Effect of Oxygen on Surface Tension of Liquid Ag-Sn Alloys

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The effect of oxygen on the surface tension of liquid Ag-Sn alloys used as one of the main components in lead-free soldering alloys was measured by the sessile drop method. The surface tension of liquid Ag-Sn alloys decreased with increasing tin content. The effect of oxygen was investigated for oxygen partial pressure ranging from about $10^{-17}$ to $10^{-12}$ atm. The effect of oxygen on the surface tension of liquid Ag-Sn alloys is closer to pure tin rather than pure silver. Thermodynamic simulation using Butler’s equation showed that the surface of liquid Ag-Sn alloys is enriched with tin. Accordingly, the effect of oxygen adsorption on the surface tension of liquid Ag-Sn alloys was considered to be closer to that of tin than silver.

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1. Introduction

Since the surface tension of liquid solder alloy determines its wetting behavior, many researchers have investigated the surface tension of the lead-free soldering alloys (e.g. Ag-Sn after Moser et al.1)). Although oxygen in atmosphere is known to decrease the surface tension of liquid metals and alloys,2–10) studies on the effect of oxygen for lead-free solders have been only restricted to pure metals.8–10)

Generally, Gibbs adsorption isotherm (1) may express the oxygen adsorption ($\Gamma_0$) on liquid metals and alloys.11)

$$\Gamma_0 = -\frac{1}{R} \frac{d\sigma}{d\ln a_O} = -\frac{2}{RT} \frac{d\sigma}{d\ln p_O}$$

where $R$: universal gas constant, $T$: temperature, $\sigma$: surface tensions of liquid metal or alloy, $a_O$: oxygen activity in the metal or alloy and $p_O$: oxygen partial pressure, respectively. Hence, the information of the surface tension dependence on the oxygen partial pressure reflects the oxygen adsorption behavior in the surface of liquid metals and alloys. For example, if the surface of liquid metals and alloys is saturated with oxygen, $d\sigma/d\ln p_O$ have a constant slope, yielding the surface excess concentration of oxygen (oxygen adsorption) at saturation. The oxygen adsorption for pure metals has been investigated by many researchers. Table 1 summarizes some of the reported oxygen adsorption at saturation for pure metals after Bernard and Lupis.9) However, there is no research on the oxygen adsorption for lead-free solder alloys as far as the authors concern.

In the present work, the surface tension of liquid Ag-Sn alloys, one of the main components in lead-free solders, was measured by the sessile drop method with varying oxygen partial pressure in atmosphere. In order to investigate the surface tension in the whole composition range, the experimental temperature was determined as 1253 K. Then, the oxygen adsorption behavior on the surface of liquid Ag-Sn alloys was interpreted by the surface concentration calculated using thermodynamic database.

2. Experimental

The experimental apparatus used for the measurements of the surface tension of liquid Ag-Sn alloys consisted of an image capturing system with a He-Ne laser and a SiC heating element furnace. Figure 1 shows a schematic diagram of the experimental setup. A quartz reaction tube (5.5 cm O.D., 5.0 cm I.D., 20.0 cm high) with investigation windows from a horizontal direction was used. The tube was sealed by means of O-rings fitted onto copper water-cooled jackets at the ends of the tube. High purity samples (Ag: 99.99+% and Sn: 99.999+% installed in an alumina crucible with a hole

Fig. 1 Schematic diagram of experimental apparatus for the sessile drop measurements of surface tension.

### Table 1 Saturation parameters of oxygen at the surface of pure liquid metals.5)

<table>
<thead>
<tr>
<th>System</th>
<th>Temp, $T$/K</th>
<th>Maximum surface excess concentration, $\Gamma_{O\text{sat}}$/$10^{-6}$ mol·m$^{-2}$</th>
<th>Area per adsorbed atom, $S$/10$^{-2}$ nm$^2$</th>
<th>experiment</th>
<th>calculation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>1253</td>
<td>5</td>
<td>33</td>
<td>23$^+$</td>
<td>38$^+$</td>
</tr>
<tr>
<td>Cu</td>
<td>1423</td>
<td>9.3</td>
<td>17.8</td>
<td>18$^+$</td>
<td>30$^+$</td>
</tr>
<tr>
<td>Fe</td>
<td>1823</td>
<td>18.1–23.4</td>
<td>7.1–9.2</td>
<td>8$^+$</td>
<td></td>
</tr>
</tbody>
</table>

