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Wetting Phenomena at High Temperature (Part III) †

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Abstract

The effect of active elements such as Ti, Zr on the wettability of ceramics by liquid metals have been investigated in many systems since it is thought that the wettability phenomena in these systems gives us an important information to develop filler metals to join metals and ceramics. In this paper, the effect of alloying elements on the wettability of ceramics by liquid metals will be reviewed.

KEY WORDS: (Wettability) (Surface Tension) (Work of Adhesion) (Contact Angle)
(Metal - Ceramic Joining)

1. Introduction

It is very important to improve the wettability of ceramics such as oxides, carbides and nitrides by liquid metals since the good wetting is required to metal-ceramic joint. Active elements such as Ti and Zr are usually added to improve the wettability of ceramics by liquid metals. In this review, the effect of active elements on the wettability of ceramics by liquid metals are summarized.

2. General Consideration of a Role of Active Elements on the Wettability

It has been reported that an improvement of the wettability by adding active elements is attributed to a formation of reaction layer at the interface between liquid metal and ceramics the higher the concentration, the more improvement since a reaction layer thickness increases with an increase in a concentration of active elements in liquid metals. It should be true the improvement of the wettability results from the reaction layer at the interface but it might not be true that the reaction layer thickness affects the wettability. Because the wettability should be improved by an existence of mono atomic reaction layer. This implies that we have to consider the other mechanism of the improvement of the wettability at higher concentration of active elements.

Figures 1 and 2 show the effect of Ti on the contact angle of liquid Cu on SiC and Si content in liquid Cu-Ti alloy, respectively¹⁾. It can be seen from Fig. 1 that only 1 mass% of Ti reduces the contact angle of liquid Cu on SiC from 140 degree to 40 degree. It is generally accepted that an addition of Ti in liquid

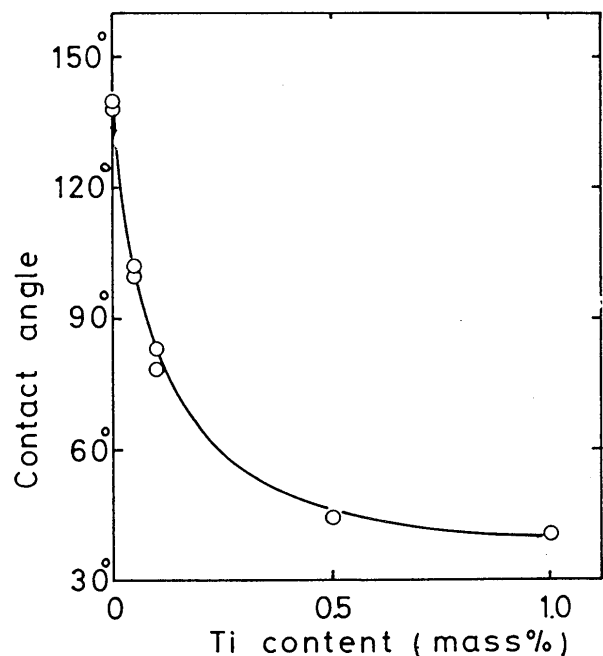


Fig. 1 Effect of Ti content on contact angle between liquid Cu and SiC at 1393K

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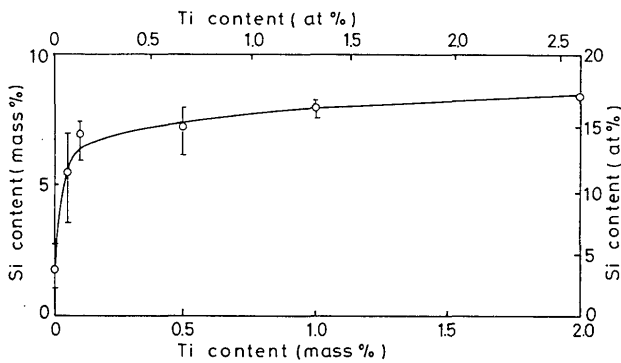


Fig. 2 Si content in liquid Cu-Ti alloy after 3.6ks

metal reduces the contact angle between liquid metals and ceramics and the higher the concentration of Ti, the more improvement the wettability of ceramics. It is also accepted that the improvement of the wettability at higher concentration of Ti results from a formation of thicker compound containing Ti at the interface between liquid metals and ceramics^{2,3}. Wetting phenomenon, however, is not a bulk phenomenon but a interface one. This means that the thickness of reaction products at the interface should not play a important role for improvement of the wettability. In other words, it is sufficient to form monolayer reaction product at the interface to improve the wettability.

