Thermodynamic Study of Phase Equilibria in the Sn-Ag-Bi-Zn Quaternary System

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The phase equilibria in the Sn-Ag-Bi-Zn quaternary system have been studied experimentally and using thermodynamic calculations. The determined values of the thermodynamic parameters of the Sn-Ag-Zn and Sn-Ag-Bi systems were applied in the calculation of the phase diagrams. Thermodynamic evaluation of the Sn-Bi-Zn and Ag-Bi-Zn systems was performed by considering a two-phase separation of the liquid phase. The phase boundaries in some vertical sections of the quaternary system were determined using differential scanning calorimetry to confirm the calculated results. The calculation of the phase diagrams when 10\%Bi was added to Sn-Ag-Zn alloy shows that the regions of the primary crystals in the quaternary system did not show a large discrepancy from the Sn-Ag-Zn ternary system. The eutectic temperature decreased to about 203.7°C on addition of Bi to Sn-Ag-Zn alloy. The rate of change was estimated to be 1°C per 1% Bi added. The solidification structure was investigated using scanning electron microscopy and energy dispersive X-ray microanalysis. The microstructure was composed of an Sn-Bi-based eutectic, Ag\textsubscript{2}Zn, Ag\textsubscript{5}Sn, and coarsened Bi of about 30\,\mu m. Based on these results, a non-equilibrium solidification process using the Scheil model was simulated and compared with the observed structures. Our calculations reasonably explain Bi-enrichment in the final solidification zone.

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\textbf{Keywords:} phase diagram, thermodynamic analysis, liquidus surface, lead-free solder, alloy design

1. Introduction

Pb-Sn eutectic alloy is widely used as a solder in high density mounting of electronic devices. The wettability and the connectivity of this alloy are excellent and the melting point is low, and thus, any thermal effects on the electronic devices from this material are confined to a small area. However, the toxicity of the lead in this alloy is well known to the public. In particular, lead leaching into underground water from scrapped electronic devices can lead to significant harmful effects on humans and the environment. The development of lead-free solder materials is, therefore, of high importance in the electronics industry.

Sn-Ag-Cu alloy has been used as a Pb-free solder, but has a melting point of 218°C, which is considerably higher than the 183°C of conventional Pb-Sn eutectic alloy. Because of this, problems will arise with workability during the reflow process if the heat resistivity of the electronic devices does not change correspondingly. Zinc is an important additive to solder alloys, because their melting point is lowered by Zn alloying, although the wettability deteriorates and oxidation is accelerated by the addition of Zn. The eutectic temperature of Sn-Ag-Zn alloy is still higher than conventional Pb-Sn alloy.\textsuperscript{1)} For the practical use of this alloy, it is necessary to add a low-melting-point metal, such as Bi. However, information on the phase equilibria of these systems is lacking, and this makes the design of an efficient alloy for practical materials very difficult. Therefore, we have carried out work to determine the phase equilibria of the Sn-Ag-Bi-Zn quaternary system using the Calculation of Phase Diagrams (CALPHAD) approach.

2. Experimental Procedures

2.1 Measurement of phase boundaries by DSC

The phase boundaries of the quaternary system were measured using differential scanning calorimetry (DSC) in the two sections with 5 mass\%Bi and 15 mass\%Bi, keeping the total quantity of Bi and Ag to around 90 mass\%. The alloys for the DSC measurements were prepared from Sn (99.999\%), Ag (99.99\%), Bi (99.99\%), and Zn (99.99\%). The alloys were prepared by enclosing each of the pure metals mixed to the desired alloy composition in a silica tube, and then homogenizing the metals at a temperature of about 400°C. After quenching the specimens in iced brine, thermal analysis was carried out using a Netzsch DSC-404 differential scanning calorimeter. Alumina was used as a standard material, and the measurements were performed under an Ar atmosphere. The sample heating and cooling rates were set to 3°C/min. The experimental results are shown in Table 1. The peak temperatures in both the heating and cooling processes are also shown in Table 1.

