

# Structure of wetting front in the Ag-Cu-Ti/SiC reactive system

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The nanostructure around the wetting triple line in the Ag-Cu-Ti/SiC reactive wetting system was studied. The reaction product consisted of an upper separated  $Ti_5Si_3$  layer more than 20 nm thick, and a lower TiC layer less than 10 nm thick was observed exceeding the front line of Ag-Cu-Ti brazing metal. At the top of the reaction product, the lower TiC layer was observed to project beyond the front line of the upper  $Ti_5Si_3$  layer. In Ag-Cu-Ti/ $Si_3N_4$  system, structural change around the wetting triple line as reactive wetting progressed has been reported, however, in the Ag-Cu-Ti/SiC system, the structure around the triple line did not change. The difference between the two systems was explained from the viewpoint of a stable phase change with the decrease of Ti activity as reactive wetting progressed. © 2000 Kluwer Academic Publishers

## 1. Introduction

A metal/ceramics interface commonly exists not only as a joint between metal and ceramics, but also as a boundary between matrix and precipitates or reinforcements in industrial materials. In many cases the metal/ceramics interface is formed via chemical reactions. Since such an interface sometimes affects the properties of the materials, the structure of the interface formed via chemical reactions has been studied [1–6]. In order to design the interface structure that will contribute to improvement of the material properties, an understanding of the interface formation mechanism is required. The structure of the interface is fixed during the interface formation process, therefore, we have focused our attention on a reactive wetting front where a new interface is continuously formed. Regarding the wetting front, many macroscopic studies on topics such as contact angle between liquid metal and ceramics as a parameter of wettability [7, 8], change in radius of the spreading molten metal as a wetting behavior [9–12] and some structures of the wetting front on the micrometer scale [13] have been conducted.

It is expected that the structure around the wetting triple line, which is defined as a liquid/solid/vapor triple junction, reflects the interface formation mechanism, because a newly formed interface appears below the triple line. To understand the interface formation mechanism, the structure around the triple line must be studied on the nanometer scale because phenomena involved in interface formation by reactive wetting, such as the dissolution of ceramics or the formation of reaction products, are expected to occur in a very small area.

In the Ag-Cu-Ti/ $Si_3N_4$  system, we have observed, in the nanometer scale, that the reaction layer lies in

front of the Ag-Cu-Ti alloy front line and the phase on top of the reaction layer changes from TiN to  $Ti_5Si_3$  as reactive wetting progresses [14]. In the present paper, the nanostructure around the wetting triple line in the Ag-Cu-Ti/SiC system was studied to understand the reactive wetting mechanism in this system, and then the macroscopic spreading behavior expressed as a change in radius, was discussed from the viewpoint of the reactive wetting mechanism.

## 2. Experimental

A brazing alloy, which is a laminated sheet consisting of 67.7 mass% Ag 27.4 mass% Cu 4.9 mass% Ti (GTE Wesgo, U.S.A.) was used as a wetting material, and a 6H-SiC singlecrystal plate whose surface has a SiC basal plane (Nippon Steel, Japan) was used as a substrate. The SiC plate was cut to a suitable size for use as the substrate, and then immersed in a 10% aqueous solution of hydrofluoric acid to remove the surface-oxidized layer immediately before the wetting experiment. The substrate was set in a vacuum chamber and the brazing alloy was placed on it. The brazing alloy melted on the substrate when heated to approximately 1300 K under a vacuum of  $10^{-3}$  Pa using a heating system equipped with a vacuum chamber. While the temperature was kept constant, changes in the spreading radius of the molten brazing alloy were measured as a function of time using an optical microscope. For comparison, a wetting experiment was also performed using polycrystalline  $Si_3N_4$  as a substrate (Toshiba, Japan) under the same conditions as mentioned above.

