



Title	Wetting of Silicon Carbide by Copper-Titanium Alloys(Physics, Process, Instrument & Measurement)
Author(s)	Naka, Masaaki; Okamoto, Ikuo; Nishino, Toshitugu et al.
Citation	Transactions of JWRI. 1989, 18(2), p. 189-194
Version Type	VoR
URL	https://doi.org/10.18910/6749
rights	
Note	

The University of Osaka Institutional Knowledge Archive : OUKA

<https://ir.library.osaka-u.ac.jp/>

The University of Osaka

Wetting of Silicon Carbide by Copper-Titanium Alloys[†]

Masaaki NAKA^{*}, Ikuo OKAMOTO^{**}, Toshitugu NISHINO^{***} and Shigeo URAI^{****}

Abstract

The contact angle of molten Cu-Ti alloys containing Ti content up to 60 at% or more on SiC was investigated by a sessile drop technique at 1373 K in a vacuum.

The contact angle of molten Cu-Ti alloys reaches the equilibrium value at 3.6 ks at 1373 K. The equilibrium contact angle of Cu-Ti alloys on SiC reduces drastically with increasing Ti content. Cu-Ti alloys containing Ti content of 30 at% or more shows the equilibrium contact angle of 7 degree or below. The addition of Ti to copper depresses the reaction of Cu with SiC by forming TiC and Ti₃SiC₂ carbides at SiC/Cu-Ti interface. This accounts for the superior wetting of the Cu-Ti alloys on SiC. The Cu-Ti alloys are applicable to the filler for joining SiC.

KEY WORDS : (Ceramic-Metal Joining) (Wetting) (Brazing) (Copper) (Copper-Titanium) (Ceramics) (Silicon Carbide) (Titanium Carbide)

1. Introduction

Wetting phenomena of metals against ceramics has received considerable interests in recent years in connection with related fields of powder sintering, composite materials processing and ceramic/metal joining.

Naka et al.^{1,2)} have reported that copper doesn't wet oxide ceramics such as alumina and zirconia in a vacuum, although aluminum wets the ceramics by increasing temperature.

Copper doesn't also wet silicon nitride and silicon carbide that possess superior mechanical properties^{3,4)}. The copper penetrates into the silicon carbide by reacting with the silicon carbide, although the metal doesn't react with silicon nitride. These works have focused on the wettability of pure copper on ceramics. Very little is known about the influence of alloying element on the wetting behavior of copper on silicon carbide.

The present work clarifies the effect of titanium addition to copper on the wetting behavior on silicon carbide, SiC by a sessile drop technique, and also the interface microstructure between the copper-titanium alloys and SiC.

2. Experimental Procedure

The ceramics used was pressureless sintered SiC with a

few percent of alumina. A series of Cu_{100-X}Ti_X alloys (X = 0 - 60) were used as shown in Table 1, where the numbers attached to the alloys designate the atomic percent of elements. The table also represents the melting points of the alloys.

The copper-titanium alloys of 6.3 mm³ in volume were placed on SiC plate in 15 mm diameter and 3 mm thickness which has been polished mechanically with diamond past in 30 μm diameter, and were heated at the rate of about 1.3 Ksec⁻¹ in a vacuum below 1.33 mPa. The contact angle between the peripheral surface of a small drop of molten metal and the horizontal surface of ceramics were photographically taken at regular intervals at 1373 K.

Table 1 Nominal composition of Cu-Ti alloys used.

	Nominal composition		Liquidus temperature (K)
	Cu(at%)	Ti(at%)	
Cu	100	0	1356
Cu ₉₅ Ti ₅	95	5	1333
Cu ₉₀ Ti ₁₀	90	10	1311
Cu ₈₀ Ti ₂₀	80	20	1243
Cu ₆₀ Ti ₄₀	60	40	1168
Cu ₅₀ Ti ₅₀	50	50	1248
Cu ₄₀ Ti ₆₀	40	60	1238

[†] Received on October, 31

^{*} Associate Professor

^{**} Professor

^{***} Instructor, Department of Metallurgical Engineering, Toyama National College of Technology

^{****} Associate Professor, Department of Metallurgical Engineering, Toyama National College of Technology

