

A study of the wetting, microstructure and bond strength in brazing SiC by Cu–X (X = Ti, V, Nb, Cr) alloys

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In the active brazing of SiC by copper-based alloys, the effects of various active elements such as titanium, vanadium, niobium and chromium on the wetting, microstructure and bond strength are investigated. In wetting, Cu–Cr alloys have the lowest wetting angles on SiC of 10°–20° depending on the chromium content. SiC is decomposed on contact with alloy melts during brazing. Carbon and silicon released from this decomposition of SiC react with active elements to produce their carbides and silicides at the interface. The reacted layers have different microstructures depending on the brazing alloys, but Cu–Ti and Cu–Cr alloys show similar microstructure, as do Cu–V and Cu–Nb alloys. In the four-point bend tests, the brazed joints of Cu–5 at% Ti, Cu–5 at% V and Cu–5 at% Nb alloys have similar bend strengths of 86.9, 80.3 and 92.4 MPa, respectively. The brazed joints of Cu–2 at% Nb alloys show a high bend strength of 154 MPa, although the wetting angle is a little higher, at about 60°. Niobium is found as a new active element of copper-based alloys to braze SiC. Cu–Nb alloys are promising for substitution for Cu–Ti alloys.

1. Introduction

Ag–Ti, Cu–Ti and Ag–Cu–Ti alloys have been expected, as active metals, to braze non-oxide ceramics such as SiC and Si₃N₄ [1, 2]. Most alloys used to braze ceramics contain titanium as an active element, but titanium is easily oxidized in the atmosphere owing to its high reactivity with oxygen. The high reactivity of titanium makes the control of the alloy composition difficult in the production of brazing alloys. Particularly brazing alloys in the form of paste can deteriorate in long-term storage because of the high reactivity of fine powders composing the brazing paste. It is required that a brazing alloy be developed which is less reactive and easily wettable on ceramics and has good bond strength with ceramics.

The role of active elements in brazing alloys is to induce the chemical reaction at the interface between the ceramic and brazing alloys. Transition elements such as titanium have been added as active elements in brazing alloys because the electrons in their unfilled d electron shell have high reactivity. Other transition elements which can be considered as active elements are zirconium and hafnium of the group IVA, vanadium and niobium and tantalum of group VA and chromium, molybdenum and tungsten of group VIA. Of these elements, zirconium and hafnium are also very reactive, whereas tantalum, molybdenum

and tungsten are refractory metals that have a high melting point and little reactivity with SiC [3]. Therefore, vanadium, niobium and chromium are chosen as elements for substitution for titanium. When vanadium, niobium or chromium were added to silver and Ag_{0.6}Cu_{0.4} alloy in our pre-experiments, the alloys did not exhibit any wettability on SiC. To braze SiC in this study, copper alloys containing vanadium, niobium or chromium were used, and compared with Cu–Ti alloys. The wettability of each alloy on SiC was studied to determine its potential as a brazing alloy. Microstructure was also investigated with scanning electron microscopy (SEM) and energy dispersive X-ray spectrometry (EDX). The bond strength of the brazed joint was evaluated by the four-point bend test and fracture surfaces were also examined using SEM.

2. Experimental procedure

SiC was sintered pressurelessly as pieces of 12.5 mm × 12.5 mm × 5 mm containing 1–2 wt% C with about 3 vol% porosity. The selected brazing alloys were Cu–2 at% X and Cu–5 at% X alloy (where X = Ti, V, Nb and Cr) and are given in Table I. Table I also describes brazing conditions and analysis methods applied to each alloy. Brazing alloys were prepared by mixing copper powder with other powders.

TABLE I Brazing alloys, brazing conditions and analysis methods

Alloy (at %)	Brazing conditions		Analysis		
	Temp. (°C)	Time (s)	Wetting	Microstructure	Strength
Cu-5Ti	1100	3600	✓	✓	-
Cu-5Ti	1100	1800	-	-	✓
Cu-2Ti	1100	3600	-	✓	-
Cu-5V	1100	3600	✓	✓	-
Cu-5V	1100	1800	-	-	✓
Cu-2V	1100	3600	✓	✓	-
Cu-2V	1100	1800	-	-	✓
Cu-5Nb	1100	3600	✓	✓	-
Cu-5Nb	1100	1800	-	-	✓
Cu-2Nb	1100	3600	✓	✓	-
Cu-2Nb	1100	1800	-	-	✓
Cu-5Cr	1100	3600	✓	✓	-
Cu-2Cr	1100	3600	✓	✓	-

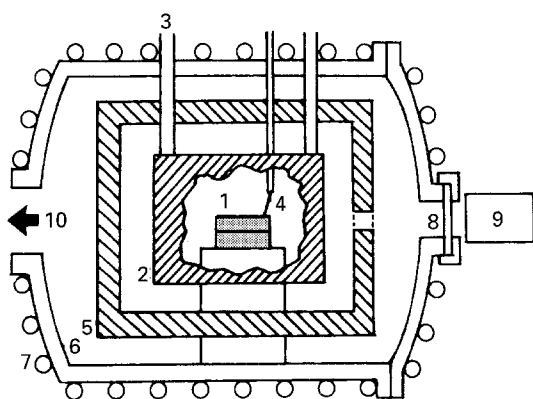


Figure 1 Schematic diagram of the vacuum furnace used in this study. 1. specimen; 2, graphite heating element; 3, water-cooled copper electrode; 4, Pt-Rh thermocouple, 5, heat-shield box; 6, vacuum chamber; 7, cooling coils; 8, viewing port; 9, telescope and camera; 10, to vacuum system.