In the Ag-Cu-Ti/SiC system, specimens wetted for 60 and 900 seconds were cooled in the vacuum chamber,

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and were then mechanically cut and ground into a thin plate, and finely etched using a focused ion beam apparatus (FIB), SMI9200 (Seiko Instruments, Japan). The cross-sectional structures around the triple lines were observed using a transmission electron microscope equipped with a cold field emission gun (FE-TEM), HF-2000 (Hitachi, Japan). The quantities of the elements in the observed phases were analyzed by energy-dispersive X-ray spectroscopy (EDS) equipped with FE-TEM.

### 3. Results and discussion

#### 3.1. Nanostructure around the triple line in Ag-Cu-Ti/SiC system

The nanostructure around the wetting triple line in the specimen wetted for 60 seconds is shown in Fig. 1. The structure of the entire area observed is presented as a schematic, and (a), (b) and (c) show typical nanostructures in the boxed areas. As shown in the schematic, reaction products were observed exceeding the front line of the Ag-Cu-Ti brazing metal, as observed in

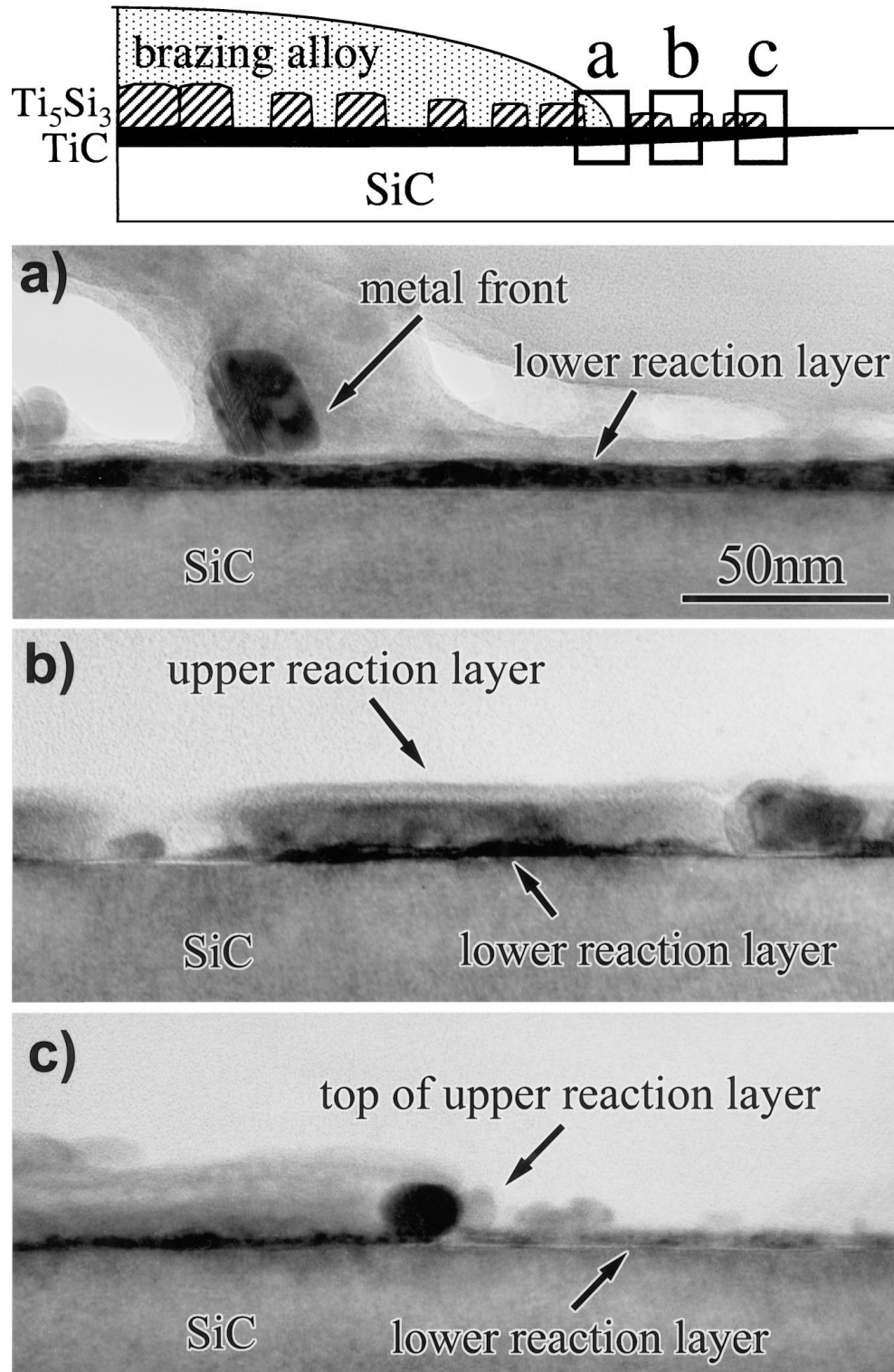


Figure 1 Nanostructure around the wetting triple line in the specimen wetted for 60 seconds. The structure in entire area observed is presented as a schematic, and (a), (b) and (c) show typical nanostructures in the boxed areas.

the Ag-Cu-Ti/Si<sub>3</sub>N<sub>4</sub> system [14]. The top of the brazing metal was detached from the specimen, as shown in Fig. 1a. The length of the brazing metal detached by debonding of the brazing metal/SiC interface was about 200 nm. This indicates the possibility of brazing metal contraction of approximately 200 nm in length due to the difference in thermal expansion coefficients between the brazing metal and SiC during the cooling of the specimen. This means some of the projection of the reaction products was caused by metal contraction. On the other hand, the projection length of the reaction products was much more than 200 nm, therefore, it is considered that the projection was formed as a precursor reaction layer at the top of the reaction layer, exceeding the front line of the brazing metal during wetting.