2.2 Analysis of the solidified structures

The solidified solder alloys obtained by cooling in air were observed using a scanning electron microscope. An Sn-1.6 mass\%Ag-8.6 mass\%Bi-1.2 mass\%Zn alloy was prepared from the pure metals, as described in Section 2.1. The alloy was prepared by enclosing the pure metals in the target composition in a silica tube, heated to 400°C, and maintaining the temperature for 3600 s. After homogenization, the specimen was removed from the furnace, and allowed to slowly cool in air. The specimen was etched using dilute hydrochloric acid solution, and the microstructure was observed using an optical microscope and a Hitachi S-4300 scanning electron microscope (SEM). The compositions of

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2.3 Thermodynamic models and evaluation of parameters

2.3.1 Description of Gibbs energy

The liquid phase (L), Ag-rich fcc phase ((Ag)), Bi-rich rhombohedral phase ((Bi)), Sn-rich diamond and bct phases ((α, β Sn)), Zn-rich hcp phase ((Zn)), disorder hcp phase (ξ Ag), Ag-Zn-based bcc disordered phase (β), Ag-Zn-based hcp ordered phase (ζ), and Ag-Zn-based hcp phase (ε) were described using a conventional regular solution model as follows

\[ G_m^\phi = x_{Ag}G_{Ag}^\phi + x_{Bi}G_{Bi}^\phi + x_{Sn}G_{Sn}^\phi + x_{Zn}G_{Zn}^\phi + \frac{RT}{x_{Ag}} \ln(x_{Ag} + x_{Bi} \ln(x_{Bi} + x_{Sn} \ln(x_{Sn} + x_{Zn} \ln(x_{Zn})) \right. \\
+ x_{Ag}x_{Bi}L_{Ag,Bi}^\phi + x_{Ag}x_{Sn}L_{Ag,Sn}^\phi + x_{Bi}x_{Sn}L_{Bi,Sn}^\phi \\
+ x_{Ag}x_{Zn}L_{Ag,Zn}^\phi + x_{Bi}x_{Zn}L_{Bi,Zn}^\phi + x_{Sn}x_{Zn}L_{Sn,Zn}^\phi \\
+ x_{Ag}x_{Bi}x_{Sn}L_{Ag,Bi,Sn}^\phi + x_{Ag}x_{Bi}x_{Zn}L_{Ag,Bi,Zn}^\phi \\
+ x_{Ag}x_{Sn}x_{Zn}L_{Ag,Sn,Zn}^\phi + x_{Bi}x_{Sn}x_{Zn}L_{Bi,Sn,Zn}^\phi \]

where \( G_m^\phi \) denotes the Gibbs energy of element \( i \) in the \( \phi \) phase. This parameter is called the lattice stability parameter, and is described by the following equation:\(^\text{2)}\)

\[ G_m^\phi - G_m^{ref} = A + BT + CT \ln T + DT^2 + ET^3 \]

\[ + FT^7 + IT^{-1} + JT^{-9} \]

(\( \dagger \): heating)

Table 1: Experimental results for phase field boundaries of quaternary alloys determined by DSC on heating.

<table>
<thead>
<tr>
<th>Alloy compositions (mass%)</th>
<th>Peak temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>Sn</td>
<td>Bi</td>
</tr>
<tr>
<td>75.8</td>
<td>13.9</td>
</tr>
<tr>
<td>74.1</td>
<td>14.1</td>
</tr>
<tr>
<td>74.5</td>
<td>17.6</td>
</tr>
<tr>
<td>81.9</td>
<td>13.1</td>
</tr>
<tr>
<td>82.9</td>
<td>14.5</td>
</tr>
<tr>
<td>79.1</td>
<td>13.4</td>
</tr>
<tr>
<td>80.9</td>
<td>13.7</td>
</tr>
<tr>
<td>77.3</td>
<td>8.3</td>
</tr>
<tr>
<td>80.4</td>
<td>12.9</td>
</tr>
<tr>
<td>85Sn-5Bi series</td>
<td></td>
</tr>
<tr>
<td>78.1</td>
<td>12.1</td>
</tr>
<tr>
<td>77.4</td>
<td>12.7</td>
</tr>
<tr>
<td>78.3</td>
<td>13.2</td>
</tr>
<tr>
<td>80.4</td>
<td>12.5</td>
</tr>
<tr>
<td>77.2</td>
<td>10.2</td>
</tr>
<tr>
<td>74.9</td>
<td>11.2</td>
</tr>
<tr>
<td>77.6</td>
<td>10.1</td>
</tr>
<tr>
<td>74.7</td>
<td>12.8</td>
</tr>
<tr>
<td>78.1</td>
<td>12.3</td>
</tr>
<tr>
<td>77.2</td>
<td>11.1</td>
</tr>
</tbody>
</table>

(\( \dagger \): heating)

the precipitates were analyzed using a Kevex 7500-type energy dispersive X-ray (EDX) microanalyser.
composition dependency of the interaction parameters \( L_{ij}^\phi \) and \( L_{ijk}^\phi \) is expressed by eqs. (3) and (4), respectively.

\[
L_{ij}^\phi = L_{ij}^{\phi 0} \pm (x_i - x_j) \cdot L_{ij}^{\phi 1} \pm (x_i - x_j)^2 \cdot L_{ij}^{\phi 2}
\]

(3)

\[
L_{ijk}^\phi = x_i \cdot L_{ijk}^{\phi 0} + x_j \cdot L_{ijk}^{\phi 1} + x_k \cdot L_{ijk}^{\phi 2}
\]

(4)

The interaction parameters for the quaternary system were not considered in this work.