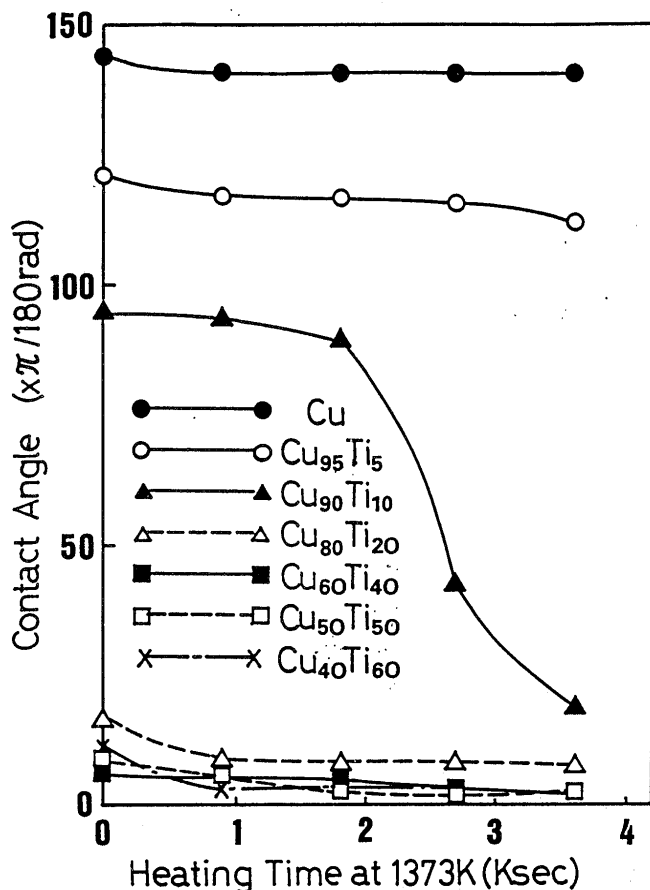


Fig. 1 Time dependence of contact angle for $\text{Cu}_{100-x}\text{Ti}_x$ alloys on SiC at 1373 K.

3. Results and Discussion

3.1 Contact angles of molten Cu-Ti alloys on SiC

The time dependence of the contact angles for Cu-Ti alloys containing titanium content up to 60 at% at 1373 K is shown in Fig. 1. The copper and $\text{Cu}_{95}\text{Ti}_5$ alloy show only a little time dependence. $\text{Cu}_{90}\text{Ti}_{10}$ alloy indicates the abrupt decrease in contact angle at 1.8 ks, and gives 20 degree of contact angle at 3.6 ksec. The dissolution of oxide film on the surface of the molten alloy is attributable to the drastic decrease in the contact angle. The Cu-Ti alloys containing titanium content of 20 at% or more represent the low contact angle of 10 degree, and definitely wet the silicon carbide.

Figure 2 shows the titanium content dependence of equilibrium contact angles for Cu-Ti alloys at 1373 K. Since the contact angles of alloys reach the constant values at 3.6 ks, the contact angles at 3.6 ks are taken as the equilibrium contact angles. The equilibrium contact angles of Cu-Ti alloys decrease effectively with increasing Ti content from 140 degree for copper to 7 degree or lower for Cu-Ti alloys containing titanium content of 20 at% or more. Cu-Ti alloys containing titanium content of

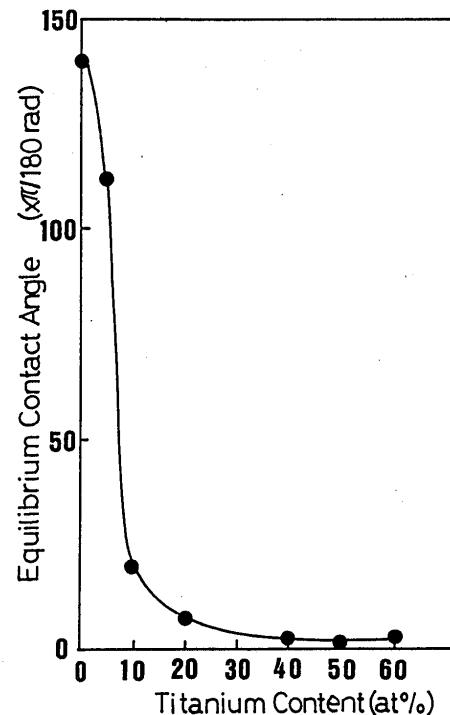


Fig. 2 Change in equilibrium contact angle for $\text{Cu}_{100-x}\text{Ti}_x$ alloys on SiC with Ti content at 1373 K.

