Characteristic Wettability of SiC by Liquid Pure Cu

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The wettabilities of α -SiC, hot pressed SiC, and reaction bonded SiC by liquid Cu were investigated using the sessile drop method under various experimental conditions.

The main results obtained are summarized as follows:

- (1) The contact angle of liquid Cu on SiC depended on SiC used.
- (2) The characteristic wetting was observed in the liquid pure Cu/ α -SiC system, which had a hexagonal wetted area.
- (3) The appearance of hexagonal wetting depended on temperature and pressure: at lower temperatures and pressures, hexagonal wetting was observed, and at relatively higher temperatures and pressures, normal wetting was observed.
- (4) The mechanism of the formation of hexagonal wetting is closely related to that of hexagonal etch pits by fused KOH solution.

(Received May 24, 1988)

Keywords: wettability, silicon carbide, contact angle, liquid copper, composites

I. Introduction

Ceramics are becoming increasingly important as engineering materials. They are generally stronger, more refractory, less thermally expansive and less reactive than metals. However, as the ceramics are weak in thermal shock, it is important to use them with metals, i.e. metal-ceramic joining and composites.

As the wettability of ceramics by liquid metals gives us important information on the production of composite materials and to metal-ceramics joinings, many reports concerning the wettability have already been published. However, the results are not in coincidence, because the wetting properties such as the contact angle of liquid metal on ceramic and the work of adhesion between liquid metal and ceramic are easily affected by the presence of small amounts of impurities both in the metal and ceramic employed, and also by atmosphere.

In this work, the wettability of a reaction bonded SiC, a hot pressed SiC, and a single crystal of α -SiC by liquid pure Cu was exam-

ined using the sessile drop method. The wettability was evaluated by measuring the contact angle of liquid Cu on SiC.

II. Experimental

1. Materials

Electrolyzed Cu was vacuum-melted in a high purity graphite crucible to remove oxygen contained. After treatment, no oxygen was detected in the sample by the inert gas carrier method.

The SiC samples used were a reaction bonded SiC which contained 10%Si as a form of metallic silicon, a hot pressed SiC, and a single crystal of α -SiC. Measurements for α -SiC were carried out on the plane of (0001).

The reaction bonded SiC obtained from Nippon Kagaku Togyo Co. Ltd. included 10 mass% of metallic Si.

The hot pressed SiC was made from SiC powder whose mean particle size was $0.05\ \mu\text{m}$ and impurities were as follows; 0.01 mass% of C, 0.03 mass% of Al, 0.03 mass% of Fe and 0.4 mass% of SiO_2 . The hot pressed SiC substrates were prepared under a pressure of c.a. $550\ \text{kg}/\text{cm}^2$ at temperatures of 2223 K or above. As graphite dies were employed, the metallic Si and SiO_2 existing on the surface of a

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substrate could be expected to change into SiC.

The single crystal of α -SiC contained 0.02 mass% of Fe, 0.02 mass% of Al and 0.01 mass% of C.

The SiC powder and the single crystal of α -SiC were purchased from Pacific Rundum Co., Ltd.

Porosities of the reaction bonded SiC and the single crystal of α -SiC were zero, and that of the hot pressed SiC was c.a. 5%.

Several experiments were carried out using SiO₂ as a substrate to clarify the effect of the oxide film which would be expected to exist on SiC.

2. Apparatus and procedures

The furnace used is shown in Fig. 1. Measurements were carried out in a reduced

Fig. 1 Apparatus for measurement. 1. Metal dropping device, 2. Water cooling pipe, 3. Exhaust hole, 4. Carbon net heater, 5. Mo radiation shield, 6. Graphite ring, 7. Alumina tube, 8. Titanium getter, 9. Observation window, 10. Levelling screw, 11. Water cooled Cu electrode, 12. Thermocouple, 13. Ionization Vacuum gauge.

pressure (c.a. 10^{-3} Pa). As the heating element was a graphite net, oxygen in an atmosphere could be reduced by eq. (1).

Oxygen in an atmosphere can be removed by the reaction which is expressed by eq. (1) and also sponge Ti which is set in the furnace.

Measurements were made mostly under a reduced pressure.

First, a SiC substrate was set horizontally in the furnace and a Cu (c.a. 1.5 g) sample in the metal dropping assembly. Then the furnace was evacuated. Pressure should be maintained at 10^{-3} Pa or lower at room temperature. After attaining a pre-set temperature, liquid Cu was dropped onto the SiC. Photographs of liquid Cu drop were taken every several hundreds seconds. Contact angles were determined by the tables of Bashforth and Adams⁽¹⁾.

III. Results and Discussion

Typical examples of shapes of liquid Cu drop on various SiC are shown in Figs. 2–4. As can be seen from Figs. 2–4, the shape of a liquid Cu drop on a single crystal of α -SiC is absolutely different from that on a reaction bonded SiC or on a hot pressed SiC. A liquid drop on a substrate must have a smooth surface as in Figs. 2 and 3. Many liquid metals/ceramics systems have been examined by the authors^{(2)–(11)} and no system like the liquid pure Cu/ α -SiC one has been observed before except for the liquid pure Fe/ Al_2O_3 system which was attempted in reduced pressure⁽¹¹⁾. In the liquid pure Fe/ Al_2O_3 system, the Al rich layer was

Fig. 2 Change in shape of liquid pure Cu on hot pressed SiC with time.