As shown in the schematic in Fig. 1, a reaction layer consisting of upper and lower reaction products was observed. The thickness of the lower layer was less than 10 nm, and that of the upper layer was more than 20 nm. In images (b) and (c), a double-layered reaction layer is observed. Around the brazing metal front in image (a), only the single lower reaction layer was observed. The upper layer had intervals, so it did not form by chance around the brazing metal front in this specimen. It is considered that lying of the single lower reaction layer is not a feature around the brazing metal front. Because the brazing metal spreads continuously on the irregular reaction layer, it is impossible for the brazing metal front to always exist on the single reaction lower layer.

Characterization of the upper and lower reaction layers was performed. From the upper layer, Ti and Si were detected as the main components by EDX analysis. The diffraction pattern of the upper layer shown in Fig. 2a coincided with that of Ti<sub>5</sub>Si<sub>3</sub>. With regard to the lower layer, Ti and a small amount of Si were detected by EDX. The diffraction pattern of the lower layer shown in Fig. 2b coincided with that of TiC. Therefore, it is considered that the upper and lower layers are considered to be Ti<sub>5</sub>Si<sub>3</sub> and TiC, respectively. In the Ag-Cu-Ti/SiC and Ti/SiC systems, the formation of Ti<sub>5</sub>Si<sub>3</sub> and TiC has been reported at the interface far from the triple line [6, 15, 16]. The fact that these reaction products were observed around the triple line indicates that the reacted interface is almost fixed at the moment of wetting. Besides Ti<sub>5</sub>Si<sub>3</sub> and TiC, Ti<sub>3</sub>SiC<sub>2</sub>

has been reported as a reaction product [6, 17, 18]. According to the free energy of formation of Ti<sub>3</sub>SiC<sub>2</sub> [19], it is possible that Ti<sub>3</sub>SiC<sub>2</sub> will also form as a reaction product. However, in our study, Ti<sub>3</sub>SiC<sub>2</sub> was not observed. It is considered that the reaction time is too short to form Ti<sub>3</sub>SiC<sub>2</sub> around the triple line.

Around the reaction layer front, the projection of the lower TiC layer was observed as shown in Fig. 1c. The thickness of the upper Ti<sub>5</sub>Si<sub>3</sub> layer was about 20 nm at the top of this layer. An upper Ti<sub>5</sub>Si<sub>3</sub> layer less than 20 nm thick was not observed in the specimen. The lower TiC layer appeared to fade out towards the top of the lower layer. The thickness of each layer will be discussed later in comparison to the thickness of the reaction layer observed around the wetting triple line in Ag-Cu-Ti/Si<sub>3</sub>N<sub>4</sub> system [14].