The Ag\(_5\)Sn phase is expressed by eq. (6), and the free energy was described by the sublattice model\(^3\) of eq. (5).

\[
G_m' = m_I (y_{Ag}^I G_{Ag:Ag:Ag:Zn}^I + y_{Zn}^I G_{Zn:Ag:Ag:Zn}^I + RT (y_{Ag}^I \ln y_{Ag}^I + y_{Zn}^I \ln y_{Zn}^I)) + m_{II} (y_{Ag}^{II} G_{Ag:Ag:Ag:Zn}^{II} + y_{Zn}^{II} G_{Zn:Ag:Ag:Zn}^{II} + RT (y_{Ag}^{II} \ln y_{Ag}^{II} + y_{Zn}^{II} \ln y_{Zn}^{II}))
\]

\[
= m_{III} (y_{Ag}^{III} G_{Ag:Ag:Ag:Zn}^{III} + y_{Zn}^{III} G_{Zn:Ag:Ag:Zn}^{III} + RT (y_{Ag}^{III} \ln y_{Ag}^{III} + y_{Zn}^{III} \ln y_{Zn}^{III}))
\]

\[
+ m_{IV} (y_{Ag}^{IV} G_{Ag:Ag:Ag:Zn}^{IV} + y_{Zn}^{IV} G_{Zn:Ag:Ag:Zn}^{IV} + RT (y_{Ag}^{IV} \ln y_{Ag}^{IV} + y_{Zn}^{IV} \ln y_{Zn}^{IV}))
\]

where, for example, \( G_{Ag:Ag:Ag:Zn}^{I} \) represents the free energy of a hypothetical compound Ag\(_8\)Ag\(_8\)Ag\(_2\)Zn\(_2\) when both the I and II sublattices are occupied by Ag atoms. The term \( y_i^s \) denotes the site fraction of elements in the sublattice \( s \). The term \( m_s \) is a variable denoting the size of the sublattice \( s \), and straightforwardly, the relationships of \( m_I = m_2 = 2/13 \), \( m_{II} = 3/13 \), and \( m_{IV} = 6/13 \) hold. An interaction parameter between atoms was excluded in this work.

Ag\(_5\)Sn was treated as a line compound in the assessment of the Sn-Ag binary system,\(^1\) because of its narrow homogeneity range. However, as described in detail by Ohtani et al.,\(^3\) Bi is assumed to preferably enter the Sn-sublattice sites. Therefore, the ternary Ag\(_5\)Sn phase is expressed by eq. (6), assuming the formula for the phase is Ag\(_{25.75}\)(Sn,Bi)\(_{0.25}\).

\[
G_{Ag:Sn} = y_{Sn} G_{Ag:Sn}^{Ag:Sn} + y_{Bi} G_{Ag:Sn}^{Ag:Bi} + 0.25RT (y_{Sn} \ln y_{Sn} + y_{Bi} \ln y_{Bi} + y_{Sn}y_{Bi} L_{Ag:Bi:Sn})
\]

(6)

The parameter \( G_{Ag:Sn}^{Ag:Sn} \) represents the Gibbs energy of the Ag\(_5\)Sn phase in the Ag\(_5\)Sn binary system, while \( G_{Ag:Bi}^{Ag:Bi} \) is the hypothetical Gibbs energy of the Ag\(_5\)Sn phase in the Ag-Bi binary system. The colon separates the constituent elements in the sublattices. The interaction energy between Sn and Bi atoms in the sublattice is denoted by the parameter \( L_{Ag:Bi:Sn} \) in eq. (6). The site fraction of elements in the Sn-sublattice sites is denoted by \( y_i \), and is related to the ordinary atom fractions as follows

\[
y_{Sn} = \frac{x_{Sn}}{x_{Sn} + x_{Bi}} = 4x_{Sn}, \quad y_{Bi} = \frac{x_{Bi}}{x_{Sn} + x_{Bi}} = 4x_{Bi}
\]

(7)

### 2.3.2 Thermodynamic description of the binary systems

To enable the thermodynamic description of the six binary systems, the results from the previous evaluation were adopted in the present study. A brief outline of each binary system will be summarized in this section. The descriptions of the lattice stability parameters for each pure element were obtained mainly from the Scientific Group Thermodata Europe (SGTE) datafile,\(^2\) and are shown in Table 2.