It is, now, necessary to consider other mechanism for the improvement at higher concentration of Ti. The reaction between liquid Cu-Ti alloy and SiC can be expressed by Eq.(1).



It is clear from Eq.(1) that one mole Ti decrease corresponds to one mole of Si increase in liquid Cu. However, it can be seen from Fig. 2 that Si concentration does not correspond to Ti concentration and amounts of Si after experiments are larger than Ti contents before experiments. Warren et al reported that it is possible to form Cu-Si-C liquid by a small amount of C-loss even at 1173K in Cu-SiC pseudobinary system⁴.

The result in the work¹) does not conflict with the Warren's proposal. This observation implies that the decrease in the contact angle, that is, the improvement of the wettability is caused by not only the reaction products (TiC) at the interface but also dissolution reaction of Si in liquid Cu. Figures 3 and 4 show a change in the contact angle with time and a change in TiC layer thickness with time, respectively. It is clear from Figs. 3 and 4 that TiC layer is formed at the initial stage but the contact angle remains constant at the initial stage. This fact suggests that a dissolution reaction of Si is more significant effect than a formation

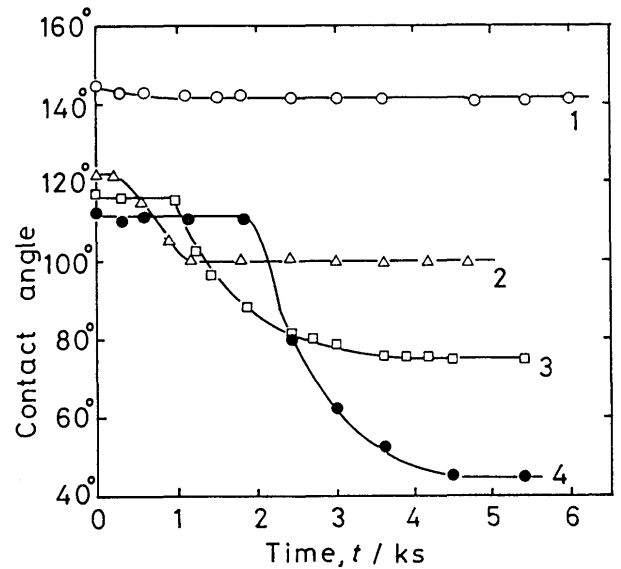


Fig. 3 Change in contact angle of liquid Cu-Ti alloy with time

○: liquid pure Cu, △: liquid Cu-0.05 mass%Ti, □: liquid Cu-0.1 mass%Ti, ●: liquid Cu-0.5 mass%Ti.

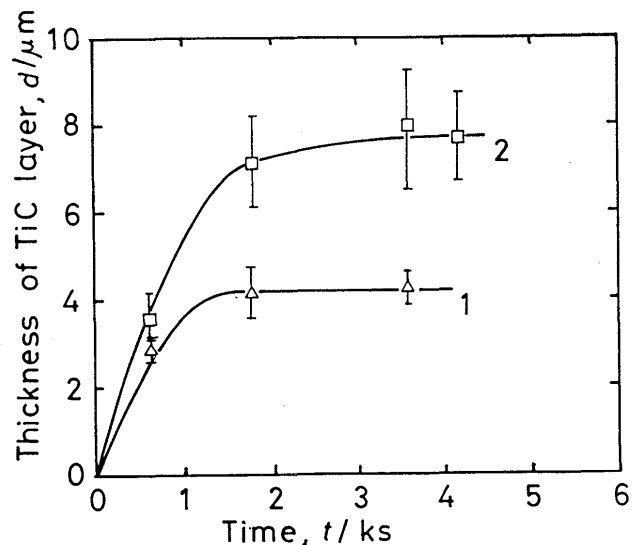


Fig. 4 Effect of Ti content and contacting time on the thickness of TiC layer

△: liquid Cu-0.05 mass%Ti, □: liquid Cu-0.1 mass%Ti.