Fig. 3 Change in shape of liquid pure Cu on reaction bonded SiC with time.

Fig. 4 Change in shape of liquid pure Cu on single crystal of α -SiC with time.

detected by EPMA analysis at the surface of a liquid Fe drop which was supposed to be an oxide layer. The EPMA analysis also revealed that the Si content at the interface between a solidified Cu drop and a single crystal of SiC was higher than that in the bulk of solidified drop, while no difference in the Si content between the bulk and the interface was observed

when the reaction bonded SiC and the hot pressed SiC were used.

Unfortunately, as the phase-diagram of the Cu-Si-C system has not been investigated yet, it is difficult to evaluate solubilities of Si and C in liquid Cu at the experimental temperature. However, Bates *et al.*⁽¹²⁾ found decomposition of SiC into liquid Cu and Naidich⁽¹³⁾ found an intermediate layer between liquid Cu and SiC. These results do not conflict with the result obtained in this work, although a quantitative analysis of C in solidified Cu samples could not be carried out, because the Cu drop was too small and too hard to take off from the α -SiC to be carried out a carbon analysis.

Contact angles of liquid Cu and Si content in liquid Cu on various SiC at 1393 K are summarized in Table 1. Considerable difference in contact angles are observed. The liquid Cu/hot pressed SiC system is a non-wetting one, while Liquid Cu/reaction bonded SiC system is a wetting one. This difference may be considered to be mainly caused by the dissolution of Si contained in a reaction bonded SiC which is shown in Table 1.

Table 1 Contact angle of liquid Cu on SiC at 1393 K.

SiC	Contact angle	Si content (at%)
Hot pressed	135.8°	0.5
	132.5°	0.8
	133.0°	0.7
Reaction bonded	83.3°	18.0
	81.6°	18.0
	79.6°	19.2
Single crystal	not determined	4.3*

*Si contents depended on analyzed position

The contact angle on reaction bonded SiC obtained here, $81.5 \pm 2^\circ$, is considerably lower than $106 \pm 2^\circ$ ⁽¹⁴⁾ at 1408 K.

The difference in contact angle might be attributed to the difference in the atmosphere, more precisely the difference in oxygen partial pressure of atmosphere. The measurements in the previous work⁽¹⁴⁾ were not carried out under a reduced pressure but in Ar atmosphere. The oxygen partial pressure in the previous work⁽¹⁴⁾ was found to be 10^{-9} Pa by an EMF measurement. On the other hand, the oxygen partial pressure in this work could not be determined precisely, since it was too low for the EMF measurement. However, it is possible to say that the oxygen partial pressure in this work was lower than 10^{-14} Pa.

The Si content in a liquid Cu was 4.3 at% and 18.0–19.2 at%, respectively, in the previous work and in this work. This difference in Si content might be caused by an oxidation of some of Si in the reaction bonded SiC in the previous work.

The contact angle of liquid Cu on SiO₂ was measured at 1393 K. The value, 127° , for the liquid Cu/SiO₂ system is comparable to the values of 106° and 81.5° for the liquid Cu/SiC system. The value, 106° , obtained in the previous work is close to that for the liquid Cu/SiC system. This can support that the oxidation of Si occurred in the previous work⁽¹⁴⁾.

The contact angle of liquid Cu on a single crystal of α -SiC could not be determined since a solid-like interface layer was formed at the interface between liquid Cu and α -SiC (see Fig. 4). Metallic Si scarcely exists in both the hot pressed SiC and α -SiC, but the Si contents in liquid Cu on the hot pressed SiC and α -SiC given in Table 1 show a big difference. This might be attributed to the difference in reactivity between the hot pressed SiC and the α -SiC, which will be discussed later.

The shape of the solidified Cu drop on α -SiC is shown in Fig. 5. The outside surface of the Cu drop is the hexagonal shape whose each rim is exactly parallel to that of α -SiC. It can be concluded that the appearance of a Cu drop on the (0001) plane of α -SiC is absolutely controlled by the nature of the surface of α -SiC.

Results obtained for liquid Cu on the α -SiC

system under various experimental conditions are summarized in Table 2. Hexagonal wetting was clearly observed at relatively lower temperatures and lower pressures, while no hexagonal wetting was observed at higher temperatures and higher pressures.

Figures 6 and 7 show etch pits on the (0001) plane of α -SiC which resulted from fused KOH treatment at 950 K. It is obvious from Fig. 6 that the hexagonal etch pits were formed on the surface of α -SiC. Each rim was parallel to an edge of α -SiC. Although the sizes of hexagons obtained by fused KOH treatment differ from those obtained by liquid Cu, their rims also run parallel to those of α -SiC.

