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A fundamental approach for the measurement of solid-liquid interfacial energy

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Abstract. Solid-liquid interfacial energies in alloys are important properties for the process design of materials production such as casting and crystal growth. Inadequate information exists on solid-liquid interfacial energies. Our aim for this study was thus to establish a method to measure solid-liquid interfacial energies in alloys from equilibrium interfacial shapes of solid-liquid-gas phases. Experiments were carried out on Cu-B and Ag-Bi systems where copper and silver were treated as solid phases, respectively. Since the determined values for solid-liquid interfacial tensions for both systems agreed with reported values or estimated values, it was clarified that solid-liquid interfacial energies can be measured by observing the interfacial shape.

1. Introduction

Solid-liquid interfacial energies are fundamental properties of materials and play a key role in material processing at the coexistence of solid and liquid phases such as for the processes of casting and crystal growth. Since little information exists on solid-liquid interfacial energies, further research is required for the simulation of the materials process including the solid-to-liquid transformation in various systems.

Solid-liquid interfacial energies have been measured based on the nucleation rate, maximum super-cooling, dihedral angles of grain boundary grooves and Young's contact angle but these techniques show considerable discrepancies in experimental results. These discrepancies are caused by experimental conditions being unsuitable for adaptation to nucleation theory. Additionally, inaccuracies in reference values of surface tensions and grain boundary energies are responsible for these discrepancies. Recently, the measurement of solid-liquid interfacial energies has been done by measuring the equilibrium interfacial shape of the solid-liquid-gas phases for Al-Si, Al-Al$_2$O$_3$ and Fe-C systems [1-3]. This method allows for the determination of the solid surface energy and the solid-interfacial energy if the liquid surface tension is available. No reports, however, exist where the measurement of solid-liquid interfacial energies of metal-metal or metal-alloy systems was undertaken.

In this work, to establish a method for the determination of both the solid-liquid interfacial energy and the solid surface energy in an alloy system, experiments measuring the equilibrium interfacial shape of solid-liquid-gas phases of Cu-B and Ag-Bi systems were carried out. The validity of this method was then verified through comparison of the experimental results with the reported or estimated values.

2. Experimental principle

2.1. Dupre's equation

When a liquid droplet is placed on a soluble solid substrate its equilibrium shape may be illustrated as in Figure 1. At physical equilibrium the three interfacial energies, the liquid surface tension (σ_L), the solid surface energy (σ_S) and the solid-liquid interfacial energy (σ_{SL}) are balanced at the triple point where the sine theorem gives Dupre's equation as expressed by equation (1).

$$\frac{\sigma_{SL}}{\sin \theta_V} = \frac{\sigma_L}{\sin \theta_S} = \frac{\sigma_S}{\sin(\theta_1 + \theta_2)} \tag{1}$$

If the value of the liquid surface tension is available we can determine the solid-liquid interfacial energy and the solid surface energy by measuring the equilibrium dihedral angles θ_V and θ_S. In this work, the liquid surface tensions of binary alloys were estimated using Butler's equation.

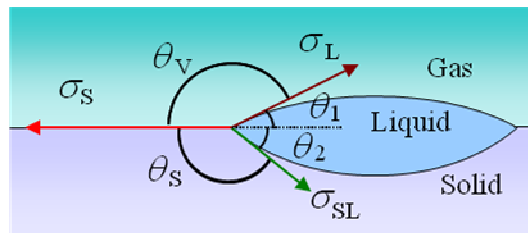**Figure 1.** The equilibrium shape of a liquid droplet on a solid substrate.

2.2. Butler's equation

The surface tension of a liquid alloy σ_L can be estimated well by Butler's equation as expressed in equation (2) with thermodynamic properties of the alloy [4].

$$
\begin{aligned}
\sigma_L &= \sigma_A + \frac{RT}{A_A} \ln \frac{\left(1 - N_B^S\right)}{\left(1 - N_B^B\right)} + \frac{1}{A_A} \overline{G}_A^{E,S}\left(T, N_B^S\right) - \frac{1}{A_A} \overline{G}_A^{E,B}\left(T, N_B^B\right) \\
&= \sigma_B + \frac{RT}{A_B} \ln \frac{N_B^S}{N_B^B} + \frac{1}{A_B} \overline{G}_B^{E,S}\left(T, N_B^S\right) - \frac{1}{A_B} \overline{G}_B^{E,B}\left(T, N_B^B\right)
\end{aligned}
\tag{2}
$$

where σ_X and A_X are the surface tension and the molar surface area of pure liquid X, respectively. $N_X^{B/S}$ is the mole fraction of component X of a bulk or a surface which is defined as the outermost monolayer. $\overline{G}_X^{E,B/S}\left(T, N_B^{B/S}\right)$ is the partial excess Gibbs energy of component X in the surface as a function of T and $N_B^{B/S}$. The partial excess Gibbs energy of the surface is obtained as equation (3) assuming it has a comparable composition dependence to that in the bulk.

