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Liquid–Liquid Interfacial Tension in Ternary Monotectic Alloys Al–Bi–Cu and Al–Bi–Si

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The liquid–liquid interfacial tension in the ternary monotectic alloys $Al_{34.5-x}Bi_{65.5}Cu_x$ and $(Al_{0.345}Bi_{0.655})_{100-x}Si_x$ (mass%) has been determined as a function of its Cu (Si) content by a tensiometric technique. It is established that the interfacial tension gradually increases when either Cu or Si is added to Al–Bi alloys. The increase of $\sigma_{\alpha\beta}$ can be related to the increase of the miscibility gap (both width and height) when Cu (Si) is added to the Al–Bi binary. The temperature dependences of the interfacial tension in binary $Al_{34.5}Bi_{65.5}$ and ternary $Al_{23.25}Bi_{65.5}Cu_{11.25}$ and $(Al_{0.345}Bi_{0.655})_{95}Si_5$ monotectic alloys are well described by the power function $\sigma_{\alpha\beta} = \sigma_0 \cdot (1 - T/T_C)^{\mu}$ with the critical-point exponent $\mu = 1.3$.

KEY WORDS: aluminum; bismuth; copper; immiscibility; interfacial tension; silicon.

1. INTRODUCTION

There exist a high scientific and industrial interest in multicomponent metallic alloys that show a miscibility gap in the liquid state. Al-based monotectic alloys are considered as potential candidates for advanced bearings in car engines. It is expected to obtain an aluminum matrix with finely distributed particles of, e.g., In, Bi, or Pb as a soft phase with a self-lubricating function. However, this idea is still far from practical implementation because the miscibility phenomenon poses problems during solidification [1].

The interfacial phenomena between two liquid phases play a crucial role in the nucleation process and Marangoni motion. Therefore,

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a knowledge of the liquid–liquid interfacial tension and its temperature dependence is of high importance for an understanding and mathematical description of the monotectic growth. However surprisingly it seems, there exist virtually no experimental data on this physical property for multicomponent monotectics.

Recently we measured the liquid–liquid interfacial tension in the binary monotectic alloy $Al_{34.5}Bi_{65.5}$ (mass%) over a wide temperature range [2]. In the present work we study experimentally how the interfacial energy between Al-rich and Bi-rich phases is changed when either Cu or Si is added to the binary $Al_{34.5}Bi_{65.5}$.

2. MEASUREMENT TECHNIQUE

The interfacial tension in the liquid monotectic alloys has been measured with a tensiometric method described in detail in Refs. 3 and 4. The principles of the experimental set-up and measuring process are schematically shown in Figs. 1 and 2. The technique is based on a relation between the force exerted on the cylindrical alumina stamp detached to the liquid–liquid interface (measured experimentally) and the shape of the meniscus (modeled by numerical solution of the Laplace equation of capillarity). Application of the submerging body in the form of the stamp reduces significantly the influence of the free surface of the upper liquid on the experimental data.

Thus, the force exerting on the stamp $F^{\exp}$ is measured as a function of the stamp's height h. The experimental curve for the liquid $Al_{29.5}Bi_{65.5}Cu_5$ alloy at 660°C is plotted in Fig. 2 as an example. After correction of the experimental data for buoyancy and geometry of the crucible and of the stamp, the volume of the meniscus $V_{\mathrm{Men}}^{\exp}$ is determined as a function of height of the contact line x_0 from the following relation:

$$F_{\mathrm{Men}}^{\exp}(x_0) = V_{\mathrm{Men}}^{\exp}(x_0) g \Delta\rho_{\alpha\beta}, \tag{1}$$

where $F_{\mathrm{Men}}^{\exp}(x_0)$ is the force caused by the meniscus, $\Delta\rho_{\alpha\beta}$ is the difference of the macroscopic densities of the two liquids, and g is the acceleration of gravity.

On the other hand, the meniscus is modeled by a numerical solution of the Laplace equation of capillarity, which describes the pressure difference ΔP across the curved liquid–liquid interface,

$$\sigma_{\alpha\beta}\left(\frac{1}{R_1} + \frac{1}{R_2}\right) = \Delta P = P_1 - P_2, \tag{2}$$

