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REACTIONS AND WETTING BEHAVIOR IN THE AuSi ALLOY - αAl_2O_3 SYSTEM

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Wetting behavior of a Au- 31 at% Si alloy (complete melting ∿540°C) on α-Al_2O_3 was studied using the sessile drop technique over the temperature range of 700 to 1450°C. The alloy was used in order to realize lower experimental temperatures (Au m.p. = 1064°C; Si m.p. = 1414°C; eutectic, 19 at% Si = 363°C). An experiment was also made with Si on α-Al_2O_3 at 1450°C.

The single crystal α-Al_2O_3 (sapphire) disks* used in this study were obtained as optically polished plates in the size of 1/2 in. diameter and 1/12 in. thickness. The surface of the plates had a 60° orientation from the c-axis. The AuSi alloy was made in the laboratory from 99.95% Au** and 99.99% Si.*** After cleaning the specimens ultrasonically in isopropyl alcohol for about 15 min. they were set in a Ta-foil resistance vacuum furnace. The experimental set up of the sessile drop furnace was previously reported.[1]

The changes of the contact angle of the AuSi alloy on α-Al_2O_3 with temperature at a pressure of 10^{-5} torr are shown in Fig. 1. The temperature was raised every 10 minutes in 50°C increments. Two curves

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are shown: one for α-Al_2O_3 as received, the other for α-Al_2O_3 heat-treated in air at 1400°C for 12 h. With as-received α-Al_2O_3, the contact angle was 150° up to ∿850°C, then decreased continuously to 78° with increase of temperature to ∿1100°C, and remained constant up to 1450°C. With the heat-treated α-Al_2O_3, the contact angle was again 150° up to ∿800°C, but then decreased abruptly to ∿117°C which was roughly maintained up to ∿950°C, then decreased continuously to 78° up to ∿1100°C where it remained up to 1200°C. The contact angle of Si on Al_2O_3 in He at 1450°C was ∿83° in 5 min and decreased to 80° after 30 min; He was necessary to raise the ambient pressure to reduce the vaporization rate of Si.

Brennan and Pask[1] also observed complex behavior in the Al-αAl_2O_3 system which was attributed to variations in the surface of the sapphire. They proposed that at low partial pressures of oxygen heat-treated Al_2O_3 had an α-surface structure whose surface energy (γ) is in the range of 560 to 700 ergs/cm^2 which changed to an oxygen deficient structure at temperatures of about 900 to 1000°C whose γ is 905 ergs/cm^2. Low energy electron diffraction (LEED) studies[2,3] also proposed such a structural change under equivalent conditions to form an oxygen-deficient surface. It was found possible to etch away this surface below the transformation temperature by evaporated silicon vapor.[2,4] Brennan and Pask[1] also indicated that surface energies and reactions were affected by the presence of a hydroxylated surface and its dehydroxylation which occurred during the wetting experiments.

The 150° contact angles in Fig. 1 are interpreted as being due to a lack of a true interface since the interfacial energy is greater than

either of the surface energies.[5] An interface forms at ∿800°C with the heat-treated α-Al_2O_3 and the contact angle becomes ∿117°. As the surface then transforms to an oxygen-deficient surface in the range of about 950 to 1100°C with an increase of γ the contact angle changes to 78°. The surface of the as-received specimen, on the other hand, undergoes a dehydroxilation over the range of 800 to 1000°C which gradually merges with the oxygen-deficiency transformation up to 1100°C beyond which point behavior is similar for both sapphires. The formation of the oxygen-deficient surface results in an interfacial reaction with Si. The Si-Al_2O_3 sessile drop specimen was cut and the cross-section was analyzed with an electron microprobe for Si and Al (Fig. 2). Presence of Al in the Si drop is evidence for a reaction. Reaction rings were also observed on the surface of Al_2O_3 both in the presence of the AuSi alloy and Si which were similar in nature to those observed in reactions of Al with Al_2O_3, also at similar low partial pressures of oxygen and high temperatures.[1] It is of interest to note that such reactions leading to saturation with aluminum resulted in adherence of the drop to the substrate.

On the basis of LEED studies with the use of silicon vapor two types of reactions between Al_2O_3 and Si have been suggested:

$$Al_2O_3(s) + 2\ Si(g) = 2\ SiO(g) + 2\ Al_2O(g) \qquad (1)$$

$$Al_2O_3(s) + 3\ Si(g) = 3\ SiO(g) + 2\ Al(g) \qquad (2)$$

Equation (2) is based on a mass spectrometer analysis of material leaving an Al_2O_3 surface heated above 1000°C during silicon deposition.[4] During a study of etching of α-Al_2O_3 by Si, Filby[6] observed the appearance of Si/Al globules on the Al_2O_3 surface at 1240°C indicating that

alumina was reduced by Si to form some free Al liquid and proposed the following equation:

