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Temperature and Oxygen Partial Pressure Dependences of the Surface Tension of Liquid Sn–Ag and Sn–Cu Lead-free Solder Alloys

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Summary. Temperature dependence of the surface tension of liquid Sn–Ag and Sn–Cu base lead-free solder alloys and oxygen partial pressure dependence of liquid Sn–Ag alloy were evaluated using the experimental data obtained, respectively, by the constrained drop method and the sessile drop method in the previous studies [1, 2]. The temperature dependences of the surface tension have maximum positive values when the mol fraction of Ag and Cu is about 0.7, while those for pure liquid Sn, Ag, and Cu have negative values. The calculated values based on *Butler*'s equations were found to be in reasonable agreement with those of the experimental data. The oxygen partial pressure dependences of the surface tension of liquid Sn–Ag alloys at 1253 K have a minimum value when the mol fraction of Ag is about 0.9 and the oxygen partial pressure is less than about 10^{-13} atm. From this, it is considered that the oxygen adsorption increased by adding Ag to Sn when the mol fraction of Ag is less than 0.9.

Keywords. Constrained drop method; Oxidation; Sn–Ag alloys; Sn–Cu alloys; Surface; Thermodynamics.

Introduction

Surface tension of liquid solder alloys is considered as one of the critical physical properties of solder. The surface tension of liquid solder alloys may influence capillary flow for pin-through-hole soldering, self-alignment of surface mounted devices, the capability to keep devices from falling off during second reflow as well as the degree of wetting [3]. The shape of solder balls in flip chip bonding is also determined by the surface tension, so that with solder alloys having comparatively large natural radius of curvature, extra care is needed as the pitch between contacts decreases [3]. Formation of intermetallic compounds during interconnection between solder and under bump metallization is also affected by the surface tension [4].

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However, there are very few surface tension data available for liquid lead-free solders [1, 2, 5–7]. In addition, the surface tension of liquid lead-free solder alloys under actual processing condition is not known precisely, which may be affected by the oxidation of the flux and the soldering environments [3].

Recently, the authors have investigated surface tension of various lead-free solder alloys such as liquid Sn–Ag [1], Sn–Cu [1], In–Ag [8], and In–Cu [8] by the constrained drop method. In addition, the surface tension of liquid Sn–Ag–O alloys was investigated by the sessile drop method at 1253 K [2]. In this contribution, temperature and oxygen partial pressure dependences of the surface tension of liquid Sn–Ag and Sn–Cu base lead-free solder alloys were evaluated using the experimental data obtained in our previous studies [1, 2], and explained with thermodynamic models such as *Butler*'s model [9] and *Gibbs* adsorption model [10].

Methods

Evaluation of the Temperature Dependence of the Surface Tension

The surface tension of liquid Sn–Ag and Sn–Cu alloys has been calculated using *Butler*'s model with thermodynamic database. This method has been applied in the previous works, successfully [1, 2, 5, 8, 11–13]. Generally, the *Butler*'s equations for A–B binary alloys are given as follows (Eq. (1)) where σ is the surface tension of liquid alloy, σ_i is the surface tension of i, R is the universal gas constant, T is the temperature, N_i^s is the mol fraction of i in the surface, N_i^b is the mol fraction of i in the bulk, $\overline{G}_i^{ex,s}$ is the partial excess free energy of i in the surface, and $\overline{G}_i^{ex,b}$ is the partial excess free energy of i in the bulk.

$$\begin{aligned}\sigma &= \sigma_{\mathrm{A}} + \frac{RT}{S_{\mathrm{A}}}\ln\frac{N_{\mathrm{A}}^s}{N_{\mathrm{A}}^b} + \frac{1}{S_{\mathrm{A}}}\left(G_{\mathrm{A}}^{ex,s} - G_{\mathrm{A}}^{ex,b}\right)\\ &= \sigma_{\mathrm{B}} + \frac{RT}{S_{\mathrm{B}}}\ln\frac{N_{\mathrm{B}}^s}{N_{\mathrm{B}}^b} + \frac{1}{S_{\mathrm{B}}}\left(G_{\mathrm{B}}^{ex,s} - G_{\mathrm{B}}^{ex,b}\right) \qquad (1)\end{aligned}$$

The molar surface area of component i was assumed to be obtained by $S_i = 1.091 \cdot (6.02 \cdot 10^{23})^{1/3} \cdot V_i^{2/3}$ [11, 14, 15], where V_i is the molar volume of the element i. For liquid Sn–Ag and Sn–Cu alloys, the molar volume of each element is constant across the whole composition range, because the molar volume of the alloys is simply proportional to the mol fraction of the component metals as shown in Fig. 1 [16]. For the excess free energy in the surface, we derived the following equation for liquid metals and alloys based on the model proposed by *Yeum et al.* [17] (Eq. (2)).

$$\overline{G}_i^{es,s}(T, N_i^s) = 0.83 \cdot \overline{G}_i^{ex,b}(T, N_i^s) \qquad (2)$$

For the calculations of the surface tension of liquid Sn–Ag and Sn–Cu alloys, the optimized thermodynamic parameters [18, 19] and physical properties [20] in the literature and the surface tension of pure liquid metals obtained in the previous work [1] were used. Finally, the temperature dependence of the surface tension is calculated for each composition with changing the temperature at a fixed composition.