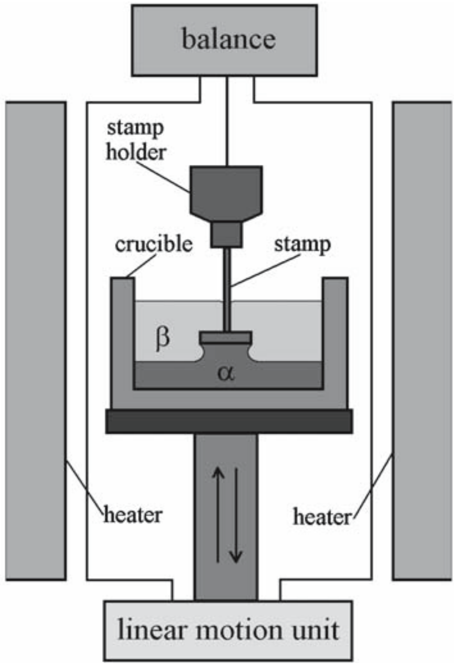

Fig. 1. Schematic diagram of the tensiometer; α and β—coexisting liquid phases.

where $\sigma_{\alpha\beta}$ is the interfacial tension between liquid α and liquid β; R_1 and R_2 are the principal radii of curvature of the interface; and P_1 and P_2 are the pressures on the concave and convex sides of the meniscus, respectively. Due to the cylindrical form of the stamp, the solution of Eq. (2) is reduced to a one-dimensional problem, so that the Laplace equation contains the curvature radii and a linear gravitation component:

$$\sigma_{\alpha\beta}\left(\frac{1}{R_1}+\frac{1}{R_2}\right)=\Delta\rho_{\alpha\beta}gx, \tag{3}$$

where x is a coordinate in the direction of the gravitational force. Substituting the principal radii of curvature by the differential geometry expressions, one obtains the following equation [5]:

$$\frac{x'}{r(1+x'^2)^{1/2}}+\frac{x''}{(1+x'^2)^{3/2}}=\frac{\Delta\rho_{\alpha\beta}gx}{\sigma_{\alpha\beta}}, \tag{4}$$

where r is the radial distance in a horizontal plane from the axis of symmetry ($r^2=y^2+z^2$), $x'=dx/dr, x''=d^2x/dr^2$.

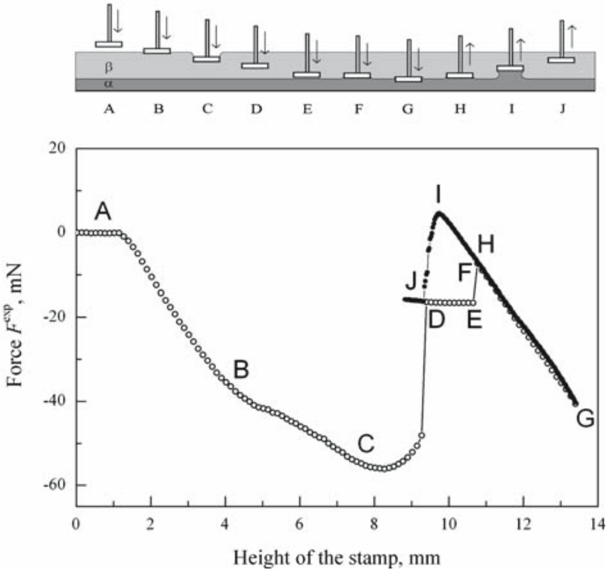

Fig. 2. Main stages of the measuring process and experimental curve for liquid $Al_{29.5}Bi_{65.5}Cu_5$ at 660°C.

The numerical solution of Eq. (4) allows modeling of the radial-symmetrical meniscus and calculation of its volume as a function of height of the contact line x_0—$V_{\mathrm{Men}}^{\mathrm{model}}(x_0)$—for different radii of the contact line (i.e., for different stamps) and for various values of the capillary constant a, which is defined as

$$a = \frac{\sigma_{\alpha\beta}}{\Delta\rho_{\alpha\beta} g}. \tag{5}$$

Then the experimental and the theoretical volume curves are compared and the capillary constant is determined as is shown in Fig. 3, for example.

The difference of the macroscopic densities of the two liquid phases is needed for calculation of the interfacial tension. It is an advantage of the measurement technique that the determination of the density difference is possible from the experimental data. The value of $\Delta\rho_{\alpha\beta}$ is calculated from the buoyancy force exerted by the liquid sample on the stamp immersed into it.

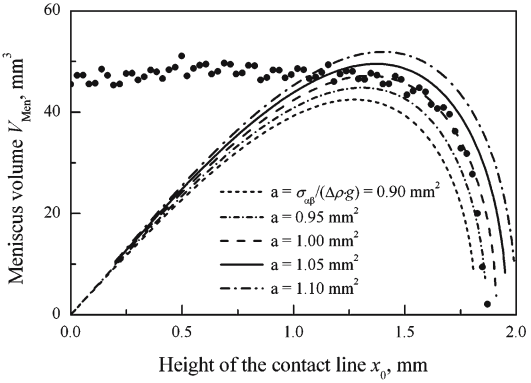

Fig. 3. Experimental meniscus volume for liquid $Al_{29.5}Bi_{65.5}Cu_5$ at 660°C obtained from the curve plotted in Fig. 2 and theoretical volume curves calculated for different capillary constants.

