Thermodynamic Properties of Liquid Sn-Bi-Sb Alloys

Iwao Katayama, Dragana Živković, Dragan Manasijević, Toshihiro Tanaka, Zivan Živković, and Hiromi Yamashita

(Received October 13, 2004; Accepted November 11, 2004)

Activity of tin in liquid Sn-Bi-Sb was derived by EMF measurement of galvanic cell with fused salt electrolyte in the temperature range of 700 to 1000 K in the whole composition range. Activity of tin at 900 K shows very small positive deviation from Raoult's law for Sn-Bi alloys and moderately negative deviation for Sn-Sb alloys. Activity of ternary alloys along Sn-Bi-Sb, Sn-Sb (γ = 0.25, 0.50 and 0.75) shows negative deviation and the deviation becomes large with increasing Sb content. Excess free energy of mixing is derived using Darken's method for Gibbs-Duhem equation and the values are compared with those by model calculations based on the three constitutive binary data.

1. INTRODUCTION

Low melting alloys such as tin-lead alloys are widely used as solder materials. Development of the lead-free solders has been tried because of the health concerns and environmental reasons. Thermodynamic properties of these alloy systems are closely related to the surface tension which is one of the important properties in the development of the solders.

The purpose of this study is to determine the activity of tin in liquid Sn-Bi-Sb alloys and in the two border systems (Sn-Bi and Sn-Sb) as one of the candidates for lead-free solder materials by fused salt EMF method and compare the results derived from the measurements with the model calculations based on the constitutive three binary data.

The Sn-Bi phase diagram is of simple eutectic type and activity of Sn in liquid Sn-Bi alloys was assessed in 1996 by Lee et al. Activity of Sn shows slightly positive deviation from Raoult's law and its temperature dependence is also very small. The activities measured by various authors were in accordance with one another. Joensson and Agren assessed thermodynamic properties of Sn-Sb systems. Activity of Sn in liquid Sn-Sb alloys deviates positively from Raoult's law and Vassiliev et al. confirmed the activity values. For these two binary systems references are shown in our previous paper.

There seem no experimental data on thermodynamic activity of Sn-Bi-Sb liquid alloys.

2. EXPERIMENTAL

As the experimental equipment, experimental procedure and some experimental results are already shown in our previous paper, only the outline is described here.

The cell with fused salt is represented as follows:

\[
\begin{align*}
\text{(-Sn-Ge)} & \underline{\text{Sn}^+} \underline{\text{KCl-LiCl}} \underline{\text{Sn-Sb-Alloy}}^{+} \\
\end{align*}
\]

Activity of tin (Sn) in the Sn alloys is calculated from the EMF (E/mV) of the cell from eq.1.

\[
\Delta G_{Sn} = RT \ln \alpha_{Sn} = -2E 
\]

where \(\Delta G_{Sn}\) is partial molar free energies of mixing of tin, \(R\) is gas constant, \(T\) is temperature and \(F\) is Faraday constant. Cell temperature was controlled at desired temperature within ±1.0 K. Under the argon atmosphere the cell temperature was raised to about 900 K and held at the temperature for equilibration. After the
equilibrium EMF was measured, the cell temperature was increased or decreased to the new temperature in about 30 min and held constant. EMF of the cell was measured at every ten min.

3. EXPERIMENTAL RESULTS

At each alloy composition of the alloys linear relations between $E$ and $T$ are obtained. The results are shown in Table 1 with the thermodynamic properties derived by well known eqs. (1), (2) and (3) at 900 K.

$$
\Delta G^{\text{mix}} = \Delta G^{\text{mix}}_{\text{ideal}} + \Delta G^{\text{mix}}_{\text{interaction}} = RT \ln \gamma
$$

(2)

Table 1 Temperature dependence of EMF of cell: SnSb$_2$|(LiCl-KCl)Eq-Sn-Alloys, and thermodynamic of the alloys at 900 K.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>800 K</th>
<th>900 K</th>
<th>1000 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$E_{\text{SnSb$_2$}}$</td>
<td>0.210</td>
<td>0.229</td>
<td>0.251</td>
</tr>
<tr>
<td>$E_{\text{SnBi}}$</td>
<td>0.330</td>
<td>0.342</td>
<td>0.356</td>
</tr>
<tr>
<td>$E_{\text{SnSb}}$</td>
<td>0.135</td>
<td>0.145</td>
<td>0.150</td>
</tr>
<tr>
<td>$E_{\text{SbBi}}$</td>
<td>0.135</td>
<td>0.145</td>
<td>0.150</td>
</tr>
<tr>
<td>$E_{\text{SnSb$_2$}}$</td>
<td>0.135</td>
<td>0.145</td>
<td>0.150</td>
</tr>
</tbody>
</table>