of TiC at the interface on the contact angle decrease. In this meaning, the previous investigators misunderstood the effect of Ti on the wettability. Iseki et al reported the effect of Ti on the wettability of SiC, TiC, Ti₅Si₃ and Ti₃SiC₂ by liquid Ag-Cu alloy⁵). It is clear from Figs. 5 and 6 that the contact angles of liquid Ag-Cu and Ag-Cu-Ti alloy on TiC are only 5 to 10 degrees smaller than those on SiC. This also means that

reaction product at the interface does not affect the contact angle.

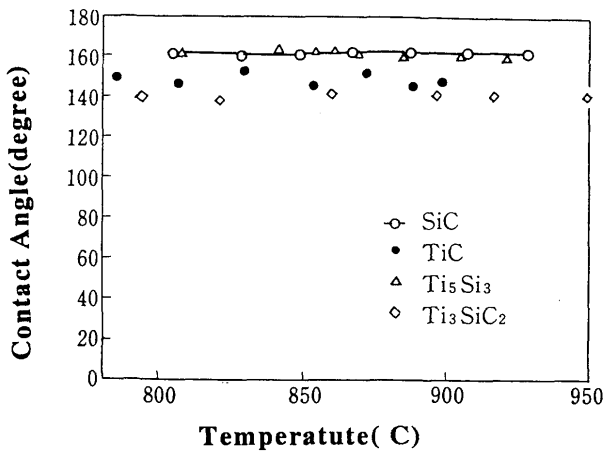


Fig. 5 Contact angle between liquid Ag-Cu alloy and various substrates

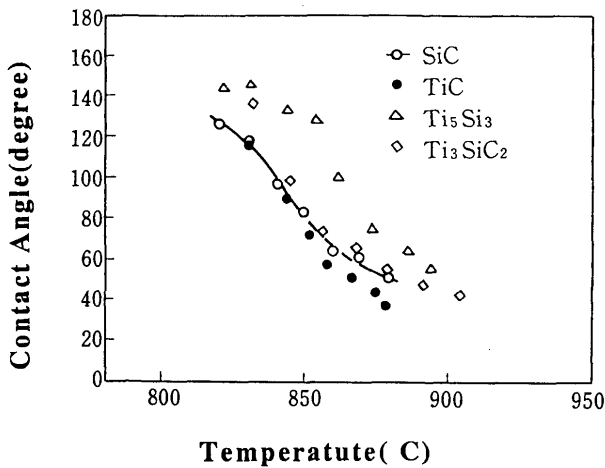


Fig. 6 Contact angle between liquid Ag-Cu-Ti alloy and various substrates

3. Effect of Ti on the Wettability of Ceramics by Liquid Metals

3.1 Effect of Ti on the Wettability of Oxides by Liquid Metals

Many reports have been published concerning the effect of Ti on wettability of ceramics by liquid metal. Figures 7, 8 and 9 show the effect of Ti on the wettability of oxides (SiO_2 , Al_2O_3 , MgO and TiO_2) by liquid metals (Cu, Sn and Au). It is clear from Figs. 7, 8 and 9 that Ti is effective to improve the wettability⁶⁻¹³. Naidich et al concluded from their