3. EXPERIMENTAL DETAILS AND RESULTS

Ternary alloys studied in this work were prepared from high-purity Al, Bi, Cu, and Si (99.999%). The measurements were performed in the tensiometer schematically shown in Fig. 1. Before heating, the chamber was evacuated to better than 1×10^{-5} mbar and filled with a gas mixture of Ar–$10H_2$ (vol.%) with a total pressure of ~1 bar. A niobium getter was used to reduce the amount of oxygen that gets into the chamber through leaks during measurements. The heating system consisted of a concentric Kanthal heater outside the chamber, power supply, and electronic temperature control device. The graphite crucible (5-cm inner diameter, 4 cm height) was moved by an ultrahigh vacuum manipulating system. The force exerted on the stamp was measured by a balance with an uncertainty of 1 mg.

The liquid–liquid interfacial tension $\sigma_{\alpha\beta}$ in the ternary $Al_{34.5-x}Bi_{65.5}$ Cu_x alloys was measured as a function of Cu concentration at 660°C. The experimental data are plotted in Fig. 4. The temperature where the monotectic reaction starts as well as the critical temperature in the ternary Al–Bi–Si system increases rapidly with increasing Si content [6]. Therefore, the interfacial tension in the $(Al_{0.345}\ Bi_{0.655})_{100-x}$ Si_x alloys was measured as a function of Si content at 660°C only up to 5 mass% Si. Figure 5 shows the experimental composition dependences of $\sigma_{\alpha\beta}$ in the $(Al_{0.345}$ $Bi_{0.655})_{100-x}Si_x$ alloys at 660 and 750°C.

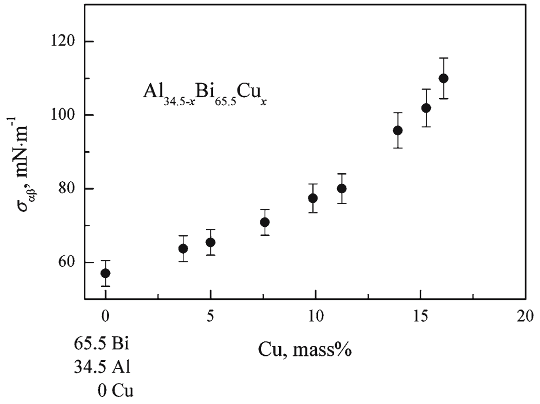

Fig. 4. Composition dependence of the liquid–liquid interfacial tension in the $Al_{34.5-x}$ $Bi_{65.5}Cu_x$ alloys at 660°C.

4. DISCUSSION

The addition of Cu to the $Al_{34.5}Bi_{65.5}$ binary causes a remarkable and continuous increase of the liquid–liquid interfacial tension over the composition range studied (Fig. 4). This result correlates with the phase diagram of the ternary Al–Bi–Cu system [7]. The main features of the Al–Bi–Cu phase equilibria, which affect the liquid–liquid interfacial tension are: (i) the miscibility gap significantly grows with increasing Cu content and (ii) the solubility of Bi in Al decreases when Cu is added; virtually all Cu is dissolved in the Al-rich phase. These facts explain the increase of the interfacial energy between Al-rich and Bi-rich phases in ternary Al–Bi–Cu immiscible alloys.

The addition of Si to $Al_{34.5}Bi_{65.5}$ also increases the interfacial energy between Al-rich and Bi-rich liquids (Fig. 5). Higher liquid–liquid interfacial tensions in the ternary $(Al_{0.345}Bi_{0.655})_{100-x}Si_x$ alloys compared to the binary $Al_{34.5}Bi_{65.5}$ can be explained by the peculiarities of the Al–Bi–Si phase diagram [6]. The solubility of Si in Bi is small and Si atoms tend to stay in the Al-rich phase when added to binary Al–Bi. Extension of the miscibility gap causes an increase of the interfacial energy between the Al-rich and Bi-rich liquid phases.

