Wettability of SiC by Liquid Pure Metals*

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The wettability of three kinds of SiC such as a reaction bonded SiC, a hot pressed SiC and a single crystal of α -SiC by liquid metals (Pb, Sn, Al, Si, Au, Ge, Ag, Fe, Ni and Co) was measured by the sessile drop method. Wettability was evaluated by the contact angle of liquid metal on SiC.

The main results obtained are as follows:

- (1) Contact angles of liquid pure Pb, Sn, Au and Ag were larger than 90° for all kinds of SiC examined.
- (2) Reactivity of reaction bonded SiC with liquid metals may be controlled by the carbon treatment, which carburates the surface of the SiC.
- (3) Contact angles of liquid pure Fe, Co and Ni were always smaller than 90° for both the reaction bonded SiC and the hot pressed SiC.
- (4) Contact angle of liquid pure Al on a single crystal of α -SiC changed considerably with time elapsing. The initial contact angle was 160° , reducing gradually with time, the final one after 6.9 ks was 56° .
- (5) Contact angle of liquid pure Ge depended on the kind of SiC used. The contact angle was obtuse on hot pressed SiC and α -SiC, while it was acute on reaction bonded SiC.
- (6) Wetting behavior of liquid metals on SiC closely is related to the solubility of Si and C.

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I. Introduction

Recently, ceramics have come into use in many fields, because they have excellent properties of heat-resistance, high-temperature strength, and corrosion resistance. Particularly, as SiC and Si_3N_4 are composed of elements which exist in sufficient abundance, it may be expected that the demand for them will increase. However, ceramics are generally weak in thermal shocks and difficult to sinter, and using them with metals and composites are of importance in solving these problems.

The wettability of ceramics by liquid metals is one of the most important properties for metal-ceramic joinings and the production of composites. However, systematic research on the wettability of ceramics by liquid metals is scarce and considerable differences are noticeable among the values reported. This

could be caused by the difficulty of measuring wettability at high temperature, and wettability being affected by the presence of small amounts of impurities.

In this work, the wettability of various SiC (reaction bonded SiC, hot pressed SiC and single crystal of α -SiC) by liquid pure metals (Pb, Sn, Al, Si, Au, Ge, Ag, Fe, Ni, Co) was investigated by the sessile drop method.

II. Experiments

1. Materials

(1) Metal samples

The metal samples used were Pb, Sn, Al, Si, Au, Ge, Ag, Fe, Ni and Co.

Of the metals used, Pb, Si, Au, Ge and Ag were of over 99.99% purity, Al, Sn, Ni and Co were of over 99.9%, and the Fe used was electrolyzed Fe that had been vacuum-melted with a small amount of carbon saturated iron for deoxidation.

(2) SiC samples

The SiC samples used were a reaction bond-

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ed SiC which contained 10%Si, a hot pressed SiC, and a single crystal of α -SiC. Wetting measurement for α -SiC was carried out on (0001).

Several experiments were carried out using the reaction bonded SiC whose surface were treated by carbon. The details of this procedure will be explained in chapter III.

2. Apparatus and method

Two types of furnaces were used in this work. The furnace used for the liquid pure metals/reaction bonded SiC and/hot pressed SiC systems is shown in Fig. 1(a). The other furnace used in the liquid pure metals/hot pressed SiC and/single crystal of the α -SiC system is shown in Fig. 1(b).

Measurements were carried out in an Ar atmosphere under a reduced pressure.

To avoid the reaction between liquid metals and SiC, the pure metal samples were set in the metal dropping assembly. After attaining the specific temperature, liquid metals were dropped onto SiC substrates. Photographs were then taken at one-minute intervals.

When the contact angle between liquid pure metal and SiC was an acute one, it was directly obtained from the shape of liquid metal drop

Fig. 1(b) Apparatus for measurement. 1. Metal dropping assembly, 2. Water cooled pipe, 3. Liquid metal drop on SiC, 4. Heating element (carbon net), 5. Mo radiation shield, 6. Graphite ring, 7. Alumina pipe, 8. Ti shots, 9. Observing window, 10. Levelling screw, 11. Water cooled copper electrode, 12. Thermocouple, 13. Vacuum gauge.

on the SiC substrate, on the other hand, when it was an obtuse one, it was calculated by Bashforth and Adams' tables⁽¹⁾.

After the experiments, solidified samples were examined by means of optical microscopy and EPMA.

III. Results and Discussion

The contact angles between liquid pure metals (Pb, Sn, Al, Si, Au, Ge, Ag, Fe, Ni and Co) and SiC are shown in Figs. 2~10. As is clear from Figs. 2~10, a difference is observed in the contact angles of liquid pure metals on

Fig. 1(a) Apparatus for measurement. 1. Gas inlet, 2. Water-cooled electrode, 3. Metal dropping assembly, 4. Carbon heater, 5. Metal droplet, 6. SiC plate, 7. Alumina refractories, 8. W-5Re/W-26Re thermocouple, 9. Observing window, 10. Water cooling pipe, 11. Gas outlet, 12. Levelling screw.