$$Al_2O_3(s) + 3\ Si(g) = 3\ SiO(g) + 2\ Al\ (\ell) \qquad (3)$$

Marumo and Pask[7] in wetting studies of Al on fused SiO_2 found that an extensive reaction readily occurred to form Al_2O_3 and SiO(g) or Si. Thermodynamically, it then would not be expected that a reaction of Si with an α-Al_2O_3 surface whose structure is contiguous with the bulk structure would be favorable unless the pressures of the possible reaction products of SiO(g), Al_2O(g), or Al(g) are kept low to provide favorable reaction conditions. It is thus proposed that the observed reaction occurs because of the formation of the oxygen-deficient surface on bulk α-Al_2O_3 under low partial pressures of oxygen at temperatures above ~1000°C. This reaction is assumed to be thermodynamically favorable for both the AuSi alloy and Si. This study and that of Brennan and Pask[1] indicate that under the existing conditions of low partial pressures of oxygen within the system the reaction depleted oxygen-deficient surface keeps reforming at the interface, thus allowing the reaction to continue. The coupled Eqs. (4) and (5)

$$3(\alpha Al_2O_3)(\text{surface}) = 2(AlO\cdot Al_2O_3)(\text{surface}) + 1/2\ O_2(g) \qquad (4)$$

$$AlO\cdot Al_2O_3(\text{surface}) + Si(\ell \text{ or } g) = Al_2O_3(s) + SiO(g) + Al(\ell \text{ or } g) \qquad (5)$$

can be used to represent this reaction.

ACKNOWLEDGMENTS

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Figure Captions

Fig. 1. Change in contact angle with temperature in the Au-3lat% Si — αAl_2O_3 system.

Fig. 2. X-ray fluorescence micrographs of cross-section of Si drop placed on α-Al_2O_3 and kept at 1450°C for 30 min in He. Aℓ is indicated in the Si drop: (Top) Aℓ-Kα, (Bottom) Si-Kα.

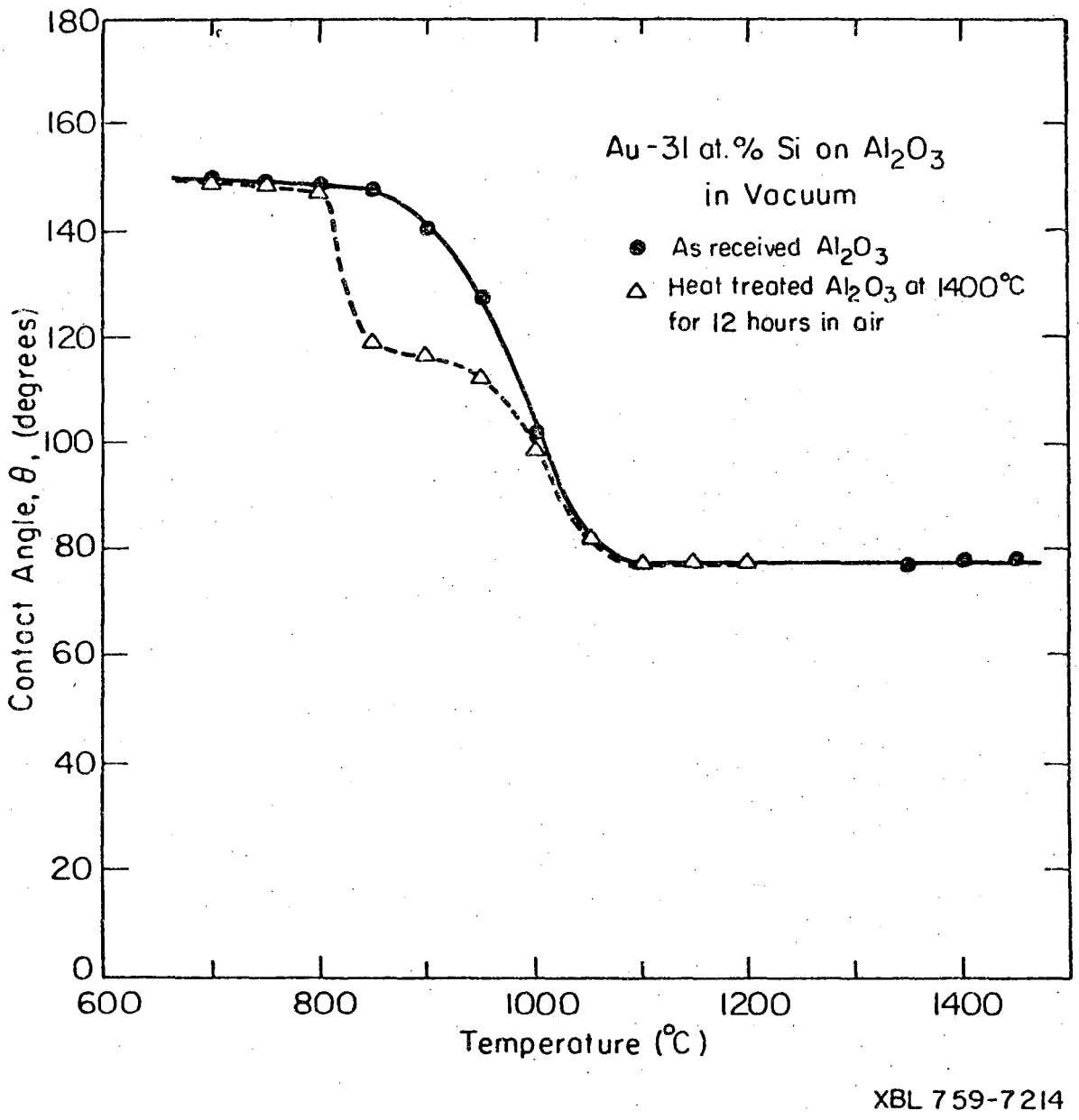
Au-31 at.% Si on Al_2O_3
in Vacuum
As received Al_2O_3
Heat treated Al_2O_3 at 1400°C
for 12 hours in air
Contact Angle, θ, (degrees)
Temperature (°C)
180
160
140
120
100
80
60
40
20
0
600
800
1000
1200
1400
XBL 759-7214