The temperature dependences of the interfacial tension for two alloys—$Al_{23.25}Bi_{65.5}Cu_{11.25}$ and $(Al_{0.345}Bi_{0.655})_{95}Si_5$—have been studied in Ref. 8. These compositions were chosen because they allowed investigations over the widest temperature range experimentally accessible. The results are plotted in Fig. 6 together with the experimental data for $Al_{34.5}Bi_{65.5}$ [2]. As is seen in this figure, the interfacial tension in ternaries is higher than

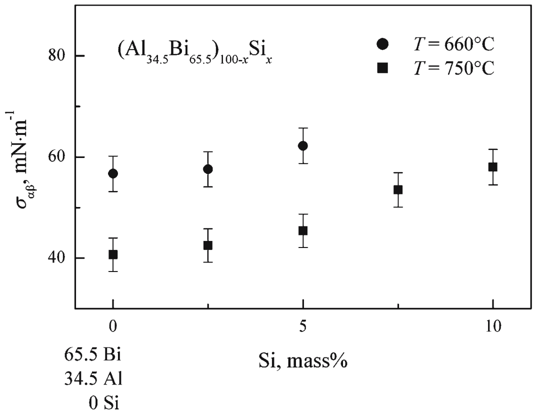

Fig. 5. Composition dependences of the liquid–liquid interfacial tension in the $(Al_{0.345}Bi_{0.655})_{100-x}Si_x$ alloys at 660 and 750°C.

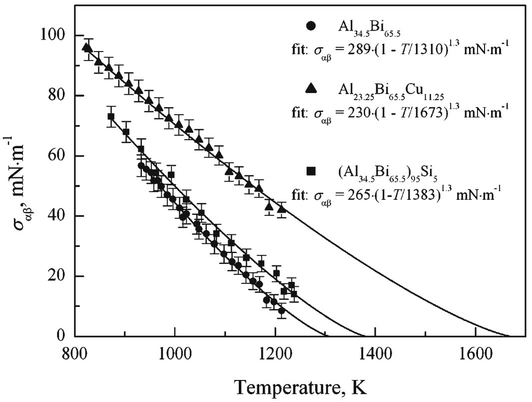

Fig. 6. Temperature dependences of the liquid–liquid interfacial tension in the binary $Al_{34.5}Bi_{65.5}$ [2] and ternary $Al_{23.25}Bi_{65.5}Cu_{11.25}$ and $(Al_{0.345}Bi_{0.655})_{95}Si_5$ [8] alloys.

that of the $Al_{34.5}Bi_{65.5}$ binary over a wide temperature range. The difference in $\sigma_{\alpha\beta}$ for the ternary and binary alloys is even more pronounced at higher temperatures since the critical temperature increases when Cu or Si is added to Al–Bi.

The temperature dependence of the interfacial tension in liquid monotectic alloys can be described by the expression,

$$\sigma_{\alpha\beta} = \sigma_0 (1 - T/T_C)^{\mu} \tag{6}$$

where σ_0 is a constant, T is the absolute temperature, T_C is the critical temperature, and μ is the so-called critical-point exponent. Such a temperature dependence of $\sigma_{\alpha\beta}$ is very convenient for the mathematical description of solidification processes in monotectic systems. The classical mean-field theory of van der Waals [9] or the later work of Cahn and Hilliard [10] predicts $\mu = 1.5$, while the renormalization theory [11] gives $\mu = 1.26$. It was shown in Ref. 2 that the experimental temperature dependence of the interfacial tension for liquid $Al_{34.5}Bi_{65.5}$ is well described by Eq. (6) with $\sigma_0 = 289\,\mathrm{mN \cdot m^{-1}}$ and $\mu \approx 1.3$ (see Fig. 6). The critical temperature $T_C = 1310\,\mathrm{K}$ as given by the Al–Bi phase diagram [12] was taken for the fit. Therefore, the same value of the critical exponent ($\mu = 1.3$) was applied by fitting of the experimental data for ternary $Al_{23.25}Bi_{65.5}Cu_{11.25}$ and $(Al_{0.345}Bi_{0.655})_{95}Si_5$ alloys [8]. Since no experimental data on the critical temperature for ternary Al–Bi–Cu and Al–Bi–Si systems are available, T_C was a fitting parameter along with σ_0. The fitting lines and parameters of the fits are shown in Fig. 6.

5. CONCLUSIONS

The interfacial tension gradually increases when either Cu or Si is added to Al–Bi alloys. The temperature dependences of the liquid–liquid interfacial tension in binary $Al_{34.5}Bi_{65.5}$ and ternary $Al_{23.25}Bi_{65.5}Cu_{11.25}$ and $(Al_{0.345}Bi_{0.655})_{95}Si_5$ monotectic alloys are well described by the power function $\sigma_{\alpha\beta} = \sigma_0 (1 - T/T_C)^{\mu}$ where σ_0 is a constant, μ is the critical-point exponent, and T_C is the critical temperature. It was possible to estimate the critical temperature for the alloys studied by fitting the experimental values of the interfacial tension with the power function.

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