1. **Sn-Ag**

The Sn-Ag binary system is composed of liquid and terminal solid solutions of (\(\alpha,\beta\) Sn) and (Ag), \(\zeta\) Ag, and Ag\(_3\)Sn, with a relatively narrow homogeneity range. The thermodynamic parameters of this system have been analyzed by Ohtani et al.,\(^1\) and their values are shown in Table 3.

2. **Sn-Bi**

The Sn-Bi binary system exhibits a simple eutectic-type phase diagram composed of liquid, (\(\alpha,\beta\) Sn), and (Bi). The thermodynamic parameters of this system, as analyzed by Ohtani and Ishida,\(^5\) are shown in Table 3.

3. **Sn-Zn**

The Sn-Zn binary system is a simple eutectic-type phase diagram, composed of liquid, (\(\alpha,\beta\) Sn), and (Zn) solutions. The adopted thermodynamic description\(^1\) is shown in Table 3.

4. **Ag-Bi**

The Ag-Bi binary system is also a simple eutectic-type with a liquid and two terminal solid solutions, (Ag) and (Bi). Kattner and Boettinger\(^6\) presented a thermodynamic description of this binary system. However, considering solubility of Bi in \(\zeta\) Ag using the lattice stability parameters shown in Table 2, an interaction parameter was added by Ohtani et al.\(^4\) so that the hcp \(\zeta\) Ag phase would not be stable in this system.

### 5. **Ag-Zn**

The Ag-Zn binary system is composed of a liquid, (Ag), a bcc disordered phase (\(\beta\)), an hcp ordered phase (\(\zeta\), Ag\(_2\)Zn\(_8\) (\(\gamma\)), an hcp phase (\(\epsilon\)), and a (Zn) solution. The metastable CsCl-type ordered phase, obtained on rapid cooling from the \(\beta\) phase, was excluded in the thermodynamic analysis.\(^1\) The parameters for this binary system are shown in Table 3.