Brazing and wetting experiments were carried out in a vacuum furnace. A schematic diagram of a vacuum furnace is shown in Fig. 1. The specimens (1) were heated at the rate of $6.7^{\circ}\text{C min}^{-1}$ by a graphite heating element (2). The temperature was measured with a Pt-Rh thermocouple (4) in contact with the SiC block. The specimens were cooled at the rate of $6^{\circ}\text{C min}^{-1}$ to 600°C and $3^{\circ}\text{C min}^{-1}$ to room temperature. The heating and cooling rates were controlled by a programmable controller. A vacuum of about 10^{-5} torr ($1 \text{ torr} = 133.322 \text{ Pa}$) was maintained before melting of the brazing alloy. To measure wetting angles, a telescope and a camera (9) were positioned at the viewing port (8) of the furnace.

Before brazing, the SiC blocks were polished using $6 \mu\text{m}$ diamond paste and ultrasonically cleaned in acetone. To keep the brazing gap constant, a 0.2 mm diameter tungsten wire was inserted, together with the brazing alloy, between the SiC blocks. To measure the wetting angles, a brazing alloy of a pre-packed disc form of 5 mm diameter \times 5 mm thickness was placed on the SiC block. Variations of wetting angles with time at 1100°C were observed and the equilibrium wetting angle was obtained after 3600 s. Wetting angles for Cu-2 at % Ti alloy could not be measured because of

the difficulty of the observation of wetting contours, but are much higher than those for Cu-5 at % Ti alloy. Microstructural analysis was performed using SEM and EDX on the cross-section of the specimen heated for 3600 s.

The specimens for bend tests were brazed for 1800 s. The preparation procedure of the specimens for the four-point bend tests is explained schematically in Fig. 2. Both sides of the brazed specimen were removed and the middle parts were sliced to the size of $5 \text{ mm} \times 2.8 \text{ mm} \times 25 \text{ mm}$ using a low-speed diamond saw. All the specimens were polished up to $1 \mu\text{m}$ diamond paste. The specimens without any microcracks observed using an optical microscope, were used in the bend tests. The four-point bend tests were carried out using an Instron universal testing machine with a special jig that had an inner span of 6 mm and an outer span of 18 mm. The crosshead speed was 0.5 mm min^{-1} . The results were evaluated from at least three measured values. Fracture surfaces after the bend test were investigated by SEM. For Cu-2 at % Ti alloy, the specimens for bend tests could not be prepared because of bad wettability and flowability. The specimens brazed by Cu-5 at % Cr and Cu-2 at % Cr alloy were broken through the SiC, owing to thermal and residual stresses; therefore bend tests could not be performed.

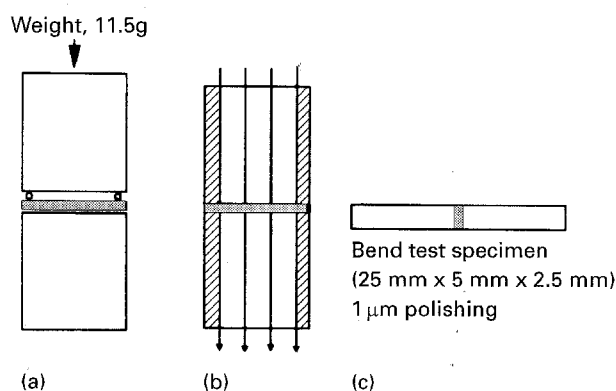


Figure 2 Preparation procedure of the specimens for the four-point bend tests. (a) Brazing, (b) cutting, (c) polishing.

3. Results

3.1. Wetting angle and microstructural analysis

3.1.1. Cu-Ti alloys

Fig. 3 shows that wetting angles of Cu-5 at % Ti alloy on SiC are continuously decreased during heating and are nearly invariable at 35°–40° at 1100 °C with time. Fig. 4 shows the microstructure and element distribution at the interface for the specimen reacted by Cu-5 at % Ti alloy for 3600 s. Results of chemical analysis by EDX on each phase are listed in Table II.