Fig. 2 Time dependence of contact angle of liquid pure Pb on SiC at 603 K. ○: Reaction-bonded SiC, □: Hot-pressed SiC.

Fig. 3 Time dependence of contact angle of liquid pure Sn on SiC. ○: Reaction-bonded SiC at 1373 K, □: Hot-pressed SiC at 1373 K, △: Single crystal of α -SiC at 1297 K, ▲: Single crystal of α -SiC at 1473 K.

Fig. 4 Time dependence of contact angle of liquid pure Al on α -SiC at 1474 K.

Fig. 5 Time dependence of contact angle of liquid pure Au on α -SiC. △: at 1373 K, ▲: at 1453 K.

SiC. This is caused not only by the metals employed but also by the SiC used.

It is obvious from Fig. 2 that the contact angles of liquid Pb on SiC show higher values

Fig. 6 Time dependence of contact angle of liquid pure Ge on SiC. ○: Reaction-bonded SiC at 1293 K, ●: Reaction-bonded SiC at 1473 K, ●: Reaction-bonded SiC at 1573 K, ●: Reaction-bonded SiC at 1693 K, □: Hot-pressed SiC at 1503 K, △: Single crystal of α -SiC at 1503 K.

Fig. 7 Time dependence of contact angle of liquid pure Ag on SiC at 1283 K. ○: Reaction-bonded SiC, ●: Carbon treated reaction-bonded SiC, □: Hot-pressed SiC.

Fig. 8 Time dependence of contact angle of liquid pure Ni on SiC at 1773 K. ○: Reaction-bonded SiC, □: Hot-pressed SiC.

Fig. 9 Time dependence of contact angle of liquid pure Co on SiC at 1803 K. $\circ$: Reaction-bonded SiC, $\square$: Hot-pressed SiC.

Fig. 10 Time dependence of contact angle of liquid pure Fe on SiC at 1873 K. $\circ$, $\bullet$: Reaction-bonded SiC, $\square$, $\blacksquare$: Hot-pressed SiC.

than 160° at 603 K in Ar atmosphere. No time dependence of contact angle can be observed in the liquid Pb/SiC system. This higher angle in both reaction bonded SiC and hot pressed SiC can be attributed to the insolubility of Si or C in liquid Pb⁽²⁾, i.e. the nonreaction between Pb and SiC.

The time dependence of contact angles of liquid Sn on SiC is shown in Fig. 3. As the experimental temperature for a SiC single crystal differed from that for a reaction bonded SiC and hot pressed SiC, it is difficult to compare the contact angles obtained. It is, however, possible to say that the contact angles depend on the SiC used. It has generally been reported that the contact angle of liquid metal on ceramics decreases with increasing tempera-

ture⁽³⁾⁽⁴⁾. This tendency has also been observed in liquid metal/SiC systems⁽⁵⁾.

The difference between the contact angle of liquid Sn on the hot pressed SiC and on the reaction bonded SiC may be observed at 1373 K from Fig. 3. This may be caused by the dissolution of the Si into liquid Sn which had been contained in the reaction bonded SiC. It has been reported that the solubility of Si in liquid Sn is c.a. 2.6 mass% at the experimental temperature⁽²⁾.

The contact angle of liquid Sn on SiC has been reported by Allen *et al.*⁽⁶⁾ and Naidich⁽⁵⁾. Allen *et al.* reported that the value of the contact angle was 165° at 1373 K in H₂ atmosphere and in *vacuo* and Naidich reported the value as 135° at 1323 K.

It is difficult to compare the values obtained here with those by Allen *et al.* and Naidich. However, it is interesting to find that the value for the reaction bonded SiC, 131° , is close to that obtained by Naidich and the value for the hot pressed SiC, 151° , is close to that by Allen *et al.*

Time dependence of contact angles of liquid Al on a single crystal of α -SiC is shown in Fig. 4. As is clear from Fig. 4, the contact angle of liquid Al decreased rapidly with the elapse of time. This can be attributed by a formation of Al₄C₃ at the interface between liquid Al and SiC. The reaction between liquid Al and SiC can be expressed by eq. (1)⁽⁷⁾.

This reaction was confirmed by a Si analysis of Al and an X-ray diffraction analysis for the interface between Al and SiC after removing the Al by NaOH solution.

The existence of Al₄C₃ at the interface was proved by the X-ray diffraction analysis and 8.7 at% of Si was detected by an EDX analysis of solidified Al sample.

The wettability of α -SiC by liquid Si was measured at 1773 K under reduced pressure (10^{-3} Pa). Since the liquid Si spread completely over the α -SiC, the contact angle could not be determined.

As shown in Fig. 5, the contact angle of liquid Au on α -SiC was almost constant during

the experiments. This is the same tendency as in the case of liquid Sn.

The effects of temperature and time on the contact angle of liquid Ge on various SiC are summarized in Fig. 6. The time dependence of the contact angle differed according to SiC used. The contact angles on the hot pressed SiC and the single crystal of α -SiC did not change with time. On the other hand, the contact angle on the reaction bonded SiC changed considerably with time, particularly at higher temperatures.