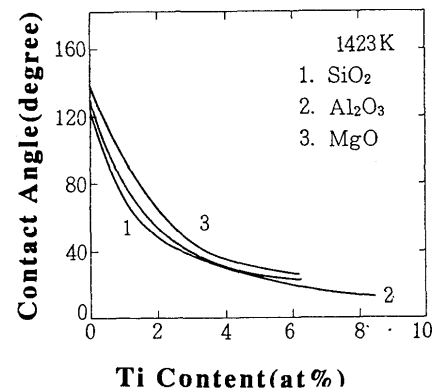


Fig. 7 Effect of Ti on the contact angle between liquid Cu and oxides

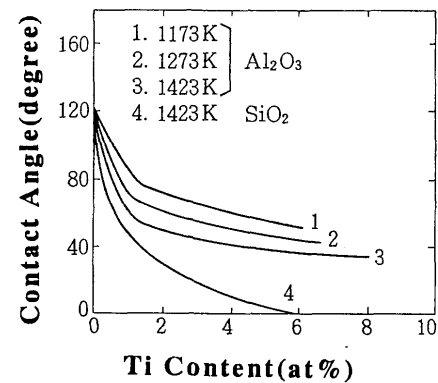


Fig. 8 Effect of Ti on the contact angle between liquid Sn and oxides

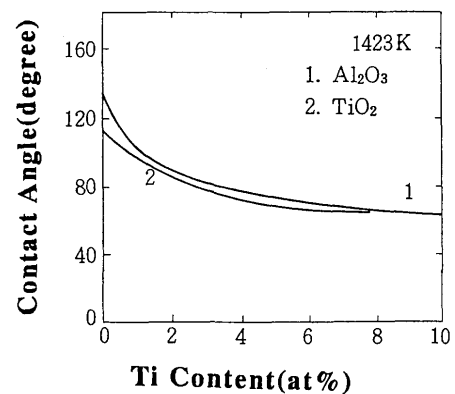


Fig. 9 Effect of Ti on the contact angle between liquid Au and oxides

results that the improvement of the wettability is caused by the TiO_2 at the interface between liquid metal and oxide^{10,11}). Their conclusion, however, is not correct as mentioned in the chapter 2.

Nicholas et al revealed the effect of third elements (In, Sn, Au, Ag, Al, Ga and Ni) on the contact angle between liquid Cu-Ti alloy and Al_2O_3 at 1423K¹²).

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Figures 10 and 11 show iso-contact angle curves for 90 degree and 25 degree, respectively. It can be seen from these figures that Sn and In have significant effect on the wettability. Effect of In and Sn can be attributed to reduce surface tension of liquid Cu-Ti alloy and to diminish a solubility limit of Ti.

Figures 12 and 13 show the effect of Ti on the interfacial energy between liquid Ni and Al_2O_3 ¹³⁾ and on the interfacial energy between liquid Sn and Al_2O_3 ¹⁴⁾, respectively. It is possible to calculate the extra quantities of Ti at the interface from the dashed line in figures. Calculated results implies the interfaces are saturated by Ti.

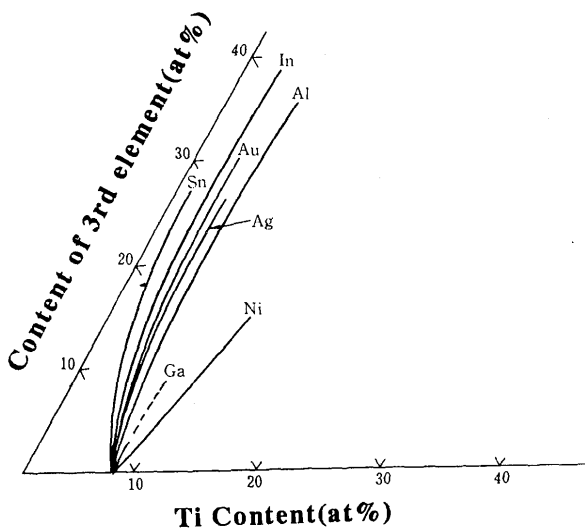


Fig. 10 Effect of 3rd elements on iso-contact angle curves(90degree) for Cu-Ti alloy / Al_2O_3 system