As for the specimen wetted for 900 seconds, almost the same nanostructure was observed around the wetting triple line as for the specimen wetted for 60 seconds.

### 3.2. Comparison of nanostructure between Ag-Cu-Ti/SiC and Ag-Cu-Ti/Si<sub>3</sub>N<sub>4</sub> systems

As shown in Fig. 1, the features of the structure around the triple line in the Ag-Cu-Ti/SiC system were the small thickness of the lower TiC layer of less than 10 nm and the intervals of the upper Ti<sub>5</sub>Si<sub>3</sub> layer. These features will be discussed in comparison to the structure around the triple line in the Ag-Cu-Ti/Si<sub>3</sub>N<sub>4</sub> system which has been previously reported [14].

In the Ag-Cu-Ti/Si<sub>3</sub>N<sub>4</sub> system, a similar double-layered reaction product consisting of an upper Ti<sub>5</sub>Si<sub>3</sub> layer and a lower TiN layer has been observed exceeding the front line of the brazing metal. However, the upper Ti<sub>5</sub>Si<sub>3</sub> layer had no intervals and the lower TiN layer was about ten times thicker than the lower TiC layer in the Ag-Cu-Ti/SiC system, as shown in Fig. 3 [14]. This implies that the amount of dissolved SiC, which supplies the component materials of the reaction products, was less than that of Si<sub>3</sub>N<sub>4</sub>. It has been reported that the interface between the Ag-Cu-Ti alloy and SiC tends to become flat by facing nucleated TiC to the basal plane of SiC [20]. This means that the most resistive plane

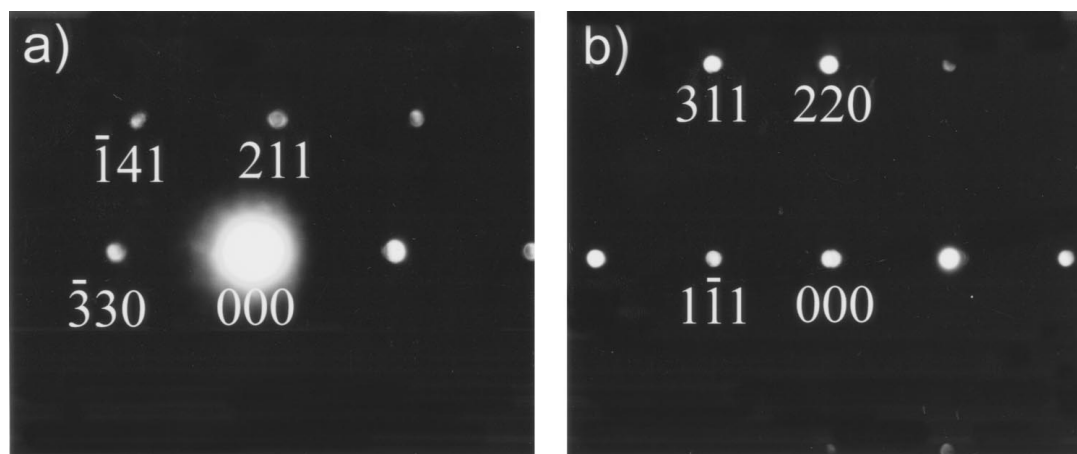


Figure 2 Diffraction patterns of the upper reaction layer (a) and the lower reaction layer (b) coincided with that of Ti<sub>5</sub>Si<sub>3</sub> and TiC, respectively.