6. **Bi-Zn**

The Bi-Zn binary system is composed of the liquid and two terminal solutions (Bi) and (Zn). The remarkable flat and asymmetric miscibility gap of the liquid phase is characteristic of this phase diagram. The possibility of a metastable
<table>
<thead>
<tr>
<th>Element</th>
<th>Phase</th>
<th>Lattice stability parameter, J/mol</th>
<th>Temperature range, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2 Lattice stability parameters for Sn, Ag, Bi, and Zn.
<table>
<thead>
<tr>
<th>System</th>
<th>Phase</th>
<th>Thermodynamic parameter, J/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>(βSn)</td>
<td>( L_{\text{Ag,Sn}}^G ) = 19096.3</td>
<td></td>
</tr>
<tr>
<td>(Ag)</td>
<td>( L_{\text{Ag}}^G ) = 9998.4 + 6.28658T ( - (x_{\text{Ag}} - x_{\text{Sn}}) \cdot 44740.4 )</td>
<td></td>
</tr>
<tr>
<td>Sn-Ag</td>
<td>( L_{\text{Ag,Sn}}^{\text{free}} ) = 5590 + 3.56T ( - (x_{\text{Ag}} - x_{\text{Sn}}) \cdot 42400 )</td>
<td>1)</td>
</tr>
<tr>
<td>( \alpha,\beta )</td>
<td>( \alpha_{\text{Ag,Sn}}^G = -0.75 \cdot \alpha_{\text{Ag}}^G - 0.25 \cdot \alpha_{\text{Sn}}^G = -2876.9 - 3.57565T )</td>
<td></td>
</tr>
<tr>
<td>( \gamma )</td>
<td>( L_{\text{Ag,Sn}} = -4902.5 - 4.30532T \cdot (x_{\text{Ag}} - x_{\text{Sn}}) \cdot (-16474 + 3.12507T) \cdot (x_{\text{Ag}} - x_{\text{Sn}})^2 \cdot 7298.6 )</td>
<td>25)</td>
</tr>
<tr>
<td>(βSn)</td>
<td>( L_{\text{Bi,Sn}}^{\text{free}} ) = 2120 - 1.438T ( - (x_{\text{Bi}} - x_{\text{Sn}}) \cdot 3710 )</td>
<td></td>
</tr>
<tr>
<td>Sn-Bi</td>
<td>( L_{\text{Bi,Sn}} = 487 + 0.966T \cdot (x_{\text{Bi}} - x_{\text{Sn}}) \cdot (32 + 0.235T) )</td>
<td>5)</td>
</tr>
<tr>
<td>Sn-Zn</td>
<td>( L_{\text{Sn,Zn}} ) = 7000</td>
<td></td>
</tr>
<tr>
<td>( \alpha,\beta )</td>
<td>( L_{\text{Sn,Zn}}^{\text{free}} ) = 40000</td>
<td>1)</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>( L_{\text{Sn,Zn}} = 12700 - 9.16T \cdot (x_{\text{Sn}} - x_{\text{Zn}}) \cdot (-5400 + 3.45T) + (x_{\text{Sn}} - x_{\text{Zn}})^2 \cdot 840 )</td>
<td></td>
</tr>
<tr>
<td>(Ag)</td>
<td>( L_{\text{Ag}}^{\text{free}} ) = 27975.7 - 16T</td>
<td>6)</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>( L_{\text{Ag}}^G ) = 10000</td>
<td></td>
</tr>
<tr>
<td>Ag-Bi</td>
<td>( \alpha_{\text{Ag,Sn}}^G = -0.75 \cdot \alpha_{\text{Ag}}^G - 0.25 \cdot \alpha_{\text{Sn}}^G = 0 )</td>
<td>4)</td>
</tr>
<tr>
<td>( \beta )</td>
<td>( L_{\text{Ag,Sn}} = 4589.8 + 23.7304T \cdot 3.93814T \cdot \ln T \cdot (x_{\text{Ag}} - x_{\text{Sn}}) \cdot (5716.6 + 0.91452T) \cdot (x_{\text{Ag}} - x_{\text{Sn}})^2 \cdot (-2630.2 + 0.88522T) )</td>
<td>6)</td>
</tr>
<tr>
<td>(Ag)</td>
<td>( L_{\text{Ag}}^{\text{free}} ) = -22135 ( + (x_{\text{Ag}} - x_{\text{Zn}}) \cdot 4060 ) ( + (x_{\text{Ag}} - x_{\text{Zn}})^2 \cdot 4340 )</td>
<td></td>
</tr>
<tr>
<td>( \alpha,\beta )</td>
<td>( L_{\text{Ag,Zn}}^{\text{free}} ) = 3880 - 14.3T ( + (x_{\text{Ag}} - x_{\text{Zn}}) \cdot 10000 )</td>
<td></td>
</tr>
<tr>
<td>( \gamma )</td>
<td>( L_{\text{Ag,Zn}} = -30430 + 3.12T \cdot (x_{\text{Ag}} - x_{\text{Zn}}) \cdot 920 ) ( + (x_{\text{Ag}} - x_{\text{Zn}})^2 \cdot 2860 )</td>
<td></td>
</tr>
<tr>
<td>Ag-Zn</td>
<td>( \alpha_{\text{Ag,Ag,Ag}}^G = -7/13 \cdot \alpha_{\text{Ag}}^G - 6/13 \cdot \alpha_{\text{Zn}}^G = -3990 - 5.71T )</td>
<td>1)</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>( \alpha_{\text{Ag,Ag,Ag}}^G = -5/13 \cdot \alpha_{\text{Ag}}^G - 8/13 \cdot \alpha_{\text{Zn}}^G = -1250 - 5.71T )</td>
<td></td>
</tr>
<tr>
<td>( \gamma )</td>
<td>( \alpha_{\text{Ag,Ag,Ag}}^G = -5/13 \cdot \alpha_{\text{Ag}}^G - 8/13 \cdot \alpha_{\text{Zn}}^G = -5400 - 4.91T )</td>
<td></td>
</tr>
<tr>
<td>( \beta )</td>
<td>( L_{\text{Ag,Zn}} = -35080 + 7.167T \cdot (x_{\text{Ag}} - x_{\text{Zn}}) \cdot 1440 ) ( + (x_{\text{Ag}} - x_{\text{Zn}})^2 \cdot 24500 )</td>
<td></td>
</tr>
<tr>
<td>( \gamma )</td>
<td>( L_{\text{Ag,Zn}} = -29500 + 8.9T \cdot (x_{\text{Ag}} - x_{\text{Zn}}) \cdot 2700 ) ( + (x_{\text{Ag}} - x_{\text{Zn}})^2 \cdot (-12700 + 6.816T) )</td>
<td></td>
</tr>
</tbody>
</table>

continued on the next page
two-peak miscibility gap was suggested by Okamoto\(^9\) to explain such a strong asymmetry. Thermodynamic analysis of this system has been carried out.\(^{8–11}\) In particular, Malakhov\(^11\) has examined the thermodynamic parameters of the liquid phase in detail, paying close attention to the shape of the two-phase separations in the liquid phase. In the present study, to maintain a correspondence of the thermodynamic parameters to those of previous reports, the results given by Girard\(^9\) have been adopted. These parameters are summarized in Table 3.