$$\overline{G}_X^{E,S}\left(T, N_B^S\right) = \frac{Z^S}{Z^B} \cdot \overline{G}_X^{E,B}\left(T, N_B^S\right) \tag{3}$$

where $Z^S / Z^B = 0.83$ which denotes the ratio of the coordination number in the surface to that in the bulk [5]. Liquid surface tensions of Cu-B and Ag-Bi systems were calculated from thermodynamic properties [6,7] at a given temperature and composition on the liquidus for each alloy system.

3. Experimental procedure

A Cu-rich Cu-B droplet was melted on a copper substrate in the Cu-B system. A copper substrate of 3 mm thickness (purity 99.96 %) into which a hole was bored to a depth of 1-2 mm in the centre was polished mechanically and chemically. Cu-B alloys for droplets were prepared by melting copper shots (purity 99.99 %) and a boron lump (purity 99.8 %) in an alumina crucible under an Ar-10%H$_2$ atmosphere at 1573 K.

The Cu-B alloy was placed in the hole of the copper substrate in a horizontal electric resistance furnace. It was heated to 1273 K within 120 min under an Ar-10%H_2 atmosphere. Water and oxygen in the atmospheric gas were removed by passing it through magnesium perchlorate and magnesium chips then heated to around 773 K. The temperature was then raised to 1348 K at a rate of 5 K/min and kept there for 5-30 min. The apparent contact angle (θ_1 in Figure 1) was measured using a CCD camera. The sample was cooled down at a rate of 6 K/min. The vertical cross-section was observed by optical microscope and the hidden angle (θ_2 in Figure 1) was determined.

Liquid bismuth was reacted with a solid silver substrate to form Ag-Bi melt for the Ag-Bi system. A silver substrate of 1-2 mm thickness (purity 99.99 %) with a hole in the centre, was polished mechanically and chemically. Bismuth shot (purity 99.999 %) was placed in the hole of the silver substrate in a horizontal infrared furnace. It was heated to 773 K at a rate of 2.5 K/min under vacuum and kept at that temperature for 5-60 min. The apparent contact angle and the hidden angle were determined as for the Cu-B system.

4. Result and discussion

4.1. Experimental results for the Cu-B system

A Cu- 10.0 mol% B alloy was melted on a copper substrate at 1348 K and kept there for 5 min. Figure 2(a) shows the liquid alloy on the copper substrate after being kept at that temperature for 5 min. The apparent contact angle θ_1 became constant within 5 min and was determined to be $6.8 \pm 0.7°$. The cross-section of the sample after quenching is shown in Figure 2(b). The liquid alloy dissolved the substrate and gave a hidden angle θ_2 of $62.4 \pm 2.5°$. Here, the volume of the liquid alloy is estimated to be 5 times the initial volume of the alloy that was placed on the substrate which indicates that the liquid composition became the Cu-liquidus (Cu- 1.9 mol% B) by taking into account the lever rule for the alloy composition. The liquid surface tension was thus estimated for the corresponding alloy composition to be 1366 mN/m using equation (2). The solid-liquid interfacial energy between solid copper and liquid Cu-B alloy and the solid surface energy of copper were determined to be 182 ± 23 mN/m and 1440 ± 17 mN/m using equation (1), respectively.

The determined interfacial energy between solid copper and liquid Cu-B alloy was in good agreement with reported values between solid and liquid copper of 177-232 mN/m [9-11]. In addition, the obtained solid surface energy of copper agrees fairly well with the reported value of 1478 mN/m [12] although it seems to be slightly smaller because of the effect of adsorption of boron on the copper surface. Hence, the possibility exists to determine the solid-liquid interfacial energy by observing the equilibrium shape of the three phase interface in the copper-based system.
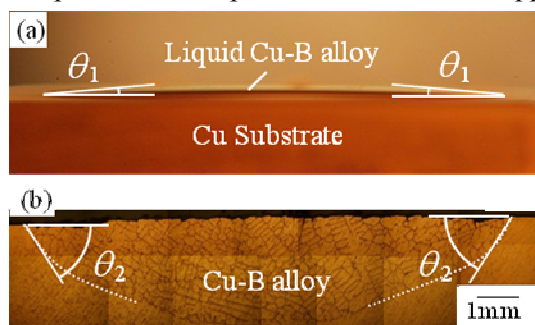

Figure 2. The liquid Cu-B droplet on the solid Cu substrate (a) at 1348 K and (b) the cross-section after the experiment.

