<table>
<thead>
<tr>
<th><strong>Title</strong></th>
<th>Thermodynamic Evaluation of Binary Phase Diagrams in Small Particle Systems</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Author(s)</strong></td>
<td>Tanaka, Toshihiro; Hara, shigeta</td>
</tr>
<tr>
<td><strong>Citation</strong></td>
<td>Zeitschrift für Metallkunde. 92(5) P.467-P.472</td>
</tr>
<tr>
<td><strong>Issue Date</strong></td>
<td>2001</td>
</tr>
<tr>
<td><strong>Text Version</strong></td>
<td>publisher</td>
</tr>
<tr>
<td><strong>URL</strong></td>
<td><a href="http://hdl.handle.net/11094/26519">http://hdl.handle.net/11094/26519</a></td>
</tr>
<tr>
<td><strong>DOI</strong></td>
<td></td>
</tr>
<tr>
<td><strong>rights</strong></td>
<td>©Carl Hanser Verlag, München</td>
</tr>
<tr>
<td><strong>Note</strong></td>
<td></td>
</tr>
</tbody>
</table>
Binary phase diagrams of small particle systems, which consist of a liquid phase with pure solid phases, have been evaluated from the information on the Gibbs energy in the bulk and the surface tension of the liquid phase. As the size of the particle decreases, the melting point of the pure component decreases and the liquid phase region is enlarged. These changes of the phase relations with the size of the particle are dependent upon the composition dependence of the surface tension of the liquid phase.

Keywords: Nano-particle; Surface tension; Binary systems: Cu–Pb; Cu–Bi; Au–Si

1 Introduction

Various thermodynamic databases have been compiled to be mainly applied to the calculation of phase diagrams of alloys, salts and oxides [90Bal]. The accumulation and assessment of thermodynamic data and phase equilibria information to establish those databases is sometimes called CALPHAD (Computer Calculation of Phase Diagrams) approach [92Nis]. The CALPHAD approach has been recognized to be useful in various aspects of materials science and engineering [90Bal, 92Nis]. If it would be possible to use the thermodynamic databases to evaluate the surface properties as well as various properties in the bulk, we could not only widen the applicability of those thermodynamic databases but also further the understanding of the surface properties.

In previous works [94Tan, 96Tan, 98Tan1, 98Tan2, 98Tan3, 99Tan1, 99Tan2, 99Tan3, 99Ued], the authors have applied those thermodynamic databases to the evaluation of the surface tension of liquid alloys, molten ionic mixtures and the interfacial tension between liquid steel and molten slag. These works are aimed to understand the thermodynamic properties of a material system, including its surface or interface as well as the bulk. Since the effect of its surface on the total thermodynamic properties cannot be negligible in a small particle of an alloy, the phase relations in the alloy are dependent upon the size of the particle and its surface property [58Rei, 54Tak, 76Buf, 77Cou, 86All, 88Sak]. In order to understand the effect of the surface property on the phase relations, the authors try to evaluate the phase diagrams of binary alloys in small particle systems in the present work. We focus on some binary alloys, of which phase diagrams consist of the liquid phase and pure solid phases. In these alloys, their phase diagrams can be evaluated by only the information on the Gibbs energy in the bulk and the surface tension of the liquid phase, which can be also obtained as functions of temperature and compositions from the thermodynamic databases.

2 Thermodynamic Equations

If a phase diagram consists of a liquid phase and pure solid phases, and in addition, the pure solid phase is selected as the reference state of Gibbs energy, the total Gibbs energy of an alloy system in a small particle with its radius \( r \) is described in the following Eqs. (1)–(4) [48Rei, 62Swa, 76Buf]:

\[
\Delta G_{\text{Total}} = \Delta G_{\text{Bulk}} + \Delta G_{\text{Surface}}
\]

(1)

The Gibbs energy of the bulk of A–B binary alloy, \( \Delta G_{\text{Bulk}} \) in Eq. (1), which corresponds to \( \Delta G_{\text{Total}} \) with \( r \to \infty \), is expressed in Eqs. (2) and (3):

\[
\Delta G_{\text{Bulk}} = N_A \Delta G_A^{\text{LS}} + N_B \Delta G_B^{\text{LS}} + G^{\text{Excess,L}} + \frac{RT(N_A \ln N_A + N_B \ln N_B)}{}
\]

(2)

\[
G^{\text{Excess,L}} = N_A N_B \left( L_0 + L_1 (N_A - N_B) + L_2 (N_A - N_B)^2 + L_3 (N_A - N_B)^3 \right)
\]