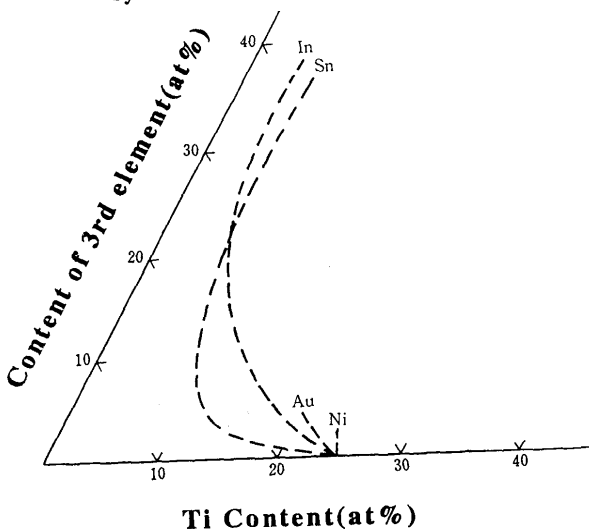


Fig. 11 Effect of 3rd elements on iso-contact angle curves (25degree) for Cu-Ti alloy / Al_2O_3 system

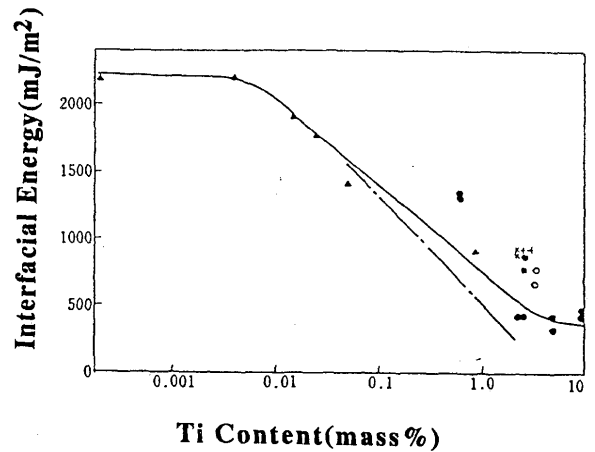


Fig. 12 Effect of Ti on the interfacial energy between liquid Ni-Ti alloy and Al_2O_3

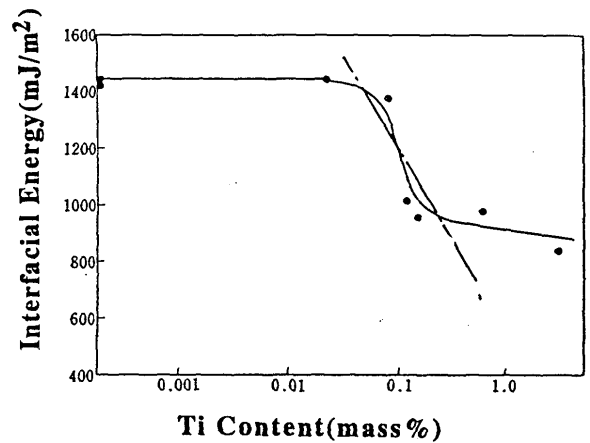


Fig. 13 Effect of Ti on the interfacial energy between liquid Sn-Ti alloy and Al_2O_3

3. 2 Effect of Ti on the Wettability of Carbides and Nitrides by Liquid Metals

It is important to understand oxides are usually more stable than carbides and nitrides in an atmosphere and the surface of carbides and nitrides is often covered by oxide film. As the wettability measurements were sometimes carried out by using oxide film coated nitrides and carbides, the results led us to an incorrect conclusion.