20 at% or more quite well wet the silicon carbide, SiC.

3.2 Microstructure observation of SiC/Cu-Ti alloys interfaces

Cu-Ti sessile drops were cooled down from the contact angle measurements at 1373 K for 3.6 ks. The reaction phases at SiC and the alloys were investigated by observing of microstructure and EPMA microanalysis.

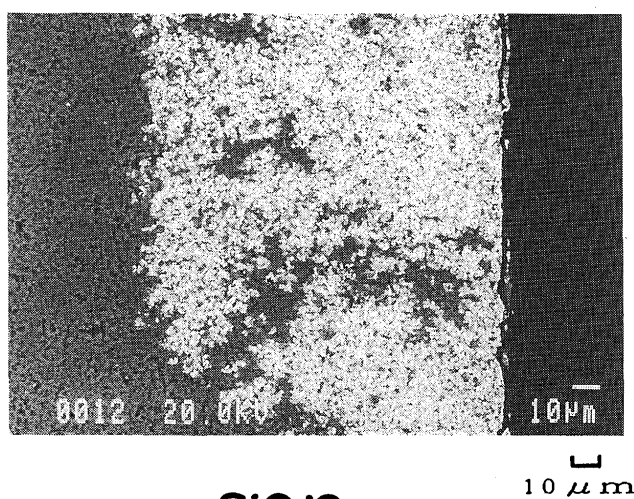
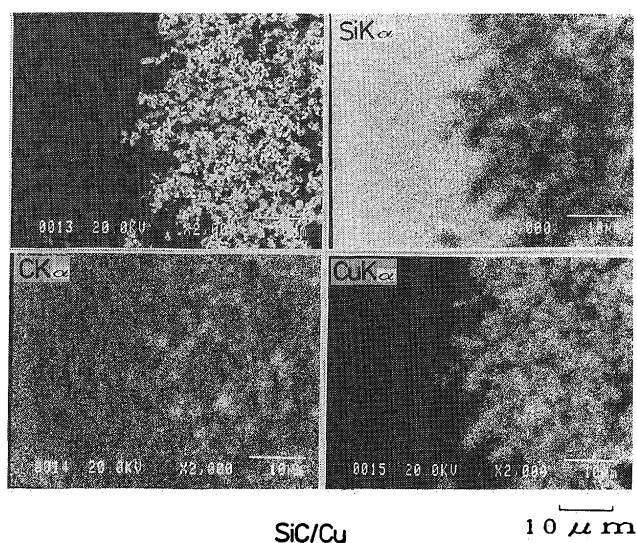
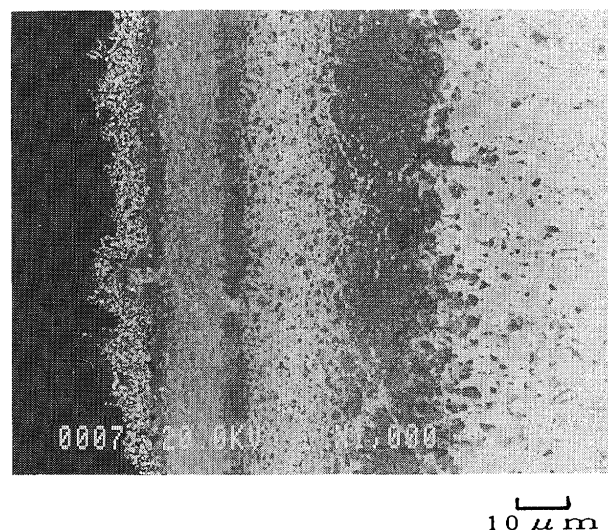
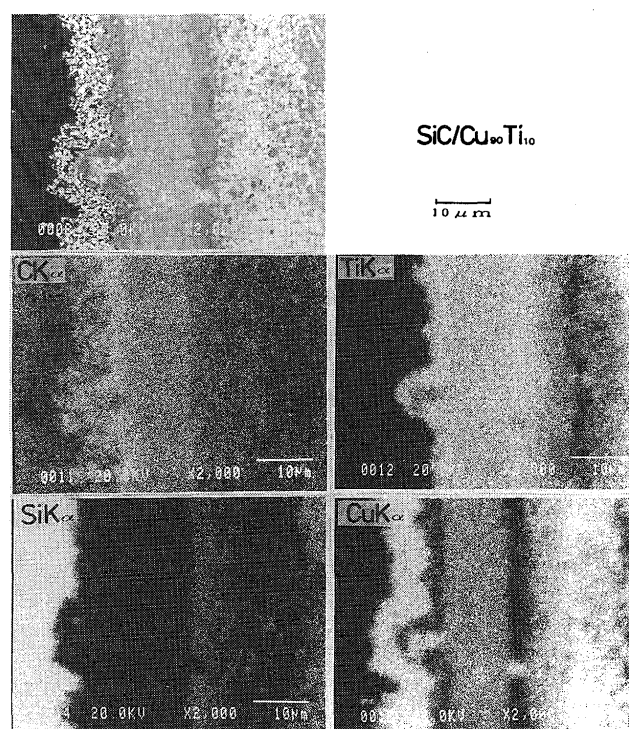
Figures 3 and 4 shows the microstructure and the image analyses of Si, C and Cu for SiC/Cu interface. Copper in the system was separated from SiC, after cooling down. The reaction layer is observed in the silicon carbide side of the system. Analyses of Cu and Si elements in Fig. 4 indicate that copper penetrated deeply into SiC, and the depth of copper-penetrating layer is 160 μm . Copper severely reacts with the silicon carbide, and forms Cu-Si alloy in the matrix and graphite in the high carbon regions. The silicon also diffuses into copper side in the distance of 100 μm and the average silicon content in copper is 3 at%. The lower free energy of copper silicide is attributable to the easy decomposition of SiC by copper.

