degree of upset deformation and the temperature of the interface cannot explain the marked improvement of the bond strength of the SiC/Cu joint with the intermediate layer of reactive metal. The enhancement of the upset deformation by the intermediate layer of reactive metals can be attributed to the increase in friction torque as suggested by Fukushima and Hasui.16)

The optical microstructure (see Fig. 2) indicates that a considerable number of SiC particles were involved in the region where the intermediate layer was mechanically mixed with Cu. This suggests that the surface layer of the SiC specimen was removed during the friction stage. The amorphous Si oxide, probably originating from the superficial oxide film of the SiC specimen, was also observed to be incorporated into this mixed region (see Fig. 14). These results suggest that the intermediate layer of the reactive metal enhances the elimination of the surface contamination of the SiC specimen and the exposure of the fresh surface. It is conceivable that this effect of the intermediate layer facilitates the intimate contact between the clean surfaces of the SiC and Cu specimens, and contributes to the improvement of the bond strength.

According to Aritoshi et al.17) and Ando et al.18) reports, a reactive-metal intermediate layer of a thickness not more than 0.1 μm was effective in improving the bond strength of friction bonding, although the Cu/intermediate-layer mixed region was decreased to less than a few μm. Therefore it can be suggested that a mixed region much thinner than those observed in the present investigation (a few 100 μm thick) is sufficient to improve the bond strength.

4.2 Effect of interfacial reaction layer on bond strength

As shown in Figs. 4, 6, 7, 8 and 13, TEM observations revealed that reaction layers composed of the silicides and carbidies of the reactive metals were formed in the joint of SiC friction-bonded to Cu, when an intermediate layer of reactive metal was applied. The observed reaction layers were much thinner than those observed in previous studies on diffusion bonding and brazing of ceramics to metal.1-7) These results suggest that a reaction layer more than a few μm thick is not essential for joining ceramics to metal, at least by friction bonding. The silicides and carbidies observed are equilibrium phases, though not all phases described in the equilibrium phase diagrams were formed.

When the Ti intermediate layer was applied, the interfacial microstructure consisting of the Cu, TiC, and Ti5Si3 layers was observed, as shown in Fig. 6. Similar microstructure was observed in the brazed joint of SiC with a filler of Ag–Cu–Ti alloy and Cu–Ti alloy.12,19,20) Kato et al. showed that in the brazing of SiC with an Ag–Cu–Ti alloy filler, the Cu (Cu–Ag alloy) layer was formed between the TiC layer and SiC matrix, depending on the free-C content of the SiC specimen.19) According to their result, the Cu layer was formed when the C content was less than 0.1%. Since the free C content of our SiC specimen was estimated to be 0.05%, the formation of the Cu layer observed in the friction-bonded joint is consistent with Kato et al. result.19) They suggested that the bond strength was significantly impaired by the formation of the Cu layer. Tamai and Naka22) also observed a similar interfacial microstructure in the brazed joint of SiC with a Cu–Ti alloy filler, and suggested that the bond strength of the joint was improved as the thickness of the Cu layer was decreased. The Cu layer observed in the present investigation was less than 20 nm thick, while those observed in the brazed joint were a few μm thick. Therefore, it can be considered that the Cu layer observed in the present investigation does not have a significant effect on the bond strength. Suganuma and Nogi23) observed, in the reactive wetting experiment of molten Cu on single-crystalline SiC, that a Cu–Si alloy layer, followed by a graphite layer, was formed at the interface after the solidification of Cu. They reported that the graphite layer was very weak. However, they did not find any evidence of a low bond strength of the interface between the Cu–Si alloy layer and SiC.24) In addition, it was also reported that when Cu and SiC specimens were brought into contact in ultrahigh vacuum after cleaning of their surfaces by Ar ion bombardment, they were firmly bonded, even at room temperature.21) A theoretical calculation based on the ASED-MO (atom-superposition and electron-delocalization molecular-orbital) method also suggested that the Cu atom was bound strongly to the SiC surface without any interfacial layer or binder.25) These experimental and theoretical results support the view that the Cu layer observed in the friction-bonded joint with the Ti intermediate layer has only slight influences on the bond strength.