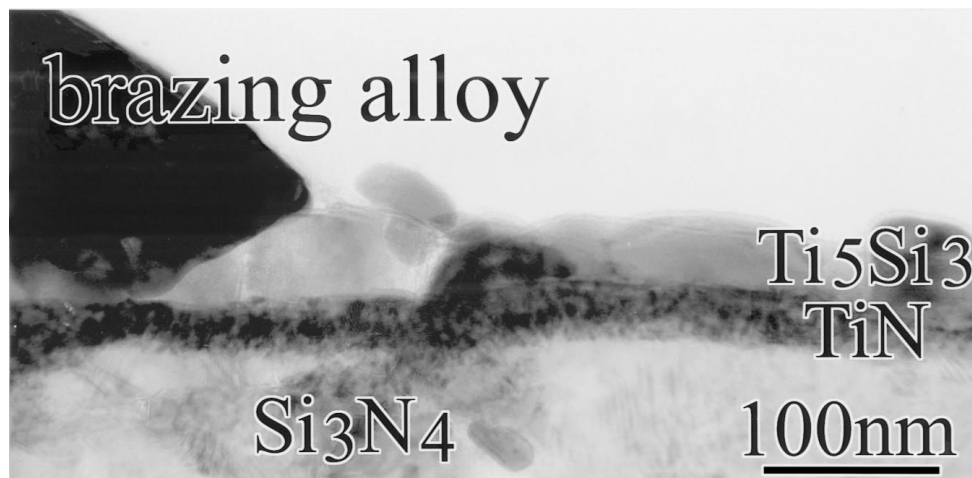


Figure 3 Nanostructure around the triple line in the Ag-Cu-Ti/Si<sub>3</sub>N<sub>4</sub> system [14]. Double-layered reaction product consists of an upper Ti<sub>5</sub>Si<sub>3</sub> and a lower TiN lay exceeding the front line of brazing alloy.

of SiC for dissolution by the Ag-Cu-Ti brazing metal is the basal plane. In our study, since wetting was performed on the basal plane of SiC, it is considered that one of the reasons for the low amount of dissolved SiC is the dissolution resistance of the SiC basal plane.

With regard to the upper Ti<sub>5</sub>Si<sub>3</sub> layer, it had intervals in the Ag-Cu-Ti/SiC system. As described above, no upper layer less than 20 nm thick was observed in the Ag-Cu-Ti/SiC system. In the Ag-Cu-Ti/Si<sub>3</sub>N<sub>4</sub> system, no upper Ti<sub>5</sub>Si<sub>3</sub> layer lying on the lower TiN layer less than 20 nm thick has been observed either around the triple line [14]. Therefore, it is considered that 20 nm is the critical thickness of Ti<sub>5</sub>Si<sub>3</sub>. In order to exceed the critical thickness, in spite of the low supply of Si by SiC dissolution, it is considered that the upper Ti<sub>5</sub>Si<sub>3</sub> was forced to form separately. It is well known that the critical nucleation size of precipitates is commonly much smaller than 20 nm. It is speculated that the observed critical size of Ti<sub>5</sub>Si<sub>3</sub> larger than expected size is caused by the surface or interface energy around Ti<sub>5</sub>Si<sub>3</sub> on TiC or Si-based substrates. In the previous study, the absence of a Ti<sub>5</sub>Si<sub>3</sub> layer with intervals at the interface between the metal phase and SiC in Ti/SiC or Ag-Cu-Ti/SiC systems has been reported [6, 15–18]. The reaction time is very short around the triple line, therefore, it is considered that the separate Ti<sub>5</sub>Si<sub>3</sub> layer was formed in our study due the short reaction time for growth.

With regard to the lower TiC layer, it appeared to fade out toward the top of this layer as describe above. This means the critical size of TiC is very small, and in fact, about 1 nm size of nucleated TiC has been reported [20]. Because of the small critical size of TiC and little supply of component materials from the SiC substrate, it is considered that TiC formed a continuous thin layer less than 10 nm thick instead of thick separate layer.