Thermodynamic Properties of Liquid Sn-Sn-Sb Alloys

Table 2 Interaction parameters and its temperature dependence.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>300 K</th>
<th>500 K</th>
<th>900 K</th>
<th>$\gamma \cdot \Delta H/K$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{\text{SnSb$_2$}}$</td>
<td>0.210</td>
<td>0.229</td>
<td>0.251</td>
<td>0.217</td>
</tr>
<tr>
<td>$B_{\text{SnSb$_2$}}$</td>
<td>0.330</td>
<td>0.342</td>
<td>0.356</td>
<td>0.342</td>
</tr>
<tr>
<td>$C_{\text{SnSb$_2$}}$</td>
<td>0.135</td>
<td>0.145</td>
<td>0.150</td>
<td>0.145</td>
</tr>
<tr>
<td>$D_{\text{SnSb$_2$}}$</td>
<td>0.135</td>
<td>0.145</td>
<td>0.150</td>
<td>0.145</td>
</tr>
<tr>
<td>$E_{\text{SnSb$_2$}}$</td>
<td>0.135</td>
<td>0.145</td>
<td>0.150</td>
<td>0.145</td>
</tr>
</tbody>
</table>

where $\Delta G^{\text{Gibbs}}$ is the Gibbs free energy of mixing for ideal solution, $\gamma$ is activity coefficient ($\propto a_{\text{SnSb$_2$}}$).

For liquid Sn-Sb and Sn-Sb-Bi systems, excess free energies of mixing $\Delta G^{\text{Ex}}$ in this study are presented in the quasi regular solution equations as follows:

$$
\Delta G^{{\text{Ex}}} = x_i x_j (A_{i-j} x_i + B_{i-j} x_j)
$$

(4)

$$
\Delta G^{{\text{Ex}}} = x_i^2 (2A_{i-j} (1-x_i) - x_i B_{i-j})
$$

(5)

$$
\Delta G^{{\text{Ex}}} = x_i (1-x_i)^2 (A_{i-j} (1-2 x_i) + B_{i-j} x_i)
$$

(6)

where $x_i$ and $x_j$ are mole fraction of component $j$ and $i$, respectively and $A_{i-j}$ and $B_{i-j}$ are interaction parameters between $i-j$. They are determined by fitting the excess free energy of mixing, which is obtained from the activity measurement and the data for each binary alloy based on the Gibbs-Duhem relation. For Sn-Sb binary alloys, the extrapolated value of the ternary data to $x_{\text{SnSb$_2$}} = 0$ is used. They are shown in Table 2.

Excess free energy of mixing for ternary alloys can be obtained by Kohler’s method in which the data of related three binary systems are used. In this study Kohler’s treatment is extended by adding the interaction in the ternary system as follows:

$$
\Delta G^{{\text{Ex}}} = x_i x_j (A_{i-j} x_i + B_{i-j} x_j)
$$

(4)

$$
\Delta G^{{\text{Ex}}} = x_i^2 (2A_{i-j} (1-x_i) - x_i B_{i-j})
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$$

(6)

where $x_i$ and $x_j$ are mole fraction of component $j$ and $i$, respectively and $A_{i-j}$ and $B_{i-j}$ are interaction parameters between $i-j$. They are determined by fitting the excess free energy of mixing, which is obtained from the activity measurement and the data for each binary alloy based on the Gibbs-Duhem relation. For Sn-Sb binary alloys, the extrapolated value of the ternary data to $x_{\text{SnSb$_2$}} = 0$ is used. They are shown in Table 2.

Excess free energy of mixing for ternary alloys can be obtained by Kohler’s method in which the data of related three binary systems are used. In this study Kohler’s treatment is extended by adding the interaction in the ternary system as follows:
excess free energy of mixing at any composition and temperature in the ternary system.

4. Model calculation from binary systems

There are several traditional models to represent the ternary thermodynamic properties based on three corresponding binary systems, which are classified into two categories according to Hillert: symmetrical model (Kohler, Muggiana) and asymmetrical model (Toop, Hillert). Chou provided a general solution model which breaks down the boundary between symmetrical and asymmetrical models. These models are applied to Ga-Sb-Bi liquid alloys by one of our groups.