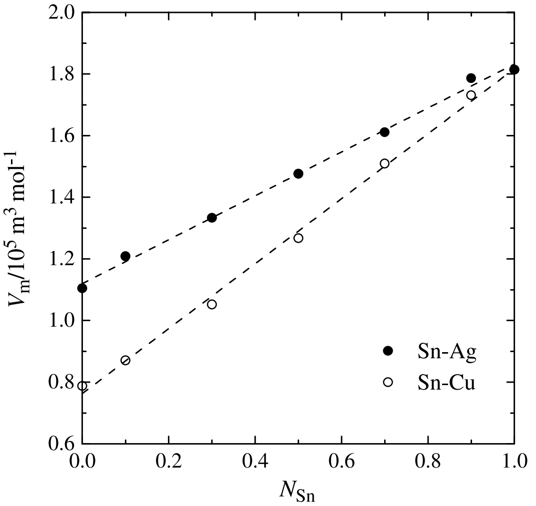

Fig. 1. Composition dependence of the molar volume of liquid Sn–Ag and Sn–Cu alloys at 1273 K

Evaluation of the Oxygen Adsorption

Generally, the oxygen adsorption (Γ_O) on liquid metals and alloys can be expressed by the *Gibbs* adsorption isotherms due to the surface active nature of oxygen in liquid metals and alloys (Eq. (3)), where σ is surface tension of liquid metal or alloy, a_O is oxygen activity in the metal or alloy, and p_{O_2} is oxygen partial pressure, respectively.

$$\Gamma_O = -\frac{1}{RT}\frac{d\sigma}{d\ln a_O} = -\frac{2}{RT}\frac{d\sigma}{d\ln p_{O_2}} \tag{3}$$

Hence, the oxygen adsorption behavior on the surface of liquid metals and alloys can be evaluated from the information of the surface tension dependence on the oxygen partial pressure. For example, when the surface of liquid metals and alloys is saturated with oxygen, $d\sigma/d\ln p_{O_2}$ has a constant value, which denotes the surface excess concentration of oxygen (oxygen adsorption) at saturation.

Results and Discussions

Temperature Dependence of the Surface Tension of Liquid Sn–Ag and Sn–Cu Alloys

In Fig. 2, the temperature dependence of the surface tension of liquid Sn–Ag alloys with concentrations of 0, 10, 30, 50, 70, 90, and 100 at% Ag measured by the constrained drop method is given as a function of the mol fraction of Ag (N_{Ag}) in the bulk (solid circles). The temperature dependence of the surface tension increases gradually with the mol fraction of Ag, when the mol fraction of Ag is less than 0.7. When $N_{Ag} = 0.7$, the temperature dependence reaches a peak, and then it drops dramatically as increasing the mol fraction of Ag. In this figure, the calculated values based on *Butler*'s model are also plotted with open squares. The calculated values were found to be in good agreement with those of the experimental data.

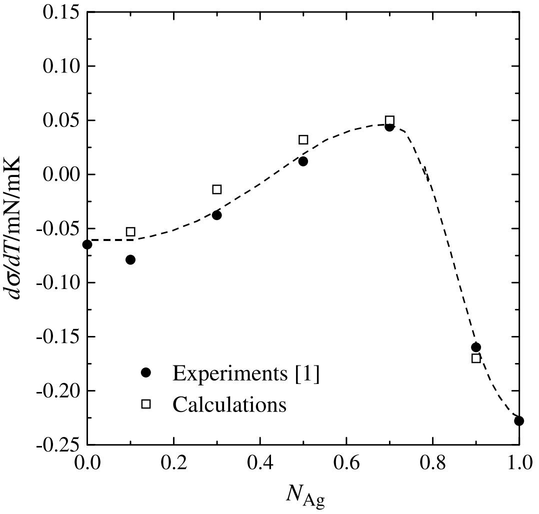

Fig. 2. Temperature dependence of the surface tension of liquid Sn–Ag alloys as a function of the mol fraction of Ag

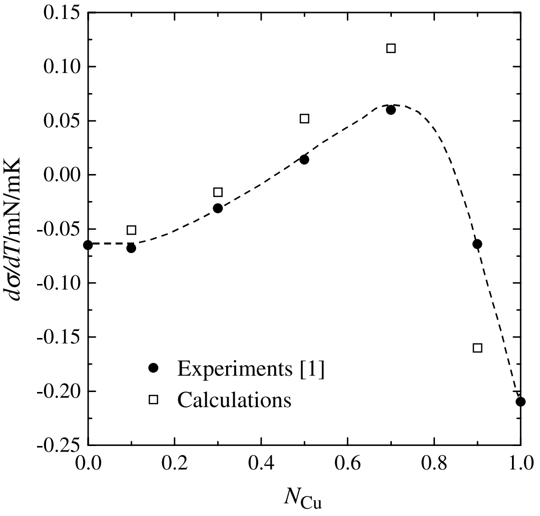

Fig. 3. Temperature dependence of the surface tension of liquid Sn–Cu alloys as a function of the mol fraction of Cu

Very similar results have been obtained from the experiments of the liquid Sn–Cu alloys [7]. In Fig. 3, the surface tension of liquid Sn–Cu alloys with concentrations of 0, 10, 30, 50, 70, 90, and 100 at% Cu is shown with respect to the mol fraction of Cu. The surface tension of liquid Sn-10 at% Cu alloys has almost the same values as pure liquid tin. When $N_{Cu} = 0.7$, the temperature dependence reaches a peak.