Figure 5 represents the microstructure of SiC/ $\text{Cu}_{90}\text{Ti}_{10}$ interface. Copper penetrates only a little into SiC and the thickness in the penetrated layer was about 10 μm . Figs. 6 and 7 show the image analyses of C, Ti, Si and Cu elements in the interface. The Ti and C enriched thin layer beside the copper-penetrating layer is the titanium carbide, TiC. The samples of No. 1 – No. 3 in Table 2

Table 2 Chemical composition of carbides in SiC/Cu-Ti interface.

No	Composition (at%)					相
	Ti	Si	C	Cu	Al	
1	58.85	0.23	40.68	5.21	0.03	TiC
2	52.31	0.37	39.20	7.87	0.27	TiC
3	52.73	0.30	40.18	6.52	0.27	TiC
4	60.07	12.66	22.03	5.22	0.02	T ₁
5	57.91	10.19	24.35	7.11	0.03	T ₁
6	60.62	13.84	22.19	3.34	0.01	T ₁
7	59.17	14.53	25.03	1.02	0.25	T ₁
8	60.45	15.08	23.06	1.16	0.24	T ₁
9	58.50	15.16	24.28	1.88	0.18	T ₁

No. 1~6: SiC/Cu₉₀Ti₁₀
 No. 7~9: SiC/Cu₅₀Ti₅₀

**Fig. 3** Microstructure and image analyses of C, Si and Cu elements for SiC/Cu interface.**Fig. 4** Microstructure for SiC/Cu₉₀Ti₁₀ interface.**Fig. 5** Microstructure and image analyses of C, Ti, Si and Cu elements for SiC/Cu₉₀Ti₁₀ interface.**Fig. 6** Microstructure and image analyses of C, Ti, Si and Cu elements for SiC/Cu₉₀Ti₁₀ interface.

indicate the quantitative analyses of the titanium carbide. The thin thickness of the carbide accounts for the lower carbon content than that of TiC. The Cu₂Ti compound is formed among the carbides layers. The second carbide layer contains the silicon as shown in Fig. 6. The quantitative spot analyses shown in Table 2 indicate that the second carbide is T₁ (Ti₃SiC₂) phase reported by ref. 5.