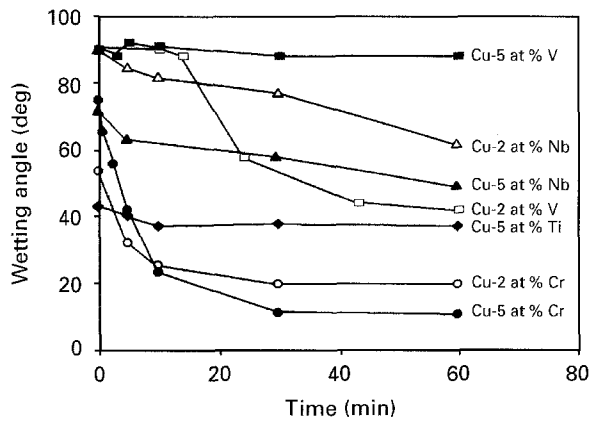
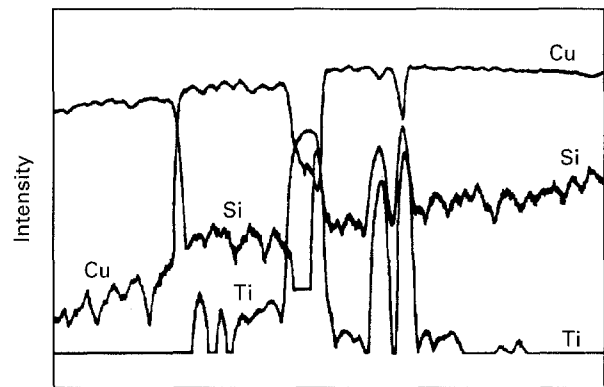
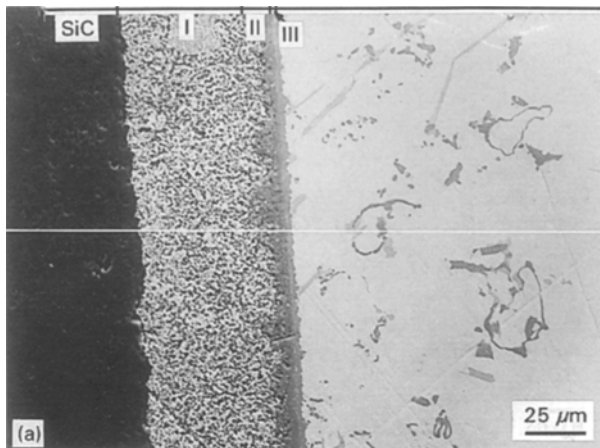


Figure 3 Changes of wetting angles of Cu-X alloys at 1100 °C with time.

TABLE II Spot analysis results (at %) by EDX at the positions indicated in Fig. 4

	Spot positions					
	1	2	3	4	5	6
Si	0.50	34.59	13.34	32.20	32.98	10.22
Ti	96.07	60.48	0.96	49.50	31.38	0.17
Cu	3.44	4.98	85.70	18.30	35.64	89.61

The detailed analyses of the microstructure and reaction mechanism between SiC and Cu-5 at % Ti alloy were presented in previous papers [4, 5]. It was identified that SiC was decomposed by the copper melt [4, 6], and that silicon liberated from the decomposition reaction causes the brazing alloy to be transformed into copper silicides, Cu_7Si and Cu_5Si [4]. Titanium reacts with carbon and silicon to create TiC and Ti_5Si_3 , respectively [4]. The reaction zone at the interface is divided into three layers. The reaction layers are formed in the order of copper silicides/graphite composite layer (reaction layer I), TiC /copper silicides composite layer (reaction layer II) and Ti_5Si_3 layer (reaction layer III) from SiC [5]. The results for the Cu-2 at % Ti alloy do not differ considerably in view of the microstructure at the interface from Cu-5 at % Ti alloy.



(b)

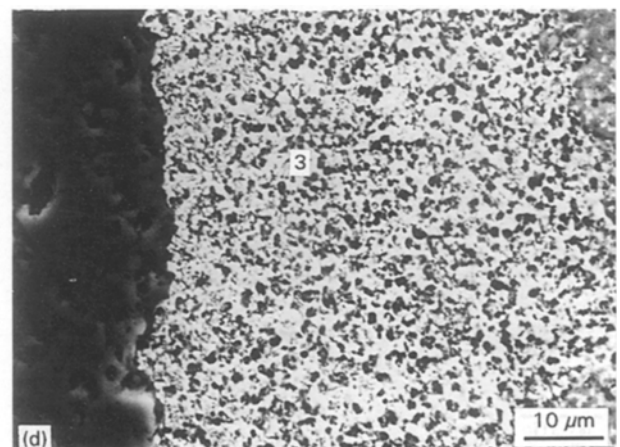
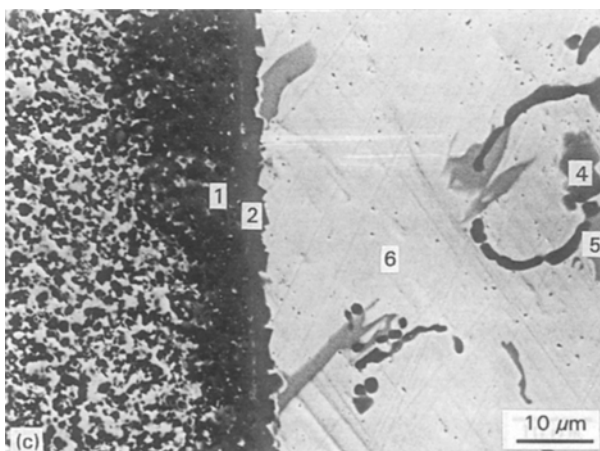


Figure 4 Microstructure and element distribution at the interfacial region in brazing by Cu-5 at % Ti alloy; (a) overall microstructure; (b) line profile for each element; (c) reaction products at the original interface; (d) decomposition layer near SiC.

3.1.2. Cu–V alloys

The variation of wetting angles at 1100 °C in Fig. 3 shows that Cu–V alloys are not accompanied by a decrease of wetting angles in heating cycle. Wetting angles after 3600 s are decreased to about 40° in Cu–2 at % V alloy, but are nearly uniform at about 90° in Cu–5 at % V alloy. The reasons why Cu–2 at % V alloy has better wettability than Cu–5 at % V alloy, are not known yet.