In the previous study, from a study on an imaginary A–B regular solution, the authors have found that, as the difference in the surface tension of component metals or the excess free energy increases, the temperature dependence of the surface tension ($d\sigma/dT$) increases in the high composition range of the component metal having higher surface tension due to the surface enhancement of the other component metal [1]. Since liquid Sn–Ag and Sn–Cu systems have negative excess free energies, the enhancement of surface concentration of Sn is considered due to the large difference in the surface tension of component metals (between Sn and Ag or Sn and Cu), yielding large (even positive) temperature dependence of the surface tension for several alloys.

Effect of Oxygen Partial Pressure on the Surface Tension of Liquid Sn–Ag Alloys

Figure 4 shows the dependence of oxygen partial pressure on the surface tension of pure Sn and Ag and Sn–Ag alloys with concentrations of 60, 70, 80, and, 90 at% Ag at 1253 K [2]. The dependence of the surface tension on the oxygen partial pressure can be evaluated from the value of $d\sigma/d\log p_{O_2}$ according to *Gibbs* adsorption isotherm. When the oxygen partial pressure is less than about 10^{-13} atm, the surface tension of liquid Ag shows almost constant values, suggesting that the oxygen adsorption is negligible. On the other hand, the dependence of surface tension on the oxygen partial pressure for other alloys containing silver less than 90 at% Ag shows negative values, yielding some amount of oxygen adsorption. It is very interesting that the value of $d\sigma/d\log p_{O_2}$ gradually decreases with the mol fraction of Ag in the bulk, yielding increase in the oxygen adsorption. It is believed that the change in the oxygen adsorption behavior may be caused by the surface structure. However, there is no appropriate model describing the oxygen adsorption on the surface of liquid alloys. Nevertheless, from the results in Fig. 4, it can be anticipated that the interaction between tin and oxygen is reinforced by addition of silver. Thus, the oxygen adsorption on the liquid Sn-90 at% Ag alloys is about three times of the pure liquid Sn. In such cases, strong oxygen adsorption may cause *Marangoni* flow during reflow, and then the solder sphere texture will not be smooth. Practical lead-free solder alloys contain only small amounts of silver.

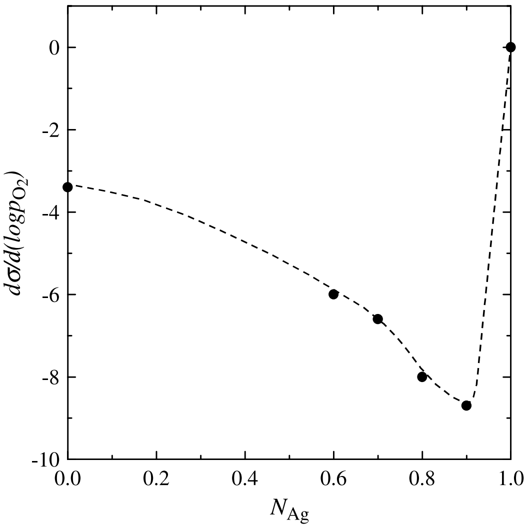

Fig. 4. The dependence of the surface tension of liquid Sn–Ag alloys at 1253 K on the oxygen partial pressure

From this, we may expect that the oxygen adsorption for liquid Sn–Ag base solder alloys for tin-rich side (generally less than 4.7% [3]) is almost the same as that of pure liquid tin, which can be confirmed in Fig. 4. Thus, if we know the surface tension of a tin-based solder alloy and the oxygen dependence of its surface tension, then we may estimate the surface tension of the alloy at a given atmosphere.

Experimental

Effect of oxygen on the surface tension of Sn–Ag alloys was investigated by using the sessile drop method [2]. The oxygen partial pressure was controlled with introducing a suitable mixture of purified Ar-10% H_2 and CO_2 gases, which was confirmed by using a zirconia oxygen sensor equipped with reference electrodes (Fe/FeO, Ni/NiO, and Cu/Cu_2O couples). Measurements were carried out after confirming the equilibrium state (Generally, it took about 60 min to establish an equilibrium state). The surface tension was determined by comparing the observed shape of a liquid drop on a solid alumina (sapphire) substrate using a CCD camera with that of the solution of the *Laplace* equation using a computer program.

Effect of temperature on the surface tension of Sn–Ag and Sn–Cu alloys was investigated by using the constrained drop method [1], which is superior to make a large axi-symmetric drop stable, yielding high accuracy in measurements. The apparatus and experimental techniques have been described in our previous contribution [21].

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