### 3.3. Formation mechanism of reactive wetting interface in the Ag-Cu-Ti/SiC system

From the observed structure, the mechanism of the reactive wetting in the Ag-Cu-Ti/SiC system is consid-

ered to be as follows. First, TiC was formed as the first reaction product through a reaction of C supplied by SiC substrate dissolution with Ti supplied by the brazing metal. From the projecting structure of the reaction layer, it is speculated that Ti diffused on the surface of the formed reaction product towards the top of the reaction product. Then, Ti<sub>5</sub>Si<sub>3</sub> was formed on the initially formed TiC by reacting Si that remained due to the formation of TiC with Ti supplied by the brazing metal. Another possible process is that TiC and Ti<sub>5</sub>Si<sub>3</sub> formations occurred simultaneously at different sites, where at the top of the reaction layer and on the TiC layer, respectively. In this case, it is considered that Ti<sub>5</sub>Si<sub>3</sub> was observed as a behind layer because of its growth beyond the critical thickness of 20 nm. In any cases, it is considered that the brazing metal spread on the formed reaction products.

The fact that almost the same structure was observed in the both specimens wetted for 60 and 900 seconds indicates that the reactive wetting mechanism is constant throughout the wetting process in the Ag-Cu-Ti/SiC system. Fig. 4 shows the change in radius of spreading Ag-Cu-Ti alloy on the SiC and Si<sub>3</sub>N<sub>4</sub> substrates as a function of time. The spreading rate became low for both systems after around 200 seconds. However, in the Ag-Cu-Ti/SiC system, the change in radius after around 200 seconds is smoother compared with that

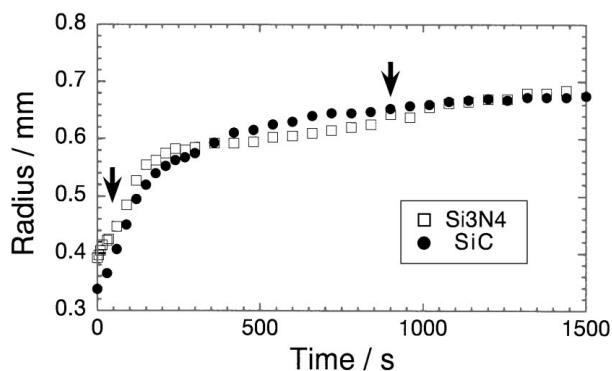


Figure 4 Change in radius of molten Ag-Cu-Ti alloy on SiC and Si<sub>3</sub>N<sub>4</sub> substrates as a function of time. The change in radius on SiC is smoother than that on Si<sub>3</sub>N<sub>4</sub>.

in the Ag-Cu-Ti/Si<sub>3</sub>N<sub>4</sub> system, where it has been reported that the structure around the wetting triple line changed before and after 200 seconds [14]. Therefore, it is considered that the smooth change in radius in the Ag-Cu-Ti/SiC system is due to the constant wetting mechanism supported by the unchanged structure around the triple line.

In the Ag-Cu-Ti/Si<sub>3</sub>N<sub>4</sub> system, the most exceeding reaction layer changed from the lower TiN layer to the upper Ti<sub>5</sub>Si<sub>3</sub> layer as reactive wetting progressed [14]. In the Ag-Cu-Ti/SiC system, the reason why the structure around the wetting triple line was not changed as reactive wetting progressed is now discussed. Fig. 5 shows the chemical potential diagrams for Ti-Si-N and Ti-Si-C ternary systems calculated using a thermodynamics database, MATL2 [21, 22]. In the diagrams, only the observed phases are presented, and effects of Ag and Cu were ignored because reaction products consisting of Cu or Ag were not observed. As has been reported [14], in the Ti-Si-N system shown, it is possible to change the stable phase from TiN to Ti<sub>5</sub>Si<sub>3</sub> as the activity of Ti decreases as shown in Fig. 5a. The activity of Ti must decrease because reactable Ti was consumed by the formation of reaction products as reactive wetting progressed. Assuming that the activity ratio of Si to nitrogen is almost constant around the triple line, the change of the stable phase from TiN to Ti<sub>5</sub>Si<sub>3</sub> is indicated by an arrow in Fig. 5a. With regard to the Ti-Si-C system, assuming that the activity ratio of Si to C is almost constant around the triple line, it is impossible to change the stable phase from TiC to Ti<sub>5</sub>Si<sub>3</sub> since the activity of Ti decreases due to the progress of reactive wetting, even if the activity ratio of Si to C