When brazed by Cu–5 at % V alloy at 1100 °C for 3600 s, the microstructure and element distribution found by EDX at the interface are shown in Fig. 5 and Table III. When referring to the analysis results for Cu–Ti alloys, titanium carbide and titanium silicide can be differentiated from the distribution of titanium and silicon at the interface. It is recognized from the distribution of vanadium and silicon that vanadium carbide (spot 1) and silicide (spot 2) are neighbouring each other in thin layers at the original interface. Spot analysis by EDX reveals that the chemical composition of the brazing alloy matrix and the decomposition region is nearly the same as that of Cu–5 at % Ti alloy. This confirms that copper in the brazing alloy is completely changed to Cu₇Si and Cu₅Si. The decomposition region in Cu–V alloys is different in

TABLE III Spot analysis results (at %) by EDX at the positions indicated in Fig. 5

	Spot positions				
	1	2	3	4	5
Si	0.82	35.59	10.49	28.16	9.63
V	91.12	63.00	0.27	67.84	0.00
Cu	8.05	1.41	89.24	4.00	90.37

morphology from that in Cu–Ti alloys. The decomposition region has a width of about 110 μm and is divided into two layers, according to the morphology. Copper silicides in the decomposition region near the original interface have been grown in the shape of distinct and angular grains surrounded with graphite. Isolated SiC particles are observed in the decomposition region near the SiC substrate. These SiC particles seem to remain undecomposed owing to the fast decomposition rate of SiC through its grain boundary. The decomposition region and brazing alloy matrix have almost no solubility of vanadium. Cu–2 at % V alloy has nearly the same microstructure at the interface as Cu–5 at % V alloy.

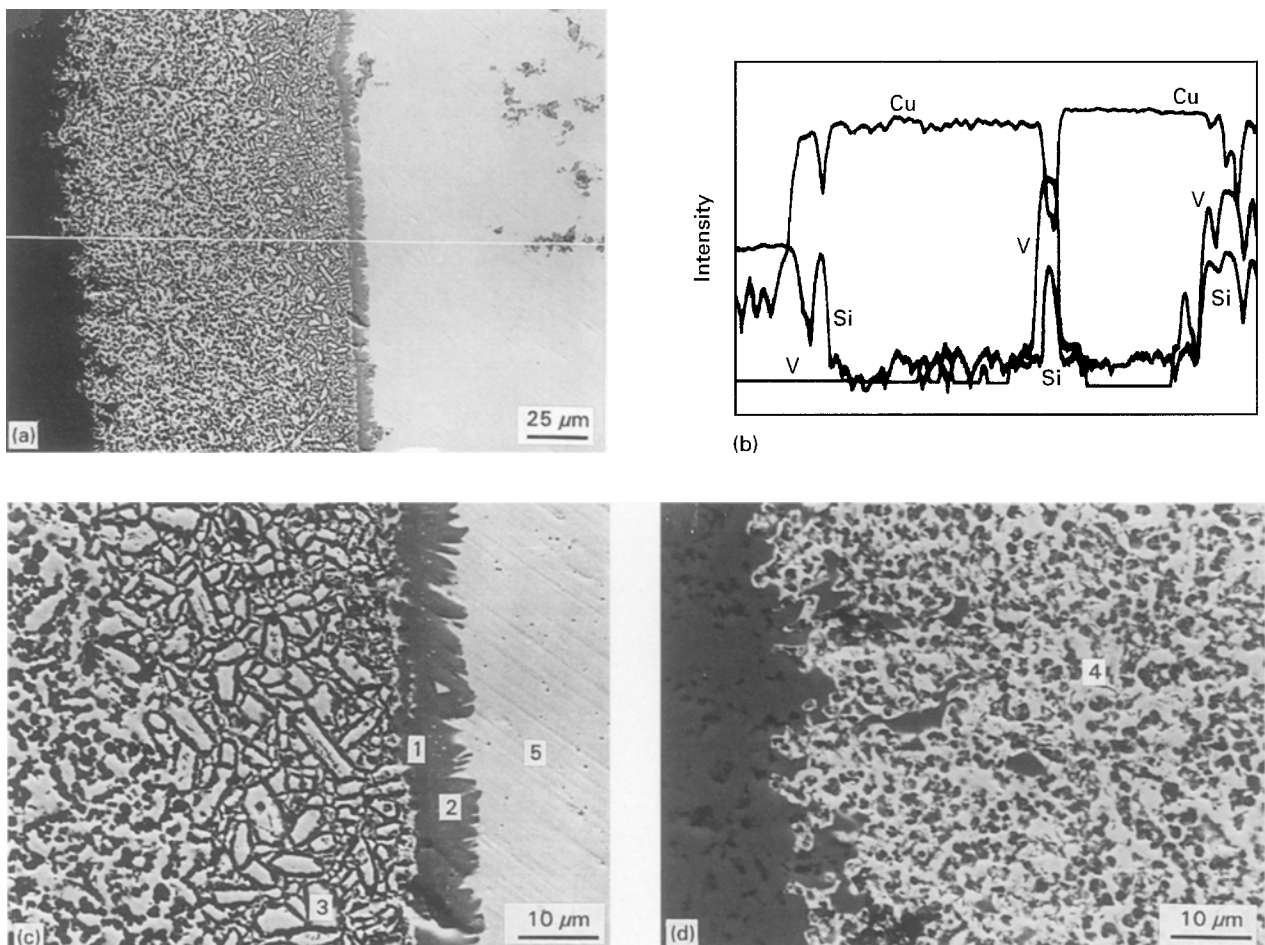


Figure 5 Microstructure and element distribution at the interfacial region in brazing by Cu–5 at % V alloy; (a) overall microstructure; (b) line profile for each element; (c) reaction products at the original interface; (d) decomposition layer near SiC.