### 2.3.3 Thermodynamic description of the ternary systems

Among the four ternary systems that compose the Sn-Ag-Bi-Zn quaternary system, the thermodynamic description of the Sn-Ag-Zn and Sn-Ag-Bi systems have been determined by our group,\(^{1,4}\) and these have been adopted in this study. The thermodynamic parameters for the Ag-Bi-Zn and Sn-Bi-Zn ternary systems were evaluated by analyzing the reported experimental data.

1. **Sn-Ag-Zn**

   This ternary system is composed of the liquid, (Ag), (α,β Sn), (Zn), disordered hcp (ξ Ag), Ag\(_2\)Sn, disordered Ag-Zn-based bcc phase (β), ordered Ag-Zn-based hcp phase (ζ), Ag\(_5\)Zn\(_8\) (γ), and a Ag-Zn-based hcp phase (ε). No data concerning the ternary compound were in the literature. By combining experimental DSC data with literature data, Ohtani et al.\(^1\) obtained a set of thermodynamic parameters for this ternary system that satisfactorily reproduces the experimental data. Thus, these parameters were used in the present study, as shown in Table 3.

2. **Sn-Ag-Bi**

   There are six phases in the Sn-Ag-Bi system: liquid, (Ag), (Bi), (α,β Sn), Ag\(_2\)Sn, and ξ Ag. No data concerning the ternary compound were available in the literature. A thermodynamic analysis of this ternary system was carried out based on experimental studies on the phase boundaries employing the DSC and EDX techniques, and these were combined with available experimental data.\(^1\) The thermodynamic parameters are listed in Table 3. The calculation of the liquidus projection reveals that this system includes three ternary invariant reactions: two ternary transitory peritectics at 263.6 °C and 262.5 °C, and a ternary eutectic at 139.2 °C. These results agree reasonably well with the estimation based on the experimental liquidus temperatures.

3. **Ag-Bi-Zn**

   This system is composed of liquid, (Ag), (Bi), (Zn), β, ζ, Ag\(_5\)Zn\(_8\) (γ), and ε phases. No ternary compounds were found. The references summarized in Villars et al.\(^{12}\) and Henglein and Köster\(^13\) investigated the liquidus surface of the ternary system by examining 62 alloys, employing thermal analysis and metallographic methods. The liquidus in the section where (mass%Bi)/(mass%Zn) = 1 was measured. However, the phase boundaries relating to the two-phase separation of the liquid phase were not obtained. According
to these results, the critical point of the miscibility gap originating in the Bi-Zn binary system is reached at $T = 660 \degree C$, and at a composition of 41 mass%Ag, 35 mass%Bi, and 24 mass%Zn. Seith et al.\cite{14} measured the two-phase separation boundary of the liquid phase in the 10 mass%Ag and 20 mass%Ag sections using a thermal analysis technique. They showed that the miscibility gap slightly extended from the Bi-Zn binary system, and that the critical temperature was about $T = 700 \degree C$. The experimental data have been compiled,\cite{15} in which the isopleths at 10 mass%Ag and 20 mass%Ag are shown. In the present study, thermodynamic analysis was performed based mainly on the experimental data for the vertical section diagram for (mass%Bi)/(mass%Zn) = 1, as well as using information on the liquidus surface.\cite{13} As a result, the ternary interaction parameter of the liquid phase was evaluated as 46 kJ/mol, as shown in Table 3.

The calculated vertical section diagram for (mass%Bi)/(mass%Zn) = 1 is compared with the experimental data\cite{13} in Fig. 1(a). The phase boundary of the miscibility gap (L/L$_1$ + L$_2$) in Fig. 1(a) was depicted by a dotted line in the work of Henglein and Köster.\cite{13} The calculated liquidus projection on the concentration triangle is shown in Fig. 1(b). The limit of the miscibility gap in the liquid phase, represented by K in Fig. 1(b), agrees well with the experimental value.\cite{13}

(4) Sn-Bi-Zn

This ternary system is composed of liquid, (Bi), ($\alpha$, $\beta$ Sn), and (Zn). Each component binary system has a eutectic-type phase diagram, although a two-phase separation in the liquid phase appears in the Bi-Zn system. No ternary compound has been reported. References on this system have been compiled in Villars et al.\cite{16} The phase boundaries were not determined sufficiently well by experiment to clarify the behaviour of this ternary system.