*$^{(00) face and ^{(111) face of the solid compound
The temperature was measured with a Pt/Pt-13%Rh thermocouple, which was set directly under the substrate. After the sample was placed in the furnace, the quartz tube was evacuated with a mechanical pump producing a vacuum of 1 Pa and filled with high-purity Ar-10%H₂ gas mixture. This procedure was repeated for three times to eliminate residual oxygen in the reaction tube. Then, the furnace was programmed for the heating cycle up to 1253 K in 3 h. When temperature in the furnace was stabilized, the sample alloys in the alumina crucible were dropped onto the alumina substrate using an alumina rod. During experiments, the oxygen partial pressure was controlled with introducing a suitable mixture of purified Ar-10%H₂ and CO₂ gases. In order to confirm the oxygen potential in the gas, zirconia oxygen sensor equipped with reference electrodes (Fe/FeO, Ni/NiO and Cu/CuO couples) was placed in the furnace. A schematic illustration of the oxygen sensor is shown in Fig. 2. Here, the “surface” is defined as outermost monolayer. The potential of reference electrodes was determined using reported values from the electromotive force (E) expressed by eq. (2) one can obtain the oxygen potential in the atmosphere (\(p_{O_2}\)).

\[
E = \frac{RT}{4F} \ln \left( \frac{p_{O_2}}{p_{O_2}^0} \right)
\]  

where \(F\): Faraday’s constant, \(p_{O_2}^0\): the oxygen potential in the reference electrode. Here, the oxygen potential in the reference electrodes was determined using reported values below. \(^{12}\) (\(p_{O_2}^0\) = exp(\(\Delta G^\circ/RT\))

\[
\begin{align*}
\text{Fe} + 1/2 \text{O}_2 &= \text{FeO} \quad \Delta G^\circ = -263.4 + 64.81T \ (\text{kJ}) \\
\text{Ni} + 1/2 \text{O}_2 &= \text{NiO} \quad \Delta G^\circ = -233.6 + 83.94 \ (\text{kJ}) \\
2\text{Cu} + 1/2 \text{O}_2 &= \text{Cu}_2 \text{O} \quad \Delta G^\circ = -166.9 + 71.13 \ (\text{kJ})
\end{align*}
\]

Preliminary experiments showed that the equilibrium oxygen potential was obtained in 60 min in the present experimental condition. Surface tension measurements, therefore, were conducted after 150 min to confirm the oxygen partial pressure. In order to capture a clear drop shadow image, a He-Ne laser (\(\lambda = 632.8 \ \text{nm}\)) was used. The drop shadow profile was taken using a CCD camera (512 × 512 pixels) fitted with an optical zoom lens and filters, where a pixel corresponds to 18.7166 μm with the CCD camera. The threshold shape of the drop was determined using image analysis software. Then, this drop profile was used to determine the surface tension by comparing the observed shape with that of the solution to the Laplace equation using a computer program developed by Krylov et al.\(^{13}\)

3. Results and Discussion

3.1 Surface tension of liquid Ag-Sn alloys

Initially the method was applied to liquid Ag-Sn alloys in Ar-10%H₂ atmosphere. In Fig. 3, the experimental results are plotted as a function of concentration of tin in the bulk phase. For comparison, the surface tension of pure silver and tin measured by Bernard and Lupis\(^{9}\) (1253 K), and Taimatsu and Sangiorgi\(^{10}\) (1273 K) are also plotted. In addition, the experimental results for alloys were compared with the calculated results based on Butler’s eq. (6) using thermodynamic database.

\[
\sigma = \sigma_{\text{Ag}} + \frac{RT}{S_{\text{Ag}}} \ln \left( \frac{1 - N_{\text{Ag}}^S}{1 - N_{\text{Ag}}^B} \right) + \frac{1}{S_{\text{Ag}}} G_{\text{Ag}}^{\text{ex,S}} (T, N_{\text{Ag}}^S) - G_{\text{Ag}}^{\text{ex,B}} (T, N_{\text{Ag}}^B) \]

\[
\text{where } R: \text{universal gas constant, } T: \text{temperature, } \sigma_{\text{Sn}}, \sigma_{\text{Ag}}: \text{surface tensions of pure liquid tin and silver, respectively, } S_{\text{Sn}}, S_{\text{Ag}}: \text{molar surface areas of pure liquid tin and silver, } N_{\text{Ag}}^S: \text{mole fraction of silver in the surface (} N_{\text{Ag}}^S = 1 - N_{\text{Ag}}^B), \]