The interface between solidified Ge and SiC was examined by EPMA. It was observed that Ge had penetrated the reaction bonded SiC along the grain boundaries where the metallic Si had existed. On the other hand, no penetration of Ge was observed when the hot pressed SiC and the single crystal of α -SiC had been used. The penetration depth through the reaction bonded SiC depended on experimental temperature. No penetration was observed at 1293 K and Ge penetrated to the bottom of the reaction bonded SiC, whose thickness had been 3 mm, at temperatures higher than 1573 K.

Si contents in the solidified Ge samples were determined by EDX analyses. No Si was detected in the samples on the hot pressed SiC and on the single crystal of α -SiC. Si contents on the reaction bonded SiC were 0.9, 34.5 and 47.6 at% at 1293, 1473 and 1673 K, respectively. The difference in Si content in the samples and in the behavior of Ge at the interface between Ge and SiC could be the reason for the difference in the time dependence of contact angles.

Kinoshita *et al.* proposed to use Ge as a reagent for metal-SiC joining⁽⁸⁾. The results obtained here supports their proposal if the reaction bonded SiC is used.

The time dependence of contact angle of liquid Ag on SiC at 1283 K is shown in Fig. 7. It is clear from Fig. 7 that the contact angle of liquid Ag on SiC depends on the properties of the SiC used. The contact angle on the carbon treated reaction bonded SiC, whose surface was carburated, was not close to that on the reaction bonded SiC but to that on the hot pressed SiC. The carbon treated reaction bond-

ed SiC was prepared by heating a reaction bonded SiC with graphite powder for 5.4 ks at 1573 K in Ar atmosphere. After the treatment, X-ray diffraction analysis revealed that free Si did not exist at the surface of the sample. This could be the reason that the value of contact angle on the carbon treated reaction bonded SiC was close to that on the hot pressed SiC. Si contents of the samples after experiments were determined by EDX and it was found that the Si content in Ag sample which was melted on the reaction bonded SiC was 4.8 at% and no Si was detected in both of the samples which were melted on the hot pressed SiC and the carbon treated reaction bonded SiC.

These facts suggest that a surface property of the carbon treated reaction bonded SiC is analogous to that of the hot pressed SiC. It might be possible to protect the reaction bonded SiC from a reaction with liquid metal by the carbon treatment.

Naidich⁽⁵⁾ reported the contact angle of liquid Ag on SiC was 128° at 1373 K. It is difficult to compare the values obtained here with the values of Naidich, since the experimental conditions are not the same. However, it is still possible to say that the value obtained by Naidich is close to that for the reaction bonded SiC. This coincidence was also found in the liquid Sn/SiC system described before. Accordingly, the SiC used by Naidich might be a reaction bonded SiC.

The time dependence of contact angles of liquid Fe, Co and Ni on SiC is shown in Figs. 8~10.

The values of the contact angles themselves shown in Figs. 8~10 and their time dependence differed from those of the other liquid metals such as Pb, Sn, Al, Au, Ge and Ag. This can be attributed to the fact that these metals can solve a considerable amount of Si and C at the experimental temperature⁽²⁾.

The difference in the values of the contact angle may be seen in Figs. 8~10. The lowest value of a contact angle was observed in the liquid Fe/SiC system and the highest in the liquid Ni/SiC system.

This may be caused mainly by a difference in the experimental temperature among the systems. It is reasonable to consider that the

higher the temperature, the more vigorous the reaction between liquid metals and SiC. The reaction between various solid metals and SiC has been reported previously⁽⁹⁾⁽¹⁰⁾. Though the metals used here are in a liquid form, the results obtained are consistent with those of previous works⁽⁹⁾⁽¹⁰⁾.

It can be said that the contact angles of liquid metals on SiC are remarkably affected by the dissolution reaction of Si and C into the liquid metals and carbide formation reaction at the interface between liquid metals and SiC.

IV. Conclusion

The wettability of three kinds of SiC, a reaction bonded SiC, a hot pressed SiC and a single crystal of α -SiC, by liquid pure metals were measured using the sessile drop method.

(1) Contact angles of liquid pure Pb, Sn, Au and Ag were always larger than 90° for all types of SiC examined.

(2) The reactivity of a reaction bonded SiC with liquid metal may be controlled by a carbon treatment.

(3) Contact angles of liquid pure Fe, Co and Ni were always less than 90° for both reaction bonded SiC and hot pressed SiC. α -SiC changed considerably with the elapse of time. The initial contact angle was 160° , reducing gradually with time, the final one after 6.9 Ks was 56° .

(4) Contact angle of liquid pure Al on a single crystal of α -SiC changed considerably with time elapsing. The initial contact angle was 160° , reducing gradually with time, the final one after 6.9 ks was 56° . This can be attributed by a formation of Al_4C_3 at the inter-

face between liquid Al and SiC.

(5) Contact angle of liquid pure Ge depended on the kind of SiC used. The contact angle on a hot pressed SiC and α -SiC was obtuse, on the other hand, that on a reaction bonded SiC was acute.

(6) Wetting behavior of liquid metals on SiC is closely related to the solubility of Si and C.

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