Thermodynamic analysis of this system was attempted in this study based on earlier reports.\cite{17–22} Alder Wright\cite{17} studied the phase equilibrium of the liquid phase at temperatures near to 650 $\degree C$, and clarified that a two-phase separation of the liquid phase exists on the Bi-Zn side. Muzaffar\cite{18} measured the freezing points and thermal arrests of the ternary alloys using thermal analysis, and determined the liquidus surface, as well as the phase boundaries at some vertical sections. Jänecke\cite{19} showed the outline of the liquidus surface of the Sn-Bi-Zn ternary system based on detailed observations of the eutectic reaction in the Bi-Cd-Pb-Sn-Zn system. The miscibility gap of the liquid phase in the temperature range between 441 < $T/\degree C$ < 604 was measured by an EMF method.\cite{20} Pelton et al.\cite{21} calculated the liquidus surface of this ternary system based on measured thermodynamic properties of the liquid phase using alloy concentration cells. According to these previous reports, it has been established that the liquidus surface of this ternary system is composed of a separate Bi-Zn rich liquid, (Sn), (Bi), and (Zn) terminal solid solutions, and the ternary eutectic point exists very close to the Sn-Bi binary system. The experimental information was analyzed in the present work, and it was revealed that the experimental data on the liquidus surface could only be reproduced well using the binary parameters. The results of calculations, shown in

![Fig. 1](image1.png)  (a) A comparison of the calculated vertical section at (mass%Bi)/(mass%Zn) = 1 with experimental data, and (b) calculated liquidus projection for the Ag-Bi-Zn system.

![Fig. 2](image2.png)  (b) Fig. 2, agree well with the phase boundaries given by Muzaffar.\cite{18}

3. Calculation of Phase Equilibrium of the Sn-Ag-Bi-Zn Quaternary System

3.1 Calculation of phase diagrams

The quaternary phase diagrams were calculated using the thermodynamic parameters of the six types of binary and four types of ternary systems described in the sections above. No extra term was added to the Gibbs energy expression.

Figure 3 shows the isopleths at the 75%Sn-15%Bi. The experimental data determined in this study are included in Fig. 3 for comparison with the calculated phase boundaries. From such a comparison, the expected experimental peaks in
the thermal analysis corresponding to the liquidus lines were not seen. This is because the peak heights of the thermal events were too small to accurately identify the liquidus temperatures. On the other hand, the peaks of the invariant reactions involving the solid phases were plainly visible, and agree well with the calculated results.

The liquidus projection on the concentration triangle when 10 mass% of Bi was added to Sn-Ag-Zn alloy are compared with the Sn-Ag-Zn ternary system in Fig. 4. Even when 10%Bi was added, the configuration of the primary crystals scarcely differed from those of the ternary system. The eutectic temperature (denoted as point “E” in Fig. 4(b) showing the enlarged portion of the Sn-rich region in Fig. 4(a)) decreased to 203.7°C on addition of Bi. The rate of decrease was estimated to be 1°C per 1% Bi addition. The melting point of the alloy fell further on adding Zn. However, Zn is an element that decreases the wettability of solders, and also promotes oxidation. Thus, the addition of a large mass of Zn to a solder alloy is not desirable. Even in Sn-Zn-Bi alloys used as reflow solders in the intermediate temperature range, the mass of added Zn is restricted to around 8 mass%. The phase diagram of the Sn-3 mass%Bi-8 mass%Zn alloy was calculated for a small mass of added Ag. The result is shown in Fig. 5. A eutectic reaction (187°C) with almost the same melting temperature as Pb-Sn alloys is formed on addition of 0.05 mass% of Ag. An improvement in the mechanical properties of the solder could be expected by the refining of the microstructure.

3.2 Examination of solidification structure by the Scheil model

When an alloy with atomic concentrations close to the eutectic point is cooled, the eutectic structure composed of Ag₃Sn and the ζ phase in the Sn matrix is expected from calculations of the phase diagram shown in Fig. 4(b). However, the result of the structural observations was different from this prediction. Figure 6 shows the solidification structure observed using the scanning electron microscope for the Sn-1.6 mass%Ag-8.6 mass%Bi-1.2 mass%Zn alloy cooled in air. According to the compositional analysis by EDX, the precipitates about 50 μm in diameter that are observed in the central part of the photograph are almost pure Bi. The fine structure scattered circumferentially consists of the Sn-Bi-based eutectic. In addition, other precipitates about 30 μm in diameter were observed. These precipitates were the Ag₃Zn₈ (γ) phase and the Ag₃Sn phase according to the EDX analysis.