The mechanical properties of bulk TiC and Ti5Si3 were measured by Iseki et al.26) According to their results, TiC showed a fracture strength comparable to that of SiC, while Ti5Si3 was fractured at much lower stresses. Naka et al.7) also reported that the diffusion-bonded joint of SiC with the Ti intermediate layer was fractured mainly at the Ti5Si3 layer. In the present investigation, however, the joint bonded with the Ti intermediate layer was fractured in the SiC away from the interface, but not at the Ti5Si3 layer. As shown in Fig. 5, the Ti5Si3 layer observed in the present investigation was very thin and discontinuous as compared with those observed in the brazed and diffusion-bonded joints. It has been reported by many authors that when a reaction layer with poor mechanical properties is formed at the joint interface, its influence on the joint performance can be mitigated by decreasing its thickness. The fine grain size of this layer also contributes to improving the mechanical properties of the layer. Probably for these reasons, the Ti5Si3 layer did not cause serious degradation of the bond strength of the friction-bonded joint.

For the interfacial layer formed through the reaction between SiC and Nb, it was reported that NbC, Nb5Si3, Nb2C, Nb5Si3C, and NbSi2 layers were formed in the solid-state diffusion bonding of SiC with a Nb intermediate layer.25) It was suggested that the NbSi2 layer was the most detrimental to the bond strength. However, as shown in Figs. 7, 8, and 9, this NbSi2 layer was not observed in the friction-bonded joint with the Nb intermediate layer. The interfacial layers observed in the present investigation were Nb5Si3, NbC, and Nb-rich layers. Since Nb5Si3 has the same crystal structure (hexagonal) as Ti5Si3, its mechanical properties are probably
poor, similar to $\text{Ti}_5\text{Si}_3$. However, the thickness of the $\text{Nb}_2\text{Si}_3$ layer was less than 0.2 $\mu$m, and its grain size was as small as a few tens of nm. Thus, the $\text{Nb}_2\text{Si}_3$ layer observed in the friction-bonded joint was much thinner than those observed in the diffusion-bonded joints, and consisted of very fine grains. Therefore, the $\text{Nb}_2\text{Si}_3$ layer does not cause a significant reduction of the bond strength of the friction-bonded joint. The reaction layer of NbC cannot be considered to be detrimental to the bond strength, similar to the TiC layer, since NbC and TiC crystals have the same cubic structure.

The phase formed in the Nb-rich layer could not be identified in the present investigation. EDX analyses suggest that Nb is the main component of this layer (see Fig. 10). Since the standard free energies of formation of Nb silicide and carbide are lower than that of $\text{SiC}_{27,28}$, it can be considered that the Nb atom can be bound more strongly to the SiC surface than the Cu atom.

The reaction layers of $\text{Nb}_2\text{Si}_3$ and NbC were formed in separate areas, as shown in Figs. 7 and 8, whereas the Nb silicide and carbide layers in the diffusion-bonded joint were reported to be in the form of multilayers. The interfacial layers in the diffusion-bonded joint were formed by the reaction between a SiC specimen and Nb foil. On the other hand, the Nb intermediate layer in the friction-bonded joint was mixed with Cu as very fine particles during the friction stage, and hence the Nb particles dispersed in Cu reacted with SiC to form the reaction layers at the interface. Considering the inhomogeneity of Nb distribution in the mixed region, the formation process of the $\text{Nb}_2\text{Si}_3$ and NbC layers will be discussed in the next paper.

As for the reaction layer between Zr and SiC particles, papers on diffusion bonding of SiC with a Zr intermediate layer have been reported. Morozumi et al. reported that interfacial reaction layers of ZrSi and ZrC were formed at a bonding temperature of 1773 K, and the bond strength of the joint was very low. The ZrSi layer seems to be responsible for the low bond strength, since ZrC probably has mechanical properties similar to those of TiC and NbC which have the same crystal structure (cubic). On the other hand, Fuku et al. observed interfacial reaction layers of ZrC, Zr$_2$Si$_3$, and Zr$_2$Si$_3$ at bonding temperatures from 1473 to 1573 K. However, they did not estimate the bond strength of the joint. At the friction-bonded interface, the predominant microstructure was the Zr-rich layer, as shown in Fig. 11. This Zr-rich layer probably contributed to the strengthening of the SiC/Cu interface, similar to the Nb-rich layer. Therefore, it may be considered that the friction-bonded joint with the Zr intermediate layer had a bond strength comparable to those bonded with the Ti and Nb intermediate layers, although its bond strength was not estimated.

