Reactive wetting in liquid Cu alloy - carbon and silicon carbide systems

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Abstract. Wettability of carbon and SiC by liquid Cu-Si alloys was measured by the sessile drop method and was mainly investigated from a thermo-dynamical view point. Penetration phenomena of liquid Cu-Si alloy into porous carbon was also investigated. It was found that it is possible to expect whether wetting system or non-wetting system from thermo-dynamic calculation.

1. Introduction

It is very important to understand wetting phenomena of liquid metals-ceramics systems in metallurgical, welding and joining fields to obtain high quality and high performance materials. For example, to understand phenomena such as a reaction between liquid alloys and refractory, deoxidation of liquid steel, metal-ceramics joining and a fabrication of metal matrix composites, information on wettability of solid oxide, nitride, carbide and carbon by liquid metals is indispensable. Accordingly, many research articles concerning the wettability of solid ceramics by liquid metals have been published. However, there is a considerable difference in the contact angle between liquid metal on solid ceramics, which is one of an index of wettability.

It is well known that the wettability is affected by many factors such as temperature, partial oxygen pressure in an atmosphere, surface condition of ceramics (surface roughness and surface crystal structure), thermo-dynamical stability of ceramics and metal and alloying element. In Al/Al₂O₃ system, there is a very large difference in contact angle among reported values and Hausner found the difference in contact angle can be attributed to the difference in oxygen partial pressure in an atmosphere [1]. As an example of the effect of surface crystal orientation on wettability, one of the present authors found a characteristic wetting in liquid pure Cu/SiC system [2]. Beta SiC has a hexagonal crystal structure and liquid Cu spreads over on SiC maintaining hexagonal shape. It is well known that thermo-dynamically active metals such as Ti, Zr and Al also affect the wettability [3]. Small amount of active metals in liquid metals reduce contact angles of liquid metals on ceramics. Furthermore, an increase in temperature usually causes a linear decrease in contact angle. However, when a surface condition such as adsorption and desorption of gas on solid changes with temperature, a change in contact angle reflects the surface condition change. In the liquid metal/diamond system, it was reported that contact angle shows sudden change at the temperature which corresponds to the desorption temperature of hydrogen from diamond surface [4,5].

In the present study, the wettability of carbon and carbide by liquid Cu-Si alloy will be mainly investigated from a view point of thermo-dynamic calculation.
2. Experimental principle

Sessile drop method was employed to measure a contact angle between liquid Cu alloy and carbon and SiC. A schematic illustration of a furnace used is shown in Fig.1. The furnace has some strong points to obtain an accurate contact angle. As graphite heater was used, oxygen potential of an atmosphere can be lowered by the reaction between carbon and O2 gas in the atmosphere, which yields CO gas. By equipping a sample dropping assembly to the furnace, it is possible to avoid a reaction between liquid Cu alloy and a substrate before starting contact angle measurement. Laser beam irradiation behind liquid Cu alloy drop enables us to obtain a clear profile of the drop. By taking photographs of the drop from 2 directions which is set a right angle, it is possible to confirm a symmetrical shape of liquid drop.

![Figure 1](image)

Figure 1 Schematic illustration of a furnace (a) side view, (b) top view

(a) (1) Sample dropping assembly, (2) Cu alloy sample, (3) Thermocouple,
(4) Carbon or SiC substrate, (5) Graphite heater, (6) Mo reflector,
(7) He-Ne laser, (8) Band-pass filter, (9) Digital camera

(b)

Two types of glassy carbon substrates whose porosity were 18% and 0% respectively were employed to observe wetting and penetration phenomena. Here after, the Glassy carbon whose porosity is 18% will be called porous carbon and the glassy carbon whose porosity is 0% will be called the dense carbon. SiC substrate was obtained by hot pressing of SiC powder with B4C as a sintering aid. Alloy samples were made by arc melting of 5N of Cu rod, 6N of Si pieces.

Measurements were conducted at the scheduled temperatures under around 1 X 10^-3 Pa.

3. Results and Discussion

Figure 2 shows the time dependence of contact angle of liquid Cu - Si alloy on a dense carbon. It can be seen from Fig. 2 that in the case of Cu - 15at.% Si, the contact angle does not change with time and in the case of Cu – 25at.% Si and Cu – 56at.% Si, the contact angle decreases with a lapse of time and a final contact angle is 40 to 50 degree. The difference of wetting behaviour between liquid Cu - 15 at.% alloy and liquid Cu - 25 at.% and liquid Cu - 56 at.% alloys can be attributed to the difference in a reactivity of liquid Cu - Si alloy with carbon.

It can be expected that SiC is produced at the interface between liquid Cu - Si alloy and carbon by a reaction expressed by equation 1. The standard Gibbs energy of the reaction (1) can be described by equation (2) [6].

\[
\text{Si (in liquid Cu)} + \text{C} = \text{SiC} \quad (1)
\]

\[
\Delta G^0 = 27100 - 2.73T \log T + 18.1T \text{ (cal/mol)} \quad (2)
\]

where \(\Delta G^0\) is the standard Gibbs energy of the reaction and \(T\) is the absolute temperature.

It can be calculated from equation (2) that the Si concentration which is required to produce SiC at the interface between liquid Cu - Si alloy and carbon is 18.3 at.% at 1300°C. As Cu - 15at.%Si alloy is
smaller than a calculated value of 18.3 at.%, no reaction occurs at the interface and contact angle does not change with time. On the other hand, as liquid Cu - 25 at.% and liquid Cu - 56 at.% alloys is larger than the calculated value of 18.3 at.%, the reaction occurs and SiC is formed at the interface. Formation of SiC was investigated by XRD at a cross section of Cu - Si alloy and carbon interface. In the case of Cu - 15at.% Si, no SiC was detected and in the Cu – 25at.% Si and Cu – 56at.% Si, on the other hand, SiC was detected as shown in Figure 3.

**Fig. 2** Change in contact angle of liquid Cu-Si alloy on carbon with time
Figure 4 shows contact angles of liquid Cu-25 at.% and liquid Cu-56 at.% alloys on SiC. It is interesting to compare Figure 4 with Figure 3. It can be clarified by comparing Figure 4 with Figure 3 that final contact angles on SiC are almost the same as that on carbon and a time dependence of decreasing in contact angle on SiC is larger than that on C. These results might suggest that reaction between Si and carbon is not a momentary one.

Figure 5 shows change in a shape of liquid Cu-56 at.% alloy drop on porous carbon substrate. It can be seen from Figure 5 that apparent contact angle on porous carbon decreases gradually with time and liquid Cu alloy absolutely penetrates in the porous carbon after 22 minutes. When a viscosity of liquid Cu-Si alloy is low enough to penetrate at high temperature, the results suggest that a low rate of penetration is caused by a low rate of reaction between Si and carbon.

Figure 3 XRD pattern at the interface between solidified Cu-25at%Si and dense carbon

Fig. 4 Change in contact angle of liquid Cu-Si alloy on SiC with time
4. Conclusion
Wettability of dense and porous carbons by liquid Cu - Si alloy and penetration phenomena of liquid Cu - Si alloy were investigated and obtained the following results.
(1) When Si content exceeds 18.3 at.% in Cu, liquid Cu - Si alloy wets carbon substrate and SiC is formed at the interface between liquid Cu and carbon in the experimental condition.
(2) Penetration of liquid Cu - Si alloy into porous carbon can be observed when liquid Cu - Si alloy wets carbon substrate
(3) It can be concluded from time dependence of contact angle and observation of penetration behavior that reaction rate of Si and carbon is not fast.

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