Figure 7 shows the image analyses of elements at the

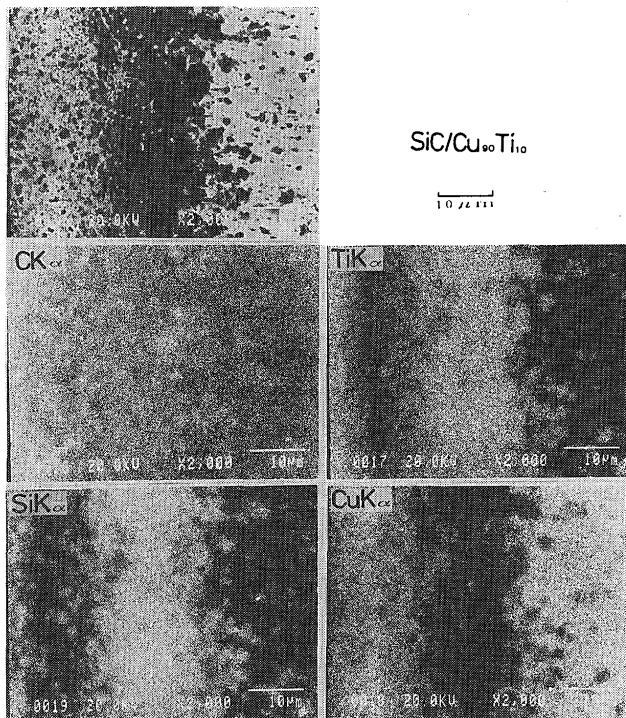


Fig. 7 Microstructure and image analyses of C, Ti, Si and Cu elements for SiC/Cu₉₀Ti₁₀ interface.

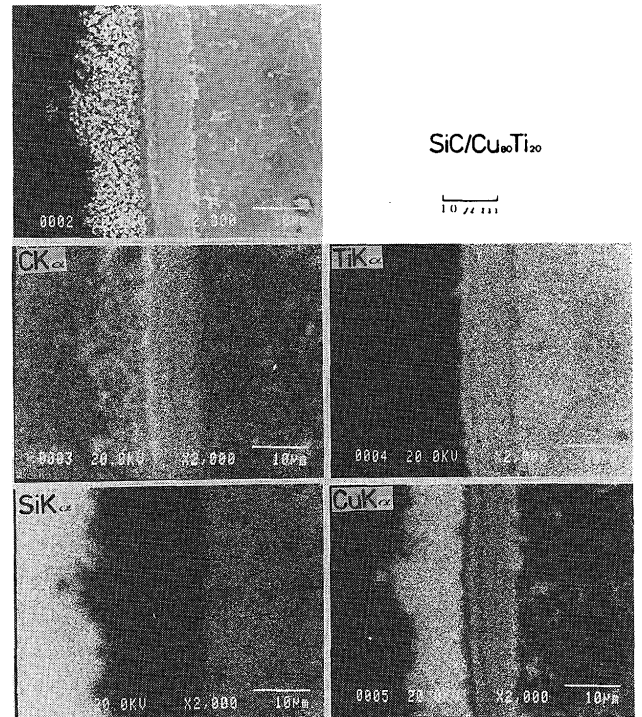


Fig. 9 Microstructure and image analyses of C, Ti, Si and Cu elements for SiC/Cu₈₀Ti₂₀ interface.

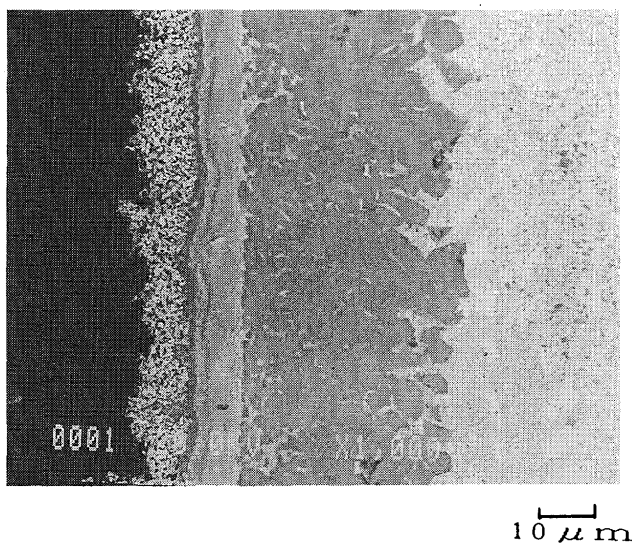


Fig. 8 Microstructure for SiC/Cu₈₀Ti₂₀ interface.

upper parts of Cu₉₀Ti₁₀ sessile drop. The thick intermediate phase is identified as Ti₅Si₃ layer contains Ti₁ phase since the silicide contains the carbon enrich phase.

The formation of two carbide, TiC and Ti₃SiC₂ phase layers and Cu-Ti alloy layer of Cu₂Ti phase prevent the penetrating of the copper into SiC.