At first, we use the literature values of constituent three binary data to get the values in ternary alloys by model calculations. For binary systems excess free energy of mixing is calculated in the Redlich-Kister polynomial form (eq.8) by data fitting.

\[
\Delta G^{\text{Ex}}_{ij} = \sum_{i,j} (a_{ij} + b_{ij} x_i c_{ij} x_j) T^{\nu_{ij}}
\]

The coefficients are shown in Table 3. From these data we can get the excess free energy of mixing in the ternary alloys from model calculations. The results at 900 K are shown in Figs.2(a)-2(c) for Sb-Bi-Sn (a:b = 0.25:0.75, 0.50:0.50 and 0.75:0.25) for the model calculations of Chou, Toop and Muggiana. Each model calculation gives little difference in the value of \(\Delta G^{\text{Ex}}\), but they can reproduce our experimental values only along the line of Sb0.25 Bi 0.75 -Sn system.

Next, we use our experimental data for Bi-Sn and Sb-Sn systems and the same data for Bi-Sb system as shown in Table 4. Then, we get the results shown in Figs.3(a)-3(c). Only Chou's model calculation is shown. In this case The discrepancy in the values between model calculation and experiment becomes bigger in Sb0.25 Bi 0.75 -Sn system, but in the other two systems model calculations can reproduce the experimental data with little uncertainty limits.

5. CONCLUSION

Activities of tin in liquid Sn-Bi, Sn-Sn and Sn-Bi-Sb alloys were derived by emf measurement of galvanic cell with fused salts electrolyte in the temperature range of 700 to 1000 K in the whole composition range. Activity of tin at 900 K shows very small positive deviation.

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Table 3: Coefficients of Redlich-Kister polynomial form of three binary systems at 900 K.

<table>
<thead>
<tr>
<th>System</th>
<th>(i,j)</th>
<th>(L_0)</th>
<th>(L_1)</th>
<th>(L_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb-Sn</td>
<td>(12)</td>
<td>7233.2</td>
<td>782.6</td>
<td>1840.9</td>
</tr>
<tr>
<td>Bi-Sn</td>
<td>(13)</td>
<td>1359.4</td>
<td>241.5</td>
<td>0</td>
</tr>
<tr>
<td>Bi-Sb</td>
<td>(13)</td>
<td>2284</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

\[
\Delta G_{ij}^{\text{Ex}} = \frac{x_i x_k}{x_i + x_k} (A_{ij}, x_i + B_{ij}, -x_k) + \frac{x_i x_j}{x_k + x_j} (A_{jk}, x_j + B_{jk}, -x_i) + \frac{x_j x_k}{x_i + x_j} (A_{ki}, x_i + B_{ki}, -x_k) + x_i x_j x_k (w_{ij} x_i + w_{jk} x_j + w_{ki} x_k)
\]

where \((i,j,k) = (\text{Sn}, \text{Bi}, \text{Sb})\).
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from Raoult's law for Sn-Bi alloys and moderately negative deviation for Sn-Sb alloys. Activity of ternary alloys with the composition ratios of Sb/Bi = 1/3, 1/1 and 3/1 shows negative deviation and the deviation becomes larger with Sb content. Excess free energy of mixing is derived using Darken's method for Gibbs-Duhem equation and interaction parameters in the ternary alloys are obtained.

The experimental values in the excess free energy of mixing were compared with the model calculations based on the constituent three binary data at 900 K.

Table 4 Coefficients of Redlich-Kister polynomial form (this work at 900 K).

<table>
<thead>
<tr>
<th>System</th>
<th>$L^{0}_{ij}$</th>
<th>$L^{1}_{ij}$</th>
<th>$L^{2}_{ij}$</th>
<th>$L^{3}_{ij}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn-Sb</td>
<td>-6454.1</td>
<td>235.1809</td>
<td>753.1789</td>
<td>757.3503</td>
</tr>
<tr>
<td>Sn-Bi</td>
<td>1647.773</td>
<td>305.011</td>
<td>184.4522</td>
<td>56.97726</td>
</tr>
<tr>
<td>Sb-Bi</td>
<td>2284</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Fig.3 Model calculation of the excess free energy of mixing in the ternary alloys at 900 K by using present data. (a) Sb$_{0.25}$B$_{0.75}$-Sn. (b) Sb$_{0.50}$B$_{0.50}$-Sn. (c) Sb$_{0.75}$B$_{0.25}$-Sn.

Fig.2 Model calculation of excess free energy of mixing in the ternary alloys at 900 K by using reference data. (a) Sb$_{0.25}$B$_{0.75}$-Sn. (b) Sb$_{0.50}$B$_{0.50}$-Sn. (c) Sb$_{0.75}$B$_{0.25}$-Sn.

REFERENCES

1) For example, T. Tanaka, and T. Iida, Steel Research 1, 21 (1994); T. Tanaka, K. Hack, T. Iida, and S. Hara,