3.1.3. Cu–Nb alloys

The changes of wetting angles of Cu–Nb alloys at 1100 °C with time also plotted in Fig. 3. In the case of Cu–2at % Nb alloy, wetting angles decrease slowly with time and reach about 60° after 3600 s. Cu–5 at % Nb alloy also exhibits a slowly decreasing wetting behaviour and has a wetting angle of about 50° after 3600 s.

Fig. 6 illustrates the microstructure and element distribution determined by EDX at the interface as brazed by Cu–5at % Nb alloy at 1100 °C for 3600 s. The chemical composition for each phase is listed in Table IV. In the same way as for Cu–Ti and Cu–V alloys, SiC is decomposed by Cu–Nb alloys and the decomposition region is very wide, about 160 μm . This indicates a high decomposition rate of SiC by Cu–5Nb alloy melt. The decomposition region resembles that of Cu–V alloys in that it is divided into two layers in morphology and has no niobium content. Chemical composition of the brazing alloy matrix and the decomposition region indicates that copper in the brazing alloy is completely changed to Cu₇Si and Cu₅Si. Single reaction layer (spot 1) is observed at the original interface and is in the form of the discontinuous line. This layer has a very high content of niobium, but a low content of silicon. Compared with the case of Cu–Ti and Cu–V alloys the interface is found to be niobium carbide. The niobium carbide layer is separated from the decomposition layer, while niobium silicides are not observed at the interfacial region. The same results are obtained in brazing by Cu–2at % Nb alloy.

3.1.4. Cu–Cr alloy

It is recognized from Fig. 3 that Cu–Cr alloys have good wettability on SiC. Wetting angles are rapidly decreased with time and become constant after 3600 s as about 20° for Cu–2at % Cr alloy and 10° for Cu–5 at % Cr alloy, respectively.

The results of the microstructural and chemical analysis by SEM and EDX on the interfacial region in brazing by Cu–5 at % Cr alloy are illustrated in Fig. 7 and Table V. The decomposition region has a thickness of about 90 μm . Two reaction layers are observed at both sides from the original interface. From the distribution of chromium and silicon, it is proved that the phase found at the side of the decomposition region is chromium carbide (spot 1) and the phase found at the side of brazing alloy matrix is chromium silicide (the left area of spot 2). The hexagonal chromium silicide particles (spot 2) are observed in the brazing alloy matrix. Overall microstructure in the interfacial region is analogous to that of Cu–Ti alloys, in that the decomposition region is not divided into two layers and the chromium carbide layer penetrates deeply into the decomposition region. The brazing alloy matrix and decomposition region have a large solubility of chromium and a high concentration of chromium is accommodated at the decomposition region adjacent to SiC. The brazed joint by Cu–2at % Cr alloy exhibits the same microstructure at the interface as that by Cu–5 at % Cr alloy.

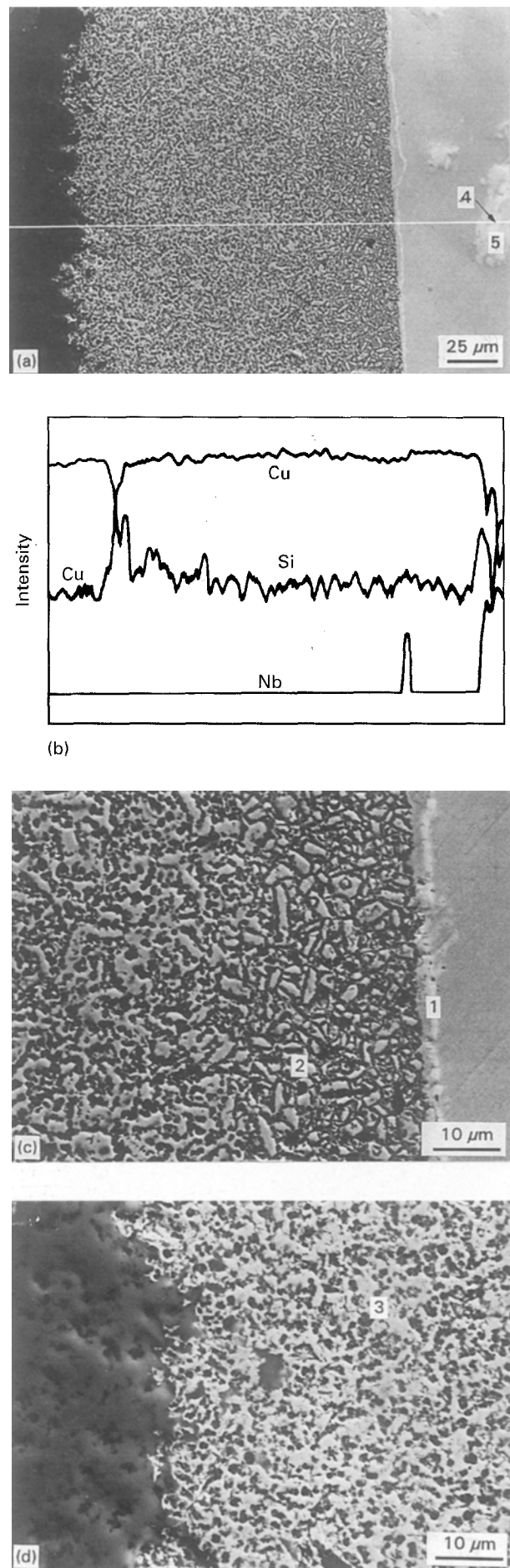


Figure 6 Microstructure and element distribution at the interfacial region in brazing by Cu–5 at % Nb alloy; (a) overall microstructure; (b) line profile for each element; (c) reaction products at the original interface; (d) decomposition layer near SiC.