As shown in Figs. 11 and 13, the formation of the reaction layer in the joint bonded with the Zr intermediate layer was limited to much narrower areas than in the joint bonded with the Ti or Nb intermediate layer. The reason for this can be explained as follows. In the Cu–Zr mixed region, a number of Cu$_2$Zr precipitates were observed. According to the phase diagram of the Cu–Zr system, the Zr content in the Cu solution in equilibrium with Cu$_2$Zr is very low. Probably because of this low Zr content, the formation of the Zr silicide and carbide at the bond interface was limited to only small amounts.

Thus it was found, through TEM observations, that interfacial reaction layers are formed in the friction-bonded joint, similar to those formed in the diffusion-bonded and brazed joints. Although some of them were reported to seriously impair the mechanical properties of the diffusion-bonded and brazed joints, their influence on the bond strength of the friction-bonded joint was not significant. The reason for this is probably because the reaction layers in the friction-bonded joint are much thinner and consist of much finer grains than those observed in the diffusion-bonded and brazed joints. The small thickness and fine grain size of the reaction layer reflect the severe and rapid plastic deformation as well as the short heating time accompanying the friction-bonding process, and these can be regarded as great advantages of friction bonding as a technique for joining dissimilar materials. It should also be noted that the Nb- and Zr-rich layers observed in the joint bonded with the Nb and Zr intermediate layers can contribute to improving the bond strength of the ceramics/metal interface, although their thickness is no more than a few nm.

5. Conclusions

The interfacial microstructures of SiC/Cu joints friction-bonded with an intermediate layer of reactive metal have been investigated mainly by TEM observations to study the effect of the reactive metal on the bond strength of the ceramics/metal interface. The results obtained are summarized as follows.

1. The application of an intermediate layer of reactive metal, Al, Ti, Nb and Zr, considerably increased the bond strength of the joint and the degree of upset deformation of the Cu specimen.

2. When an intermediate layer of reactive metal was applied, a very complicated microstructure was formed in the Cu adjacent to the bond interface through mechanical mixing of the intermediate layer and SiC particles with Cu.

3. Interfacial reaction layers ~0.1 $\mu$m thick were observed by TEM when Ti, Nb, and Zr intermediate layers were applied. They were composed of phases similar to those observed in diffusion-bonded and brazed joints, although they were much thinner.

4. In the joint bonded with the Ti intermediate layer, a TiC layer 10–30 nm thick was formed over almost the entire area along the interface, and a Cu layer few nm thick was formed between the TiC layer and SiC matrix. On the Cu side of the TiC layer, a Ti$_2$Si$_3$ layer ~100 nm thick was intermittently formed like islands.

5. At the interface of the joint bonded with the Nb intermediate layer, three types of microstructures characterized by different interfacial layers were observed: $\text{Nb}_2\text{Si}_3$ layer ~100 nm thick, NbC layer ~100 nm thick, and Nb-rich layer a few nm thick. Among these, the $\text{Nb}_2\text{Si}_3$ layer and Nb-rich layer were predominant, while the NbC layer was formed only at positions where the interface was curved toward SiC.

6. At the interface of the joint bonded with the Zr intermediate layer, a Zr-rich layer and ZrC layer were observed, similar to those observed in the joint bonded with the Nb intermediate layer.
(7) Amorphous Si oxide, which probably originated from the oxide film on the SiC surface, was occasionally observed at the interface of the joint bonded with an intermediate layer of reactive metal, suggesting that the reactive-metal intermediate layer enhanced the elimination of the oxide film from the SiC surface.

REFERENCES