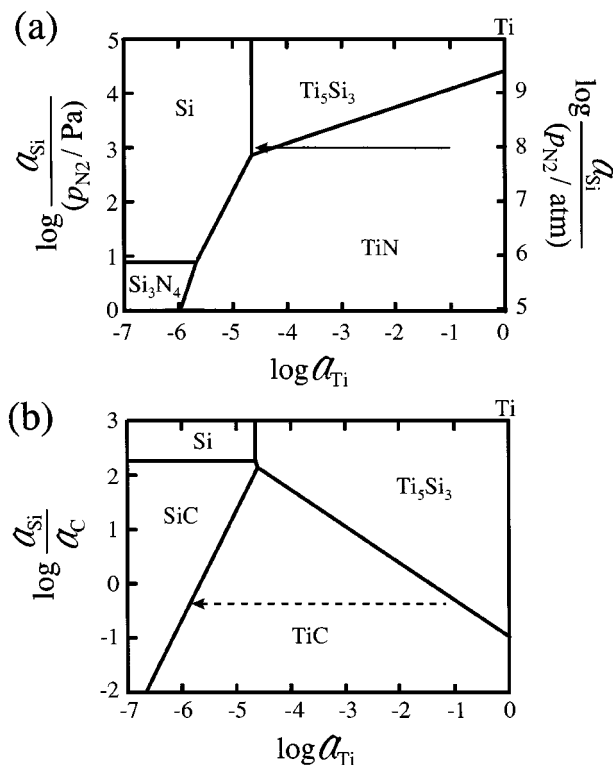


Figure 5 Chemical potential diagrams for Ti-S-N (a) and Ti-Si-C (b) ternary systems. Arrows show change of the stable phase as decreasing the activity of Ti as reactive wetting progressed.

takes any constant value, as shown in Fig. 5b. The first formed reaction product is expected to be observed at the top of the reaction layer, therefore, it is considered that the most stable phase forms there. At 60 seconds, TiC already formed at the top of the reaction product as the most stable phase, thus it is considered that the most exceeding layer could not change after 60 seconds because of the stability of TiC. Therefore, in the Ag-Cu-Ti/SiC system, an unchanged structure around the wetting triple line was observed as reactive wetting progressed. Based on Fig. 5b, there is a possibility of forming the Ti<sub>5</sub>Si<sub>3</sub> as the most exceeding layer before 60 seconds. We did not obtain the structure before 60 seconds, so this is the next key issue.

#### 4. Conclusions

In the Ag-Cu-Ti/SiC reactive wetting system, the structure around the triple line was studied, and the following conclusions were obtained.

1. The projection of the reaction product from the front line of Ag-Cu-Ti brazing metal was observed. The reaction product consisted of an upper separate Ti<sub>5</sub>Si<sub>3</sub> layer more than 20 nm thick and a lower TiC layer less than 10 nm thick. At the top of the reaction layer, the lower TiC layer exceeded from the upper Ti<sub>5</sub>Si<sub>3</sub> layer.

2. The nanostructure around the wetting triple line did not change between the specimens wetted for 60 and 900 seconds in the Ag-Cu-Ti/SiC system, though the structure did change in the Ag-Cu-Ti/Si<sub>3</sub>N<sub>4</sub> system. The unchanged structure is reasonable for the smooth change in radius of the Ag-Cu-Ti brazing metal on the SiC substrate compared with that on the Si<sub>3</sub>N<sub>4</sub> substrate. From this, it is considered that the mechanism of reactive wetting in the Ag-Cu-Ti/SiC system is constant as reactive wetting progresses.

3. It is considered that the unchanged structure in the Ag-Cu-Ti/SiC system is supported by the unchanged stable TiN phase. Based on a thermodynamic estimation, it is considered that the stable phase does not change with decreasing of activity of Ti caused by the reactive wetting progressing in this system.

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