TABLE IV Spot analysis results (at %) by EDX at the positions indicated in Fig. 6

	Spot positions				
	1	2	3	4	5
Si	4.64	11.51	9.98	4.32	31.13
Nb	83.15	0.00	0.12	94.36	51.29
Cu	12.22	88.49	89.90	1.32	17.58

3.2. Four-point bend test

The four-point bend strength was evaluated on the specimens brazed by Cu-5 at % Ti, Cu-2 at % V, Cu-5 at % V, Cu-2 at % Nb and Cu-5 at % Nb alloys. Cu-2 at % Ti alloy had too poor wetting and flowing characteristics to make specimens for the bend test, while the samples brazed by Cu-Cr alloys were broken through the SiC near the interface during cooling. The specimens for the bend test were brazed at 1100°C for 1800 s. When brazed for 1800 s, the overall microstructure was the same as that in brazing for 3600 s, whereas the thickness of reaction layers was slightly decreased. The results of four-point bend tests are given in Fig. 8. Dotted lines represent the mean strength of three measurements. The specimens brazed by Cu-5 at % Ti, Cu-5 at % V and Cu-5 at % Nb alloys have similar bend strengths of 87.9, 80.3 and

TABLE V Spot analysis results (at %) by EDX at the positions indicated in Fig. 7

	Spot positions				
	1	2	3	4	5
Si	0.87	24.35	19.41	11.78	14.49
Cr	91.17	74.00	0.62	11.33	0.97
Cu	7.96	1.65	79.98	76.89	84.54

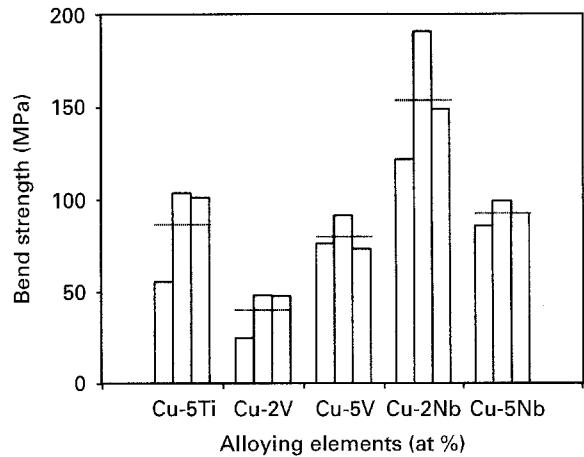


Figure 8 Four-point bend test results of the brazed joints by Cu-X alloys.

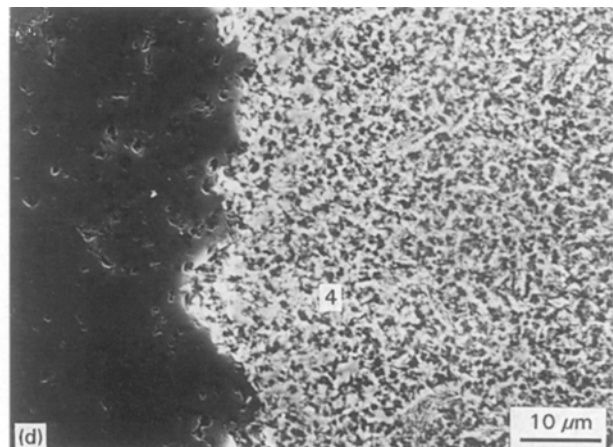
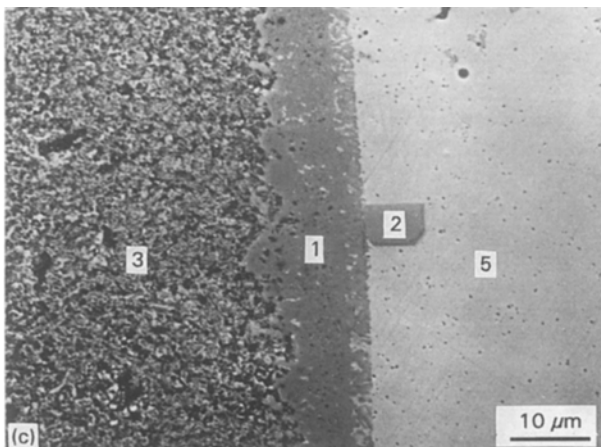
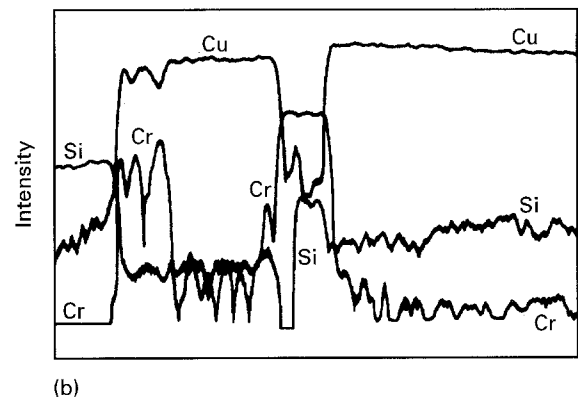
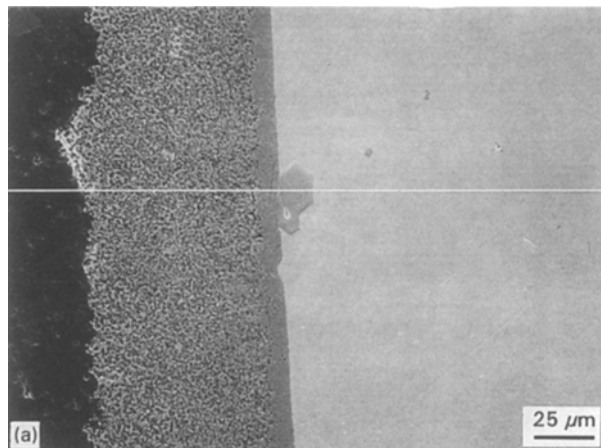