Figure 8 shows the microstructure of SiC/Cu₈₀Ti₂₀ interface. The thickness of copper-penetrating layer is 10

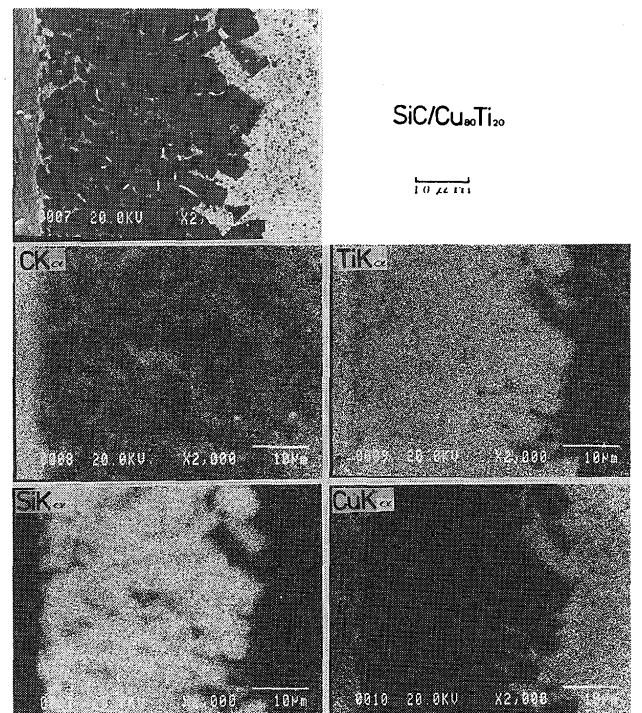


Fig. 10 Microstructure and image analyses of C, Ti, Si and Cu elements for SiC/Cu₈₀Ti₂₀ interface.

μm. The image analyses of C, Ti, Si and Cu elements in Figs. 9 and 10 indicate that the first carbide layer beside the copper-penetrating layer is composed of TiC, and the second thick carbide layer is composed of Ti₃SiC₂ phase containing the high Si and C content. The Cu-Ti phase

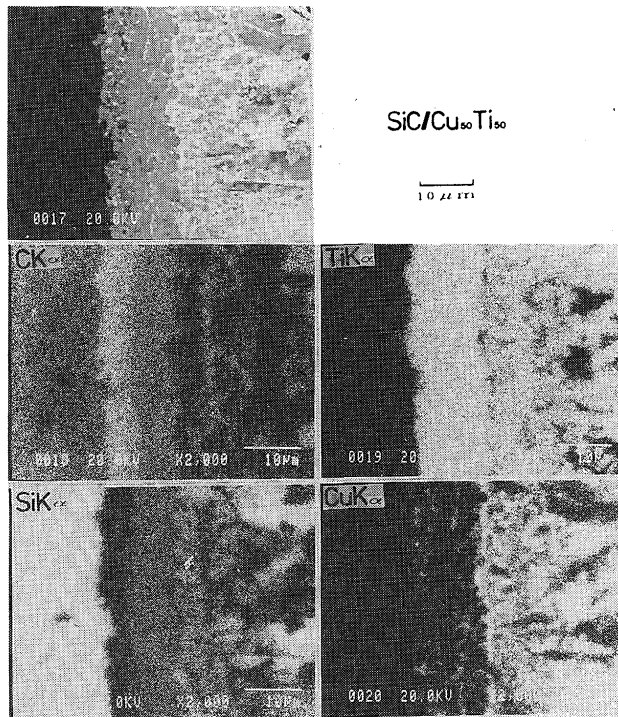


Fig. 11 Microstructure and image analyses of C, Ti, Si and Cu elements for SiC/Cu₅₀Ti₅₀ interface.

layer is formed among TiC and Ti₃SiC₂ carbides.

The microstructure and image analyses for C, Ti, Si and Cu for SiC/Cu₅₀Ti₅₀ interface are shown in Fig. 11. The copper penetrating layer is not observed in SiC/Cu₅₀Ti₅₀ and SiC/Cu₆₀Ti₄₀ systems. The carbide layer is composed of two carbides. The carbon content in the first carbide is higher than that in the second carbide. The first carbide is identified as TiC by the quantitative analysis and the second carbide is identified as Ti₃SiC₂ (T₁) phases⁵⁾ which contains large amounts of silicon of 15 at% as shown in Table 2. The formed T₁ phase layer is mixed with Cu-Ti matrix phase and others. This is attributable to that the analysed contents for silicon and carbon are relatively lower than that of nominal content in T₁ carbide.