The change in concentrations of the elements in the liquid phase during the solidification process was calculated using the thermodynamic parameters obtained in this analysis. In the simulation, the so-called “Scheil model” was employed, in which the liquid phase is super cooled several °C below the equilibrium liquidus in each calculation step. The Scheil model assumes that the atoms never diffuse in the solid phase during the solidification process was calculated using the thermodynamic parameters obtained in this analysis. In the simulation, the so-called “Scheil model” was employed, in which the liquid phase is super cooled several °C below the equilibrium liquidus in each calculation step. The Scheil model assumes that the atoms never diffuse in the solid phase and that uniform solidification occurs over the entire liquid, i.e., the concentration of each element equilibrates instantaneously. Under such assumptions, the concentration of the diffused element in the solid phase is

\[ C_S = kC_0(1 - f_S)^{k-1} \]  

where \( C_0 \) denotes the content of the original liquid. The equilibrium distribution coefficient between liquid and solid, \( k \), is assumed to have a constant value during solidification. The variable \( f_S \) represents the fraction of solid present. The cooling speed is not parameterized in this model. However, it is thought to have been in the middle of the cooling speed between equilibrium solidification and practical solidification.

Figure 7(a) shows the calculated results for the alloy shown in Fig. 6. The short dashed lines and solid lines represent the calculations of the equilibrium and non-equilibrium solidification processes, respectively. The vertical axis and horizontal axis show the temperature and the fraction of the liquid phase, respectively. The solidification ends at \( T = 172°C \) in the equilibrium solidification process.
On the other hand, the liquid phase remains until about $T = 140\, ^\circ\text{C}$ in the non-equilibrium case. In the non-equilibrium solidification process, $\beta$ Sn crystallizes first out of the liquid phase. Thereafter, the Ag-Zn-based compounds, $\gamma$ and $\zeta$ phases, precipitate in the matrix. The $\gamma$ phase disappears soon after the temperature reaches $T = 170\, ^\circ\text{C}$, and $\text{Ag}_3\text{Sn}$ forms instead. As the solidification continues, the liquid becomes increasingly enriched in Bi. The concentration change of Ag, Bi, and Zn in the liquid phase is shown in Figs. 7(b), (c), and (d). As can be seen, the Ag content in the liquid phase lowers with decreasing temperature. This is due to Ag consumption by the precipitation of the Ag-Zn and Ag-Sn-based compounds. A similar tendency was observed in the change in concentration of Zn. On the other hand, Bi is not consumed by the formation of compounds during solidification. Such an enrichment of Bi in the liquid phase makes the melting point fall to near the melting point of the Sn-Bi binary system. In equilibrium solidification, the concentration of Bi in the liquid phase is about 30% when solidification is complete. The Scheil model, on the other hand, predicts the Bi concentration in the liquid phase to increase to 55%. Consequently, the coarse Bi particles observed in Fig. 6 are supposed to have formed through a non-equilibrium solidification process. It has been pointed out that the addition of Bi to solder alloys enhances the degradation of the bonding strength, and a deterioration in the mechanical properties of solders is attributed to the precipitation of brittle Bi. It is necessary to consider the cooling speed to avoid the formation of such a microstructure.

![Figure 4](image-url)
4. Conclusions

A thermodynamic analysis of the Sn-Ag-Bi-Zn quaternary system was carried out by conducting experimental studies on the phase boundaries using a DSC and by performing microstructural analysis using EDX. The Gibbs energies of the individual phases were expressed using the conventional regular solution approximation. The sublattice model was applied to some of the compound phases. The results were as follows

1) For the thermodynamic description of the six binary systems, the results of previous evaluations were adopted. Thermodynamic descriptions of the Sn-Ag-Zn and Sn-Ag-Bi systems as previously determined by our group were employed, while those for the Ag-Bi-Zn and Sn-Bi-Zn ternary systems were evaluated by analyzing earlier experimental data. No quaternary interaction between Ag, Bi, Sn, and Zn was considered.

2) The calculated phase boundaries for the Sn-Ag-Bi-Zn system agree well with the present experimental DSC values for the invariant reactions involving the solid phases. However, the liquidus lines were not detected in the experimental work because the experimental peaks in the thermal analysis corresponding to the liquidus lines were very weak. Configuration of the primary crystals in the liquidus projection of the quaternary system was not much different to that of the Sn-Ag-Zn ternary system. A 1% addition of Bi decreases the eutectic temperature by approximately 1°C.

3) The solidification structures observed by the scanning electron microscope contained coarsened Bi particles. Simulation of the solidification process using the Scheil model revealed that an enrichment of Bi in the liquid phase should occur, because the other alloying elements are consumed by the formation of metallic compounds. Control of the solidification conditions using parameters such as the cooling rate should be carried out with care, to avoid degradation in the mechanical properties of the solder from the precipitation of brittle Bi.

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