Figure 7 Microstructure and element distribution at the interfacial region in brazing by Cu-5 at % Cr alloy; (a) overall microstructure; (b) line profile for each element; (c) reaction products at the original interface; (d) decomposition layer near SiC.

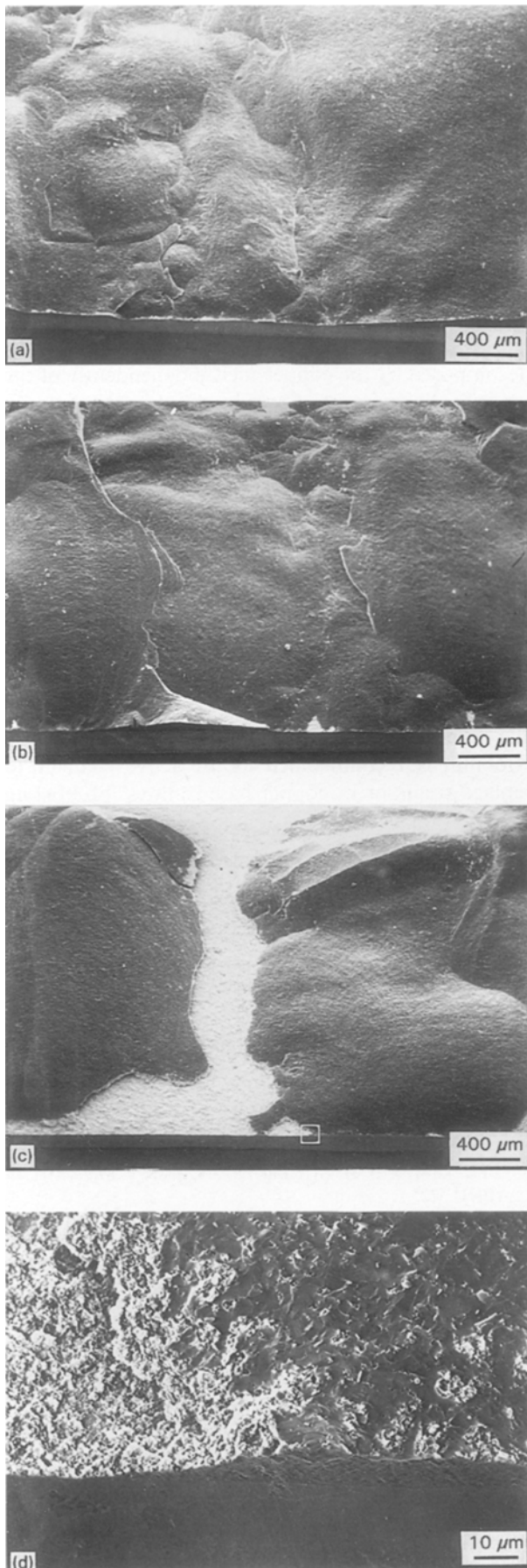


Figure 9 Fracture surfaces after four-point bend tests: (a) Cu-5 at % Ti alloy, (b) Cu-5 at % Nb alloy, (c) Cu-2 at % Nb alloy, (d) at square region indicated in (c).

92.4 MPa, respectively. When brazed by Cu-2 at % Nb alloy, the bend strength was prominently improved to 154 MPa, but brazing by Cu-2 at % V alloy lowered the bend strength to 40.1 MPa. The bend strength is influenced by the type and content of the active element in the brazing alloy. Fig. 9 shows the fracture surfaces after the bend tests for the specimens brazed by Cu-Nb alloys. Fracture surfaces in the cases of Cu-V and Cu-Ti alloys were nearly identical to those of Cu-5 at % Nb alloy. It seems that fracture was predominantly initiated at the interface between SiC and the decomposition layer and propagated through SiC. In the case of Cu-2 at % Nb alloy which can obtain good bend strength, fracture on the tensile surface was mainly initiated at the decomposition layer and interfacial region, and overall fracture was propagated through the decomposition layer in addition to SiC.