The change in thickness of copper-penetrating layer for SiC with Ti content in Cu-Ti alloys is shown in Fig. 12. The thickness decreases drastically with Ti content, and the formation of TiC and Ti₃SiC₂ carbides prevents the copper-penetrating into SiC.

In Cu-Ti alloys with Ti content of 30 at% or more the formation of carbides depresses the reaction of copper with SiC, and the reaction of Ti with SiC preceeds the reaction of Cu with SiC. Therefore, the Cu-Ti alloys extremely wet SiC, and show the low equilibrium contact angles below 10 degree.

The schematic structures of SiC/Cu and SiC/Cu₉₀Ti₁₀ interfaces are shown in Figs. 13 (a) and (b). The copper penetrates into SiC, and decomposes SiC to Cu-Si alloy

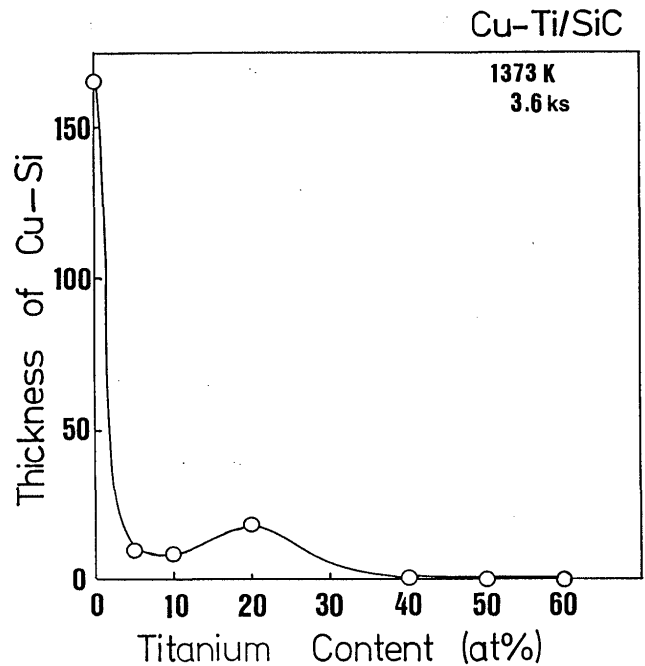
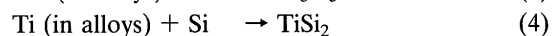
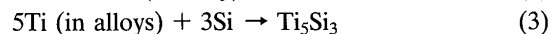
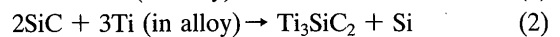
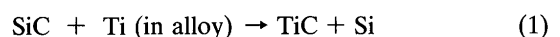


Fig. 12 Change in copper-penetrating thickness in SiC with Ti content in Cu-Ti alloy at 1373 K.

and graphite.

Figures 14 (a) and (b) represents the schematic structures of SiC/Cu₈₀Ti₂₀ and SiC/Cu₅₀Ti₅₀ interfaces. The addition of Ti content of 10 at% or more to copper depresses the copper-penetrating into SiC by forming TiC and Ti₃SiC₂ carbides.

Ti in Cu-Ti alloys reacts with SiC, and forms TiC and Ti₃SiC₂ carbides, Ti₅Si₃ and TiSi₂ silicides as following reactions.



At SiC/Cu₅₀Ti₅₀ interface the penetration of copper into SiC is suppressed by the formation of (TiC, Ti₃SiC₂) thick carbide layers. This accounts for the superior wetting of Cu-Ti alloy against silicon carbide.

4. Conclusion

The wettability of molten Cu-Ti alloys containing copper content up to 60 at% on SiC was evaluated by measuring contact angles at 1373 K in a vacuum. Further, the interfaces of SiC/Cu-Ti sessile drops were investigated by observing the microstructure, and analysing the reaction phases.