4.2. Experimental results for the Ag-Bi system

A bismuth shot was melted on a silver substrate at 773 K and kept there for 60 min. Figure 3(a) shows the liquid alloy on the silver substrate after being kept at that temperature for 60 min. The apparent contact angle θ_1 became constant within 10 min and was determined to be $21.8 \pm 0.3°$. The cross-section of the sample after quenching is shown in Figure 3(b). The liquid alloy dissolved the substrate and gave a hidden angle θ_2 of $55.5 \pm 1.7°$. Here, the liquid size is estimated to be 3 times that

of the initial size of the bismuth granule that was placed on the silver substrate which indicates that the liquid composition was the Ag-liquidus (Ag- 38.8 mol% Bi). The liquid surface tension was thus estimated for the corresponding alloy composition to be 416 mN/m using equation (2). The solid-liquid interfacial energy between solid silver and liquid Ag-Bi alloy, and the solid surface energy of silver were determined to be 187 ± 6 mN/m and 493 ± 8 mN/m using equation (1).

The determined interfacial energy between solid silver and liquid Ag-Bi alloy was in good agreement with the estimated value of the solid-liquid interfacial energy through the prediction proposed by Eustathopoulos [8,9] for the corresponding solid silver and liquid alloy of 178 mN/m. On the other hand, the solid surface energy of silver was much smaller than the reported value for pure silver of 1339 mN/m at 773K [12]. This might be influenced by the absorption of bismuth onto the silver surface although this should be confirmed by further investigation.

The applicability of this new method for the determination of the solid-liquid interfacial energy by observing the equilibrium interfacial shape of the three phases was also confirmed for the silver-based system.
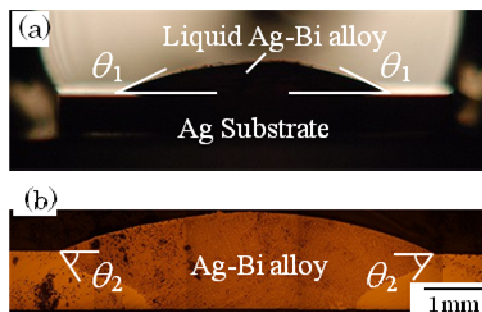

Figure 3. The liquid Ag-Bi droplet on the solid Ag substrate (a) at 773 K and (b) the cross-section after the experiment.

5. Conclusions

A measurement method was established for interfacial energies in alloy systems by observing the equilibrium shape of the solid-liquid-gas interface of an alloy system. Experiments were conducted on Cu-B and Ag-Bi systems. The determined interfacial energies from the observed interfacial shapes were in accordance with reported or estimated values. Hence, it is possible to measure the solid-liquid interfacial energies in alloy systems from the interfacial shape of the three phases.

References

[1]   Nakae H and Katoh H 1999 *J. Japan Inst. Metals* **63** 1356
[2]   Levi G and Kaplan W D 2003 *Acta Materialia* **51** 2793
[3]   Shinozaki N, Satoh N, Shinozaki H , Wasai K and Era H 2006 *J. Japan Inst. Metals* **70** 950
[4]   Butler J A V 1932 *Procedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character* **135** 348
[5]   Tanaka T, Hack K, Iida T and Hara S 1996 *Z. Metallkunde* **87** 380
[6]   Weber L and Tavangar R 2007 *Scripta Materialia* **57** 988
[7]   Zoro E, Servant C and Legendre B 2007 *Calphad* **31** 89
[8]   Eustathopoulos N 1983 *Int. Met. Rev.* **28** 189
[9]   Turnbull D 1950 *J. Applied Physics* **21** 1022
[10]   Vinet B, Magnusson L, Fredriksson H and Desre P J 2002 *J. Colloid Interf. Sci.* **255** 363
[11]   Kaptay G 2001 *Trans. JWRI* **30** 245
[12]   Alchagiro A B, Alchagirov B B, Taova T M and Khokonov K B 2001 *Trans. JWRI* **30** 287