(3)

where \( \Delta G_A^{\text{LS}} \) and \( \Delta G_B^{\text{LS}} \) are the Gibbs energies of the pure liquid phases relative to those of pure solid phases, the temperature dependence of which is listed in Table 2 [86Nie, 91Din]. \( G^{\text{Excess,L}} \) is the excess Gibbs energy of the liquid phase in the A–B alloy. The interaction parameters \( L_i \) (\( i = 0 \ldots 3 \)) of \( G^{\text{Excess,L}} \) in Eq. (3) are also listed in Table 3 [86Hay, 86Nie, 88Spe]. \( N_A \) and \( N_B \) are the mole fractions of the components A and B.

\[
\Delta G_{\text{Surface}} \text{ in Eq. (1), the effect of the surface on } \Delta G_{\text{Total}}, \text{ is assumed as follows [62Swa]:}
\]

\[
\Delta G_{\text{Surface}} = \frac{2\sigma_l V_l}{r} - \frac{2(N_A \sigma_A^S V_A^S + N_B \sigma_B^S V_B^S)}{r}
\]

(4)

where \( \sigma_l \) and \( V_l \) are the surface tension and molar volume of the liquid alloy, respectively, \( r \) is the radius of a particle, \( \sigma_A^S \) and \( \sigma_B^S \) are the surface tensions and \( V_A^S \) and \( V_B^S \) are the molar volumes of pure solid A and B.

As shown in Eq. (4), we need the value of the surface tension \( \sigma_A^S \) of pure solid X, but the precise information on the value of \( \sigma_A^S \) and its temperature dependence are insufficient [59All, 75Mur, 83Kum]. From the data reported in some Refs. [59All, 75Mur, 83Kum], the value of \( \sigma_A^S \) of a pure solid at the melting point is found to be 25% larger than the surface tension of the pure liquid on the average. Equation (5) is, therefore, assumed to express the surface tension \( \sigma_A^S \) of a pure solid X in the present work:

\[
\sigma_A^S = 1.25 \sigma_{A,\text{mp}} + \frac{\partial \sigma_A^S}{\partial T} (T - T_{\text{mp}}) \quad (X = \text{A or B})
\]

(5)

where \( \sigma_{A,\text{mp}} \) is the surface tension of the pure liquid X at its melting point \( T_{\text{mp}} \). The temperature dependence of \( \sigma_A^S \) in Eq. (5) is assumed to be the same as that of \( \sigma_X^S \), which is summarized in Table 1 [88Sid]. In addition, the effects of crystal faces on \( \sigma_A^S \) is ignored in the present work.
Table 1. Data of physical properties.

<table>
<thead>
<tr>
<th>Element</th>
<th>Surface tension (\sigma^L (\text{Nm}^{-1})) of the pure liquid components [88Lid]</th>
<th>(\frac{\partial \sigma^L}{\partial T} (\text{Nm}^{-1} \cdot T^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>(\sigma^L_{\text{Cu}} = 1.303 - 0.00023 \cdot (T - 1356.15))</td>
<td>-0.00023</td>
</tr>
<tr>
<td>Pb</td>
<td>(\sigma^L_{\text{Pb}} = 0.458 - 0.00013 \cdot (T - 600.55))</td>
<td>-0.00013</td>
</tr>
<tr>
<td>Bi</td>
<td>(\sigma^L_{\text{Bi}} = 0.378 - 0.00007 \cdot (T - 544.1))</td>
<td>-0.00007</td>
</tr>
<tr>
<td>Au</td>
<td>(\sigma^L_{\text{Au}} = 1.169 - 0.00025 \cdot (T - 1356.15))</td>
<td>-0.00025</td>
</tr>
<tr>
<td>Si</td>
<td>(\sigma^L_{\text{Si}} = 0.865 - 0.00013 \cdot (T - 1687.15))</td>
<td>-0.00013</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Element</th>
<th>Molar volume (m(^3)mol(^{-1})) of the pure liquid components [88Lid]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>(V^L_{\text{Cu}} = 7.94 \times 10^{-6} \cdot (1.0 + 0.0001 \cdot (T - 1356.15)))</td>
</tr>
<tr>
<td>Pb</td>
<td>(V^L_{\text{Pb}} = 19.42 \times 10^{-6} \cdot (1.0 + 0.000124 \cdot (T - 600.55)))</td>
</tr>
<tr>
<td>Bi</td>
<td>(V^L_{\text{Bi}} = 20.80 \times 10^{-6} \cdot (1.0 + 0.000117 \cdot (T - 544.1)))</td>
</tr>
<tr>
<td>Au</td>
<td>(V^L_{\text{Au}} = 11.3 \times 10^{-6} \cdot (1.0 + 0.000069 \cdot (T - 1356.15)))</td>
</tr>
<tr>
<td>Si</td>
<td>(V^L_{\text{Si}} = 11.1 \times 10^{-6} \cdot (1.0 + 0.000014 \cdot (T - 1687.15)))</td>
</tr>
</tbody>
</table>

Table 2. Data of the Gibbs energies of the pure components.