N_{\text{Ag}}^B: mole fraction of silver in the bulk (\(N_{\text{Ag}}^B = 1 - N_{\text{Ag}}^S\)), \(G_{\text{i}}^{\text{ex,S}} (T, N_{\text{i}}^S)\): partial excess Gibbs energy of i in the surface as a function of T and \(N_{\text{i}}^S\), \(G_{\text{i}}^{\text{ex,B}} (T, N_{\text{i}}^B)\): partial excess Gibbs energy of i in the bulk as a function of T and \(N_{\text{i}}^B\).
energy of \( i \) in the bulk as a function of \( T \) and \( N_i^B \). The molar surface area of component \( i \) can be obtained by eq. (7).15,16

\[
S_i = 1.091 \cdot (6.02 \cdot 10^{23})^{1/3} \cdot V_i^{2/3}
\]

(7)

where \( V_i \) is molar volume of the element \( i \), \( G_i^{Ex,B}(T, N_i^B) \) can be obtained directly from thermodynamic database, and \( G_i^{Ex,S}(T, N_i^S) \) is obtained using eq. (8) assuming that the partial excess Gibbs energy in the bulk and the surface have the same concentration dependence.

\[
G_i^{Ex,S}(T, N_i^S) = 0.83 \cdot G_i^{Ex,B}(T, N_i^B) \quad \text{Jmol}^{-1}
\]

(8)

The thermophysical data and excess Gibbs energy used in the present calculation are listed in Table 2.14,17,18 This method has already been applied to various alloy and slag systems by the authors with success.15,16,19-27 As shown in Fig. 3, the agreement between calculations (solid line) and measurements (solid circles) in the present work is also reasonable. Accordingly, the surface tension of liquid Ag-Sn alloys at different temperatures could be obtained by the above calculation method.

The thermodynamic calculations using eq. (6) also suggest us information on the surface concentration of tin as shown in Fig. 4. Even though the actual surface concentration of tin would not be exactly the same plotted in Fig. 4 due to the simple assumption of the surface by a monolayer, it may be acceptable that tin preferentially adsorbs on the surface of liquid Ag-Sn alloys. In Fig. 4, the surface concentration at 493 K (the eutectic temperature of Sn-3.8%Ag solder alloy14) is also plotted for comparison. The surface concentration of tin dramatically increased with decreasing temperature from

3.2 Surface tension of liquid Ag-Sn-O alloys

3.2.1 Thermodynamics of Ag-Sn-O system

In order to understand oxygen behavior on the surface of Ag-Sn alloys, it is necessary to calculate the thermodynamic limits for experiments (no oxides formation). In liquid Ag-Sn alloys, SnO2 is preferentially formed by the reaction (9).

\[
\text{Sn(l)} + \text{O}_2(\text{g}) = \text{SnO}_2(\text{s})
\]

(9)

where the equilibrium constant of eq. (9) is expressed as eq. (10).

\[
K = \frac{1}{a_{\text{Sn}} \times p_{\text{O}_2}} = 2.415 \cdot 10^{13} \quad \text{(at 1253 K)}^{28}
\]

(10)

Using the reported thermodynamic data for the activity of tin in the alloys,29 the maximum limit of oxygen partial pressure to prohibit the formation of SnO2 is calculated. In Table 3, the calculated results of thermodynamic limits for experiments are shown.

3.2.2 Effect of oxygen on surface tension of liquid Ag-Sn alloys

Figure 5 shows the measured surface tensions for pure silver and tin and Ag-5, 10, 20, 30, 40%Sn alloys as a function of logarithm of the oxygen partial pressure. The dependence of the surface tension for liquid Ag-Sn alloys on the oxygen potential (the slope of \( d\sigma/d\ln p_{O_2} \) in Fig. 5) was found different from those for pure tin or silver. Nevertheless, it is noteworthy that the oxygen potential dependence on the surface tension of liquid Ag-Sn alloys was much closer to pure tin even for the samples containing 10% tin.

As described previously, when \( d\sigma/d\ln p_{O_2} \) has a constant slope, we can determine the oxygen adsorption at saturation in the surface. Table 4 shows the maximum surface excess concentration of oxygen and the minimum area occupied by single oxygen atom at saturation on the liquid metals and alloys. Here, the minimum area (5) occupied by an oxygen atom was calculated from eq. (11).

\[
S = 1/(N_A G_{O,\text{sat}})
\]

(11)
Table 4 The maximum surface excess concentration of oxygen and the minimum area occupied by single oxygen atom on liquid Ag-Sn alloys.