Fig. 1

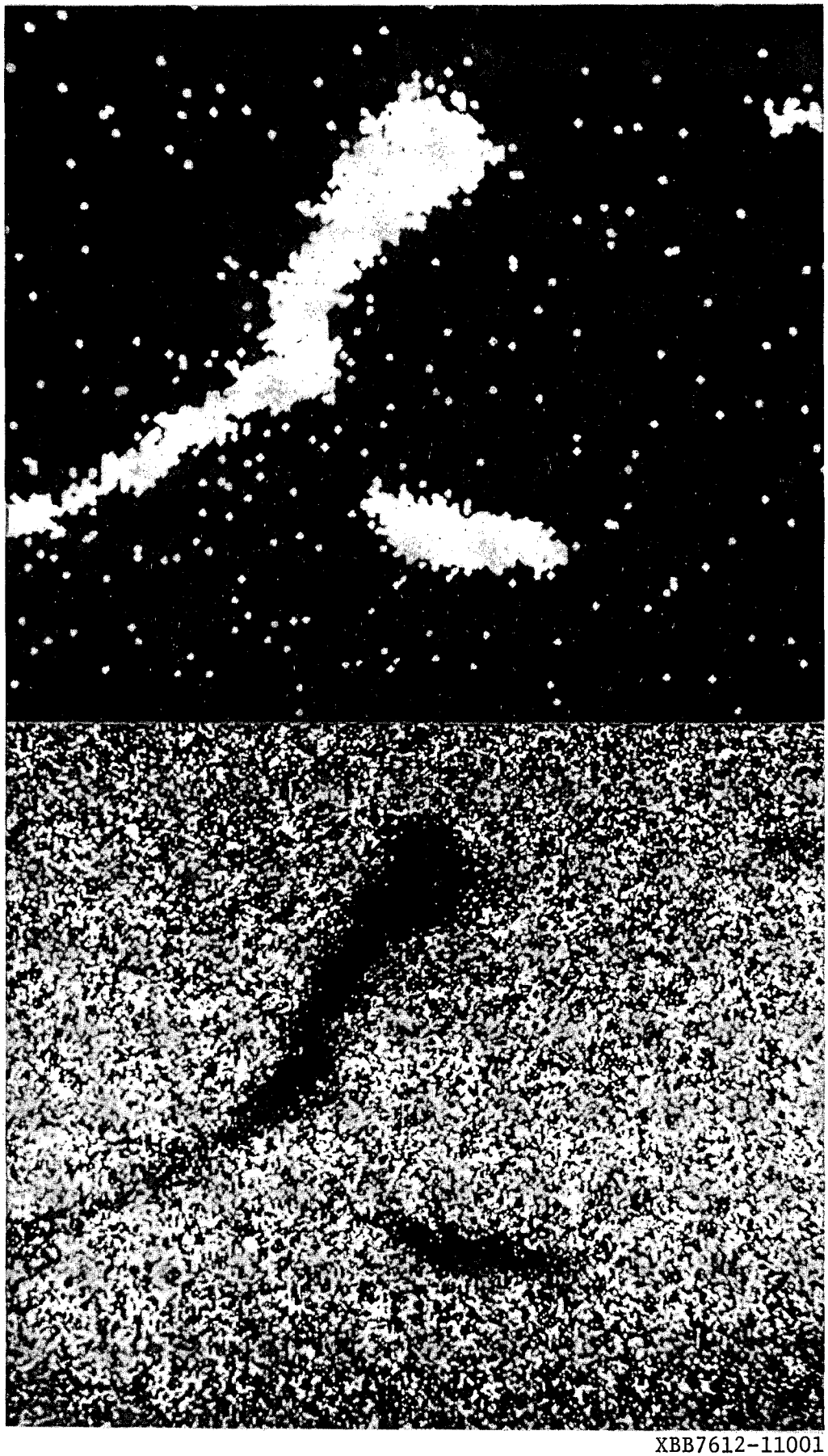

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Fig. 2

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