4. Discussion

It seems that the wetting of copper-based alloys on SiC becomes very complicated due to the decomposition reaction of SiC by the copper melt. More analyses are required to determine the wetting mechanism of copper-based alloys on SiC. For practical purposes, Moorhead and Keating [7] have reported that a wetting angle lower than 70° is satisfactory to braze ceramics. All the brazing alloys except Cu-5 at % V alloy have wetting angles below 70° and meet the prerequisite for the practical use as brazing alloys of SiC. Cu-Cr alloys have very low wetting angles of 10° - 20° , but the brazed joints are too weak to evaluate the bend strength. In Cu-Nb alloys, Cu-2 at % Nb alloy has a higher wetting angle than Cu-5 at % Nb alloy, but has a higher bend strength.

The morphology of the decomposition and the reaction layer is similar between Cu-Ti and Cu-Cr alloys and between Cu-V and Cu-Nb alloys. Brazing by Cu-Cr alloys brings about a high concentration of chromium in the decomposition layer near SiC, different from the cases using other alloys. It seems that good wettability of Cu-Cr alloys bears some relation to this behaviour. In brazing of SiC by Cu-V and Cu-Nb alloys, some SiC grains were observed in the decomposition region near SiC. The wide decomposition region in Cu-V and Cu-Nb alloys reflects the high decomposition rate of SiC by these alloy melts. The boundary advancing with the decomposition of SiC by the copper melt moves so fast that some large SiC grains remained isolated in the decomposition layer near SiC. The decomposition region in brazing by Cu-V and Cu-Nb alloys is morphologically divided into two layers. The copper melt has no solubility of carbon and little solubility of vanadium and niobium which can have affinity with carbon [8]. The low solubility of these elements in the copper melt can expedite the separation of copper and carbon, which causes some copper silicides in the decomposition layer to be grown into angular grains surrounded by a thick graphite network. A thick carbide layer in Cu-Ti and Cu-Cr alloys is formed on contact with the original interface, whereas a thin carbide layer was

formed in Cu–V and Cu–Nb alloys. It also seems to bear some relation to the solubility in the copper melt of active elements that can form carbides. The copper melt has a large solubility of titanium and chromium, therefore titanium and chromium can be supplied in sufficient amounts to develop a thick carbide layer by the continuous reaction with carbon. Vanadium and niobium are only slightly soluble in the copper melt; in this case only a thin carbide layer can be formed at the original interface where these elements first meet carbon. In brazing by Cu–Nb alloys, niobium silicides are observed not at the interfacial region but at the outer sides of the particles in the brazing alloy matrix. This may be attributed to the extremely low solubility of niobium in the copper melt [8]. The niobium carbide layer is discontinuous and detached from the decomposition layer. Thus copper silicides are continuously connected from the brazing alloy matrix to SiC. It is interesting that a high bend strength can be obtained at the joint connected directly between SiC and copper silicides without intermediate phases.

In the four-point bend test of ceramic-metal joint, the bend strength will be affected by fracture initiation on the surface subjected to a tensile load. In the specimens brazed by Cu–5 at % Ti, Cu–2 at % V, Cu–5 at % V and Cu–5 at % Nb alloys, fracture initiation on the tensile surface predominantly occurs near the interface between the decomposition layer and SiC, and finally the fracture propagates through the SiC. It is acknowledged that the interface between the decomposition layer and the SiC has to be strengthened to increase the bend strength in brazing of SiC by copper-based alloys. The specimens brazed by Cu–2 at % Nb alloy, which has the highest bend strength of 154 MPa, show that fracture on the tensile surface mainly initiates at the decomposition layer and propagates through SiC and the decomposition layer. Niobium on Cu–2 at % Nb alloy seems to improve the bond strength at the interface between the decomposition layer and SiC. Some of the strengthening mechanisms in brazing by Cu–2 at % Nb alloy can be the reduction of thermal and residual stresses owing to the wide decomposition region at the low content of active element in the decomposition region and brazing alloy matrix. It is known that a copper/graphite composite has an intermediate thermal expansion coefficient between SiC and the brazing alloy, therefore the decomposition layers can contribute to relax the thermal stress induced by the difference of the thermal expansion coefficient between SiC and the brazing alloy [9]. More detailed analyses are required to understand the strengthening mechanism in brazing by Cu–2 at % Nb alloy. Copper-based alloy added with 2 at % Nb instead of titanium, is promising as a brazing alloy of SiC.

5. Conclusions

Wetting, microstructure and bend strength in brazing of SiC using Cu–X (X = Ti, V, Nb and Cr) alloys have been investigated. The results are as follows.

1. Cu–Cr alloys have low wetting angles on SiC of 10°–20° depending on the chromium content, but the brazed joints are so weak that the bend strength cannot be measured. Cu–2 at % Nb alloy has a high wetting angle of 60° on SiC, but it can braze SiC with a high bend strength. The bend strength has no correlation with wettability in brazing of SiC by copper-based alloys.

2. In brazing of SiC by copper-based alloys, SiC is decomposed by the copper melt independently of the type of active elements. Carbides of active elements are formed at the original interface, and they have different morphologies. The microstructure at the interface is similar for Cu–Ti and Cu–Cr alloys and for Cu–V and Cu–Nb. It seems that the morphology of the decomposition layers and the interfacial reaction layers bears some relation to the solubility of the active element in the copper melt.

3. In brazing of SiC by Cu–5 at % Ti, Cu–5 at % V and Cu–5 at % Nb alloy, the bend strengths do not show a large difference, being 86.9, 80.3 and 92.4 MPa, respectively. The specimen brazed by Cu–2 at % Nb alloy can achieve a good bending strength of 154 MPa. Niobium is recommended as an active element to replace titanium in copper-based alloys for brazing of SiC.

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