The process of the formation and growth of etch pits observed is shown in Fig. 7. The formation of etch pits was observed after 0.6 ks of fused KOH treatment but the shapes were not clear. After 1.2 ks of the treatment, the shapes became clear and an incorporation of etch pits began. Finally, the incorporation of the left side and right side groups was observed.

The α -SiC surface after removing Cu by HNO₃ solution was observed by SEM as shown in Fig. 8. It may be seen from Fig. 8-a that many small hexagons were formed on the (0001) plane of a surface of α -SiC. Figure 8-b shows their growth and incorporation. On the other hand, on the sample which had not shown the hexagonal wetting, no hexagons could be observed on the (0001) plane after removing Cu but a chemical attack of the surface by liquid Cu was observed.

It can be considered that the characteristic wetting observed in the liquid Cu/ α -SiC system is caused by the difference in the dissolution rate of SiC into liquid Cu which depends on the orientation of surface of α -SiC.

Many reports on the wettability of single crystals of ceramics such as oxides and carbides have been published, but none of the characteristic wetting observed in this work has been reported.

The mechanism of hexagonal wetting may be considered as follows:

(1) The formation and growth of etch pits resulting from the difference in the dissolution rate of α -SiC into liquid Cu which depends on the surface orientation of α -SiC.

Fig. 5 Appearance of solidified Cu drop on α -SiC.

Table 2 Experimental results.

Temp (K)	Atmosphere (Pa)	Hexagonal wetting	Temp (K)	Atmosphere (Pa)	Hexagonal wetting
1371	10^{-3}	⊙	1440	10^{-3}	○
1393	10^{-3}	⊙	1473	10^{-3}	×
1393	10^{-2}	⊙	1393	10	○
1393	10^{-1}	○	1393	10^5 Ar	×

⊙: Clearly observed, ○: Observed, ×: Not observed

Fig. 6 Etch pits resulting from fused KOH.

Fig. 7 Etch pits resulting from fused KOH.

Fig. 8 SEM observation of the (0001) plane of α -SiC after removing Cu.

(2) Supersaturation of Si and C in liquid Cu attributed to the evaporation of Cu under reduced pressure.

(3) Precipitation of supersaturated Si and C at the liquid Cu/SiC interface.

In the case of stage (1), it is reasonable to consider that the same phenomena as KOH treatment occurred in the case of the liquid Cu/ α -SiC comparing Fig. 8 with Figs. 6 and 7.

Berg⁽¹⁵⁾ found a triangular and a hexagonal wetting of liquid In on the (111) plane of Ge, while Goldstein⁽¹⁶⁾ found that the dissolution rate of Ge into liquid In depended on the crystal plane of Ge, and the difference in the dissolution rate was dominant at lower temperature. If the difference in the dissolution rate of α -SiC into liquid Cu was also dominant at lower temperature, the results in Table 2 are understandable, i.e. the lower the temperature, the clearer becomes the shape of hexagon.

In stage (2) and (3), as it was not possible to determine a loss in weight during the experiment because of vigorous reaction between liquid Cu and α -SiC, the loss was expected by a thermodynamic calculation. The vapor pressure of pure Cu, Si and C was compared at experimental temperature, since no data were available for activities of Cu, Si and C in Cu-Si-C ternary system. The vapor pressures of

Cu, Si and C are 1.3×10^{-2} Pa, 3.3×10^{-5} Pa, and 7.5×10^{-15} , respectively, at 1371 K⁽¹⁷⁾. It is evident from the comparison of these values that as the vapor pressure of Cu is higher than those of Si and C, it is possible for stage (2) to occur.

Two possibilities can be considered for stage (3).

(a) An epitaxial growth of solid from supersaturated liquid on (0001) plane of α -SiC.

(b) The precipitation of solid from supersaturated liquid whose shape is regulated by the shape of the hollow formed by etching with liquid Cu.

The Laue method was applied to the sample which had been cut parallel to the interface layer to investigate the possibility of epitaxial growth. The diffraction pattern did not reveal that the structure at the vicinity of the interface corresponded to the structure of SiC. Accordingly, this possibility can be denied, although a slight possibility remains.

It may be reasonable to conclude from the similarity between the hexagons resulting from fused KOH and the hexagons observed in Fig. 8 that (b) is the mechanism of the hexagonal wetting.

Although the characteristic wetting found in the present work has not been reported yet on

liquid metals/single crystal of ceramics systems, it has been clarified that the wettability of a single crystal of ceramics by liquid metal can be affected by a crystal structure of α -SiC.

IV. Conclusion

The wettability of SiC by liquid Cu was investigated using the sessile drop method.

(1) The contact angle of liquid Cu on SiC depended on SiC used.

(2) Hexagonal wetting was observed in liquid Cu/ α -SiC system.

(3) The mechanism of the formation of hexagonal wetting closely relates to that of hexagonal etch pits by fused KOH solution.

(4) Hexagonal wetting depended on temperature and pressure.

Acknowledgments

The authors are indebted to Mr. K. Ikeda and Mr. T. Ueda for their devoted experimental work and to the Ministry of Education, Science and Culture, Japan for its financial support in the form of a Grant-in-Aid for Scientific Research.

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