A characteristic wetting behaviour has been reported in the liquid pure Cu- α SiC single crystal¹⁵⁾. As shown in Figs. 14 and 15, liquid Cu spreads over the SiC forming hexagonal shape which corresponds to a crystal structure of SiC. This is a direct evidence which shows the wettability depends on a surface structure of a substrate. It is very important to know the hexagonal wetting is not necessary to be observed in any

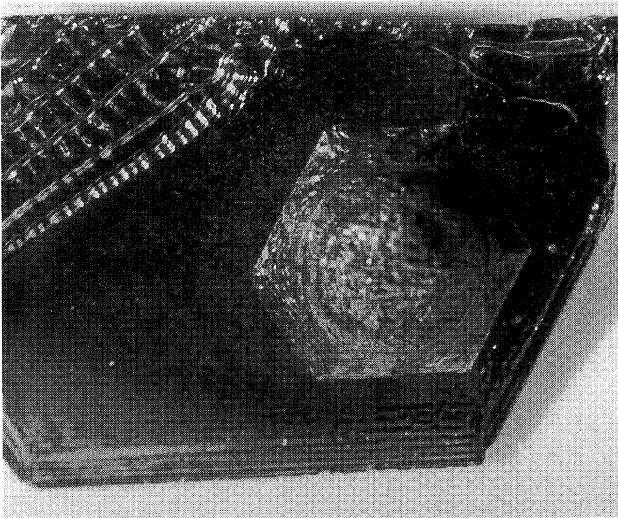


Fig. 14 Top view of pure Cu drop on SiC single crystal

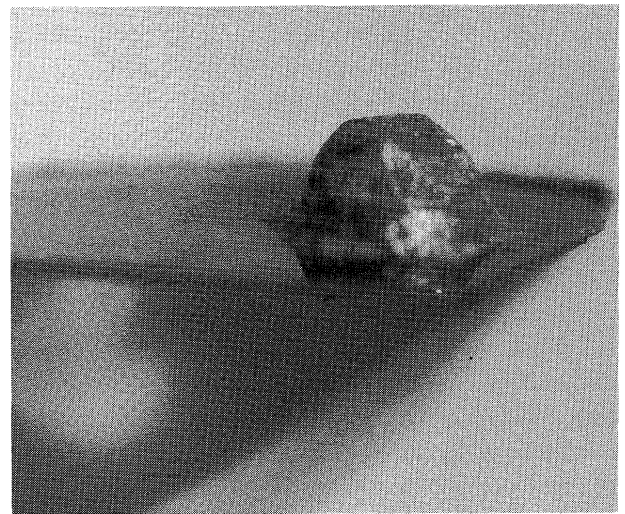


Fig. 15 Side view of pure Cu drop on SiC single crystal

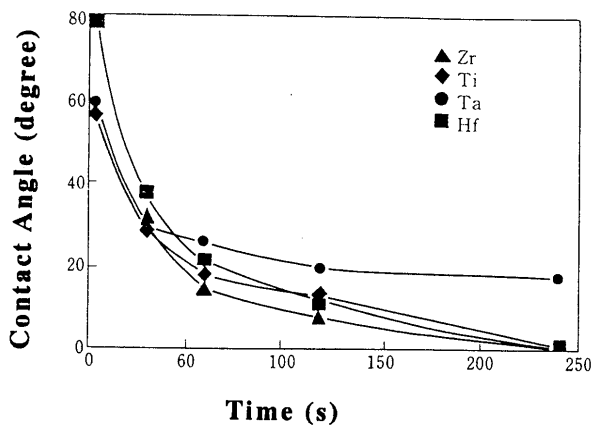


Fig. 16 Effect of Zr, Ti, Ta and Hf on time dependence of contact angle of Au-18mass%Ni on Si_3N_4

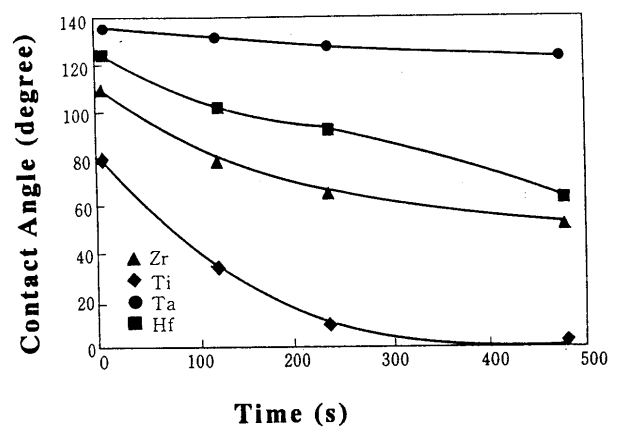


Fig. 17 Effect of Zr, Ti, Ta and Hf on time dependence of contact angle of Ag-28mass%Cu on Si_3N_4