<table>
<thead>
<tr>
<th>Composition, at%</th>
<th>Maximum surface excess concentration, $\Gamma_{O,sat}$, $10^{-2}$ mol m$^{-2}$</th>
<th>Area per adsorbed atom, $S_{2}/10^{-2}$ nm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag</td>
<td>46.7</td>
<td>36.0</td>
</tr>
<tr>
<td>Ag-10%Sn</td>
<td>9.24</td>
<td>180</td>
</tr>
<tr>
<td>Ag-20%Sn</td>
<td>8.49</td>
<td>196</td>
</tr>
<tr>
<td>Ag-30%Sn</td>
<td>7.01</td>
<td>237</td>
</tr>
<tr>
<td>Ag-40%Sn</td>
<td>6.37</td>
<td>261</td>
</tr>
<tr>
<td>Sn</td>
<td>3.61</td>
<td>460</td>
</tr>
</tbody>
</table>

where $N_A$ and $\Gamma_{O,sat}$ denote Avogadro number and the maximum surface excess concentration of oxygen at saturation, respectively. Even though the present results for pure metals slightly differ from those after previous researchers, the tendency of the variation with metals is acceptable, i.e., oxygen adsorption for pure silver was relatively higher than those for pure tin and Ag-Sn alloys. Thereafter, the minimum area occupied by single oxygen atom at saturation for pure silver (0.36 nm$^2$) has much smaller value than those for pure tin (4.60 nm$^2$) and Ag-Sn alloys (1.80~2.61 nm$^2$). Since tin preferentially adsorbs on the surface of liquid Ag-Sn alloys as predicted in Fig. 4, the oxygen adsorption on liquid Ag-Sn alloys is considered closer to that of tin rather than silver. Many researchers have shown that the minimum area occupied by single oxygen atom at saturation on the surface of metal M is close to those for oxide compound M$_2$O (2,9,26,27,30,31). If we assume Ag$_2$O structure is formed on the surface of liquid silver as suggested by Bernard and Lupis, the minimum areas occupied by single oxygen atom on (100) and (111) faces, respectively, are 0.32 and 0.38 nm$^2$, which are very close to the present result (0.36 nm$^2$). On the other hand, the minimum area occupied by single oxygen atom in the surface of pure tin and Ag-Sn alloys are much larger than that of pure silver. As shown in Table 4, the minimum area occupied by single oxygen atom at saturation on the surface of metal M is close to those for oxide compound M$_2$O at about the melting temperature of the metals. Taimatsu et al. and Yuan et al. reported that the dependence of oxygen partial pressure on the surface tension of pure tin increased with lowering temperature. Hence, we may consider that on the surface of liquid Ag-Sn alloys segregated with tin, oxygen adsorption would decrease with increasing temperature. Probably, the reason for the increase in the minimum area occupied by single oxygen atom in the surface of pure tin and Ag-Sn alloys is that the experimental temperature of the present work is much higher than the melting temperature of pure tin. In addition, we may expect that the oxygen adsorption on the surface of liquid Ag-Sn alloys at much lower temperature (for example, eutectic temperature of Sn-3.8%Ag alloy, 493 K as shown in Fig. 4) would be close to that of pure tin rather than pure silver, because the surface segregation of tin increases with decreasing temperature as shown in Fig. 4. Consequently, the effect of the oxygen on the surface tension of Sn-Ag based soldering alloy, of which silver content is not so much, is estimated to be almost the same as that for pure tin reported by Yuan et al. near the liquidus temperature.

4. Conclusions

In the present work, the effect of oxygen on the surface tension of liquid Ag-Sn alloys at 1253 K was investigated using the sessile drop method. The followings are the major conclusions of the present work.

1. The surface tension of liquid Ag-Sn alloys decreased with increasing the concentration of tin, and the experimental results were reasonably accord with the calculated results using Butler’s equations.

2. The dependence of the surface tension for liquid Ag-Sn alloys on the oxygen potential was found different from those for pure tin or silver. The oxygen potential dependence for liquid Ag-Sn alloys was much closer to pure tin even for the samples containing 10% tin.

REFERENCES

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