The copper doesn't show the time dependence of contact, and gives the equilibrium contact angle of 140

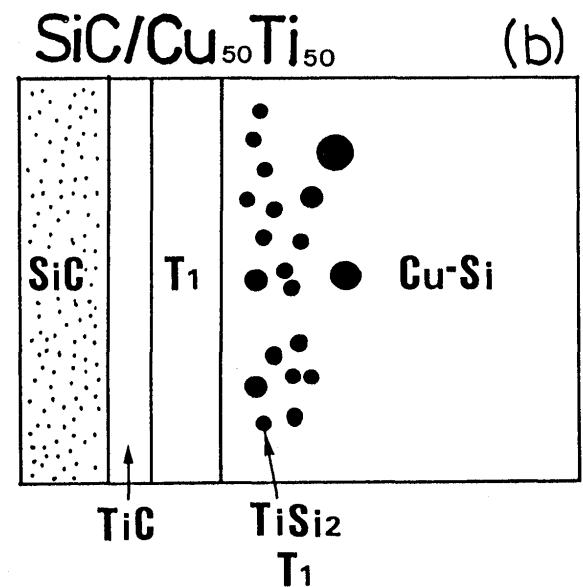
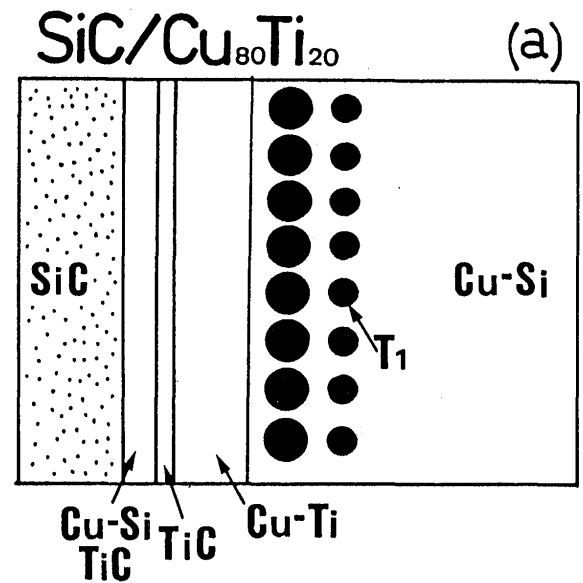
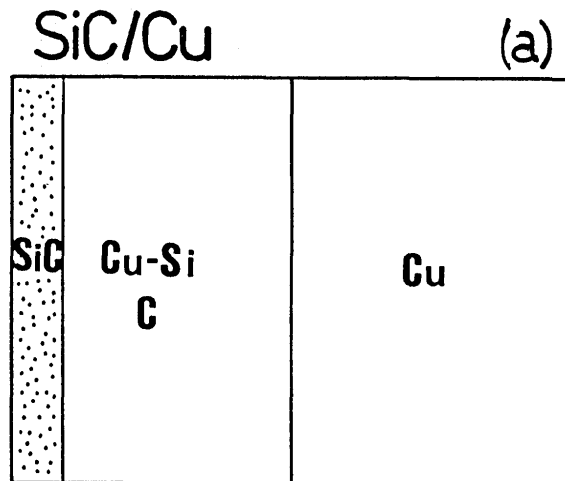


Fig. 14 Schematic structures of SiC/Cu₈₀Ti₂₀ interface (a) and SiC/Cu₅₀Ti₅₀ interface (b).

Fig. 13 Schematic structures of SiC/Cu interface (a) and SiC/Cu₉₀Ti₁₀ interface (b).

degree. The copper penetrates into SiC in depth of 160 μ m, and forms the Cu-Si alloy and graphite.

An increase in Ti content for Cu-Ti alloys definitely decreases the equilibrium contact angle on SiC. The Cu-Ti alloys containing Ti content of 30 at% or more show the equilibrium angle of 7 degree or below.

The addition of Ti to copper forms the two carbides of TiC and Ti₃SiC₂ phases at the SiC/Cu-Ti interface. The carbides depress the penetration of copper into SiC. These results in the low equilibrium contact angle and the superior wetting of Cu-Ti alloys with Ti content of 30 at% or more.

References

- 1) M. Naka, H. Hirono and I. Okamoto: High Temp. Soc., 12(1986), 250.
- 2) M. Ueki, M. Naka and I. Okamoto: J. Mater. Sci. Letters, 5(1986), 1261.
- 3) M. Naka, M. Kubo and I. Okamoto: J. Mater. Sci. Letters, 6(1987), 965.
- 4) M. Shinbo, M. Naka and I. Okamoto: J. Mater. Sci. Letters, 6(1989), 663.
- 5) S. Morozumi, M. Endo, M. Kikuchi and K. Hamazumi: J. Mater. Sci., 20(1985), 3976.