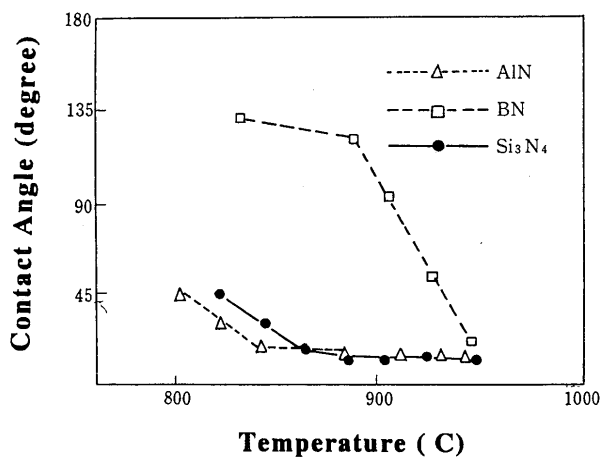


Fig. 18 Temperature dependence of contact angle of Ag-27.5Cu-2Ti on nitrides

experimental conditions¹⁵). When the experiment is carried out in Ar atmosphere whose oxygen potential might be higher than reduced pressure, normal wetting can be observed. The reason for a different wetting behaviour can be attributed to a difference in an atmosphere. As the oxygen potential in Ar gas is high, the α -SiC surface is easy to change to SiO_2 and liquid pure Cu- SiO_2 shows a normal wetting¹⁶).

Kong investigated the effect of Ti, Zr, Ta and Hf on the wettability of Si_3N_4 by liquid Au-Ni and Ag-Cu alloys¹⁷). Figures 16 and 17 show the effect of active elements, Zr, Ti, Ta and Hf, on the contact angle of liquid Au-18mass%Ni alloy and Ag-28mass%Cu alloy on Si_3N_4 , respectively. It can be seen from Fig. 16 that all elements investigated reduce the contact angle. On the other hand, as can be seen From Fig. 17, Ta in

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liquid Ag alloy does not reduce the contact angle and others do. Iwamoto et al support the reason for no improvement on the wettability by adding Ta should be attributed to its high melting point⁽⁸⁾. It should not, however, have any relationship between the improvement of wettability and melting point.

Nicholas reported the temperature dependence of contact angle between Ti containing alloy and nitrides, AlN, BN, and Si₃N₄⁽¹⁹⁾. As can be seen from Fig. 18, the contact angles do not reduce linearly but do suddenly at certain temperatures. The author investigated the temperature dependence of contact angle between liquid pure metals and various oxides⁽⁶⁾ and Rhee also studied the contact angle between liquid pure metals and carbides and nitrides⁽²⁰⁻²²⁾. It can be concluded from these results that the contact angle for non reactive system reduces linearly with temperature. The reason for steep decrease in the contact angle containing active elements can be attributed to a vigorous reaction between the active elements and nitrides at high temperature.

4. Conclusion

It can be concluded that the adding active elements in liquid metals is effective to improve the wettability of ceramics by them. The reason for an improvement of the wettability by adding active elements, however, should not usually be attributed to a formation of reaction layer at the interface between liquid alloys and ceramics. The formation of the reaction layer, of course, reduces the contact angle itself. Its contribution is only 10 to 20 degrees at most. The reduce in the contact angle is mainly caused by a dissolution reaction of ceramics into liquid alloys.

It is easy to reduce the contact angle between ceramics and liquid metals by adding active elements, in other words, when we add active element such as Ti in liquid metals, the wettability is always improved. In this meaning, the wettability measurement to develop a filler metal should not be done, since an answer is well

known before the measurements. Important factor for the filler metals is not how to improve the wettability, but how to reduce a residual stress in joints as long as the filler metals which contain active elements.

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