<table>
<thead>
<tr>
<th>Element</th>
<th>Gibbs energies of the pure components (J \cdot \text{mol}^{-1})</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>(G^S_{\text{Cu}} = -48.7 - (-142.53101) \cdot T + 31.380005 \cdot T^2 / 2 - (-138909)/2T)</td>
<td>[86Nie]</td>
</tr>
<tr>
<td>Pb</td>
<td>(G^S_{\text{Pb}} = -37.8 - (-133.83501) \cdot T + 35.112106 \cdot T^2 / 2 - (-130909)/2T)</td>
<td>[86Nie]</td>
</tr>
<tr>
<td>Bi</td>
<td>(G^S_{\text{Bi}} = -78.1 - (-137.84653) \cdot T + 24.221176 \cdot T^2 / 2 - (-100911) \cdot T^3 / 6)</td>
<td>[86Nie]</td>
</tr>
<tr>
<td>Au</td>
<td>(G^S_{\text{Au}} = 12552.0 - 9.385866 \cdot T)</td>
<td>[91Din]</td>
</tr>
<tr>
<td>Si</td>
<td>(G^S_{\text{Si}} = 5069.36 - 30.099439 \cdot T + 2.0931 \times 10^{-21} \cdot T^2)</td>
<td>[91Din]</td>
</tr>
</tbody>
</table>

The molar volume of a liquid alloy, \(V^L\) in Eq. (4), is obtained from the following equation:
\[
V^L = N^A V^L_{\text{A}} + N^B V^L_{\text{B}}
\]
(6)
where \(V^L_{\text{A}}\) and \(V^L_{\text{B}}\) are the molar volumes of pure liquid A and B. Their temperature dependencies are given in Table 1 [88Lid]. The molar volume \(V^S_{X}\) of pure solid X is evaluated in Eq. (7), which is obtained by considering the volume change due to the fusion at the melting point of each component.
\[
V^S_{X} = \frac{V^L_{X}}{(1 + \alpha_X)}
\]
(7)
where \(\alpha_X = (V^S_{X,m} - V^S_{X,m}) / V^S_{X,m}\), which is the ratio of the volume change of solid due to the fusion, is listed in Table 1 [72Wit]. \(V^S_{X,m}\) and \(V^S_{X,m}\) are the molar volumes of pure liquid and solid X at the melting point.

When we evaluate the composition and the temperature dependence of the surface tension \(\sigma^S\) of liquid phase, we can calculate \(\Delta G^\text{Total}\) of the liquid phase from the above equations. As mentioned above, the authors have evaluated the surface tension of liquid A–B binary alloys on the basis of Butler’s equation [32But] as follows [96Tan, 98Tan2, 98Tan3, 99Tan1, 99Tan2]:
\[
\sigma^S = \sigma^S_{\text{A}} + \frac{RT}{A_A} \ln N^S_{\text{A}} - \frac{1}{A_A} G^E_{\text{A}} (T, N^S_{\text{B}}) - \frac{1}{A_A} G^E_{\text{A}} (T, N^S_{\text{B}})
\]
(8a)
\[
\sigma^S = \sigma^S_{\text{B}} + \frac{RT}{A_B} \ln N^S_{\text{B}} - \frac{1}{A_B} G^E_{\text{B}} (T, N^S_{\text{A}}) - \frac{1}{A_B} G^E_{\text{B}} (T, N^S_{\text{A}})
\]
(8b)
In Eqs. (8a) and (8b), $\sigma_A^L$ and $\sigma_B^L$ are the surface tensions of the pure molten components, and $N_B^L$ and $N_B$ are the mole fractions of element $B$ in the surface and the bulk, respectively. $A_X = L N_A (V_X)^{3/2}$ ($N_A$ is the Avogadro number: $X = A$ or $B$, $L = 1.091$) is molar surface area of pure $X$, and this is obtained from the molar volume $V_X$. $G_X^L(T,N_B^L)$ and $G_X^B(T,N_B)$ are the partial excess Gibbs energies of component $X$ in the bulk and the surface, respectively, as functions of $T$ and $N_B$ or $N_B^L$.

Since the partial molar excess Gibbs energy of component $X$ ($X = A$ or $B$) in the bulk $G_X^E(B,T,N_B^L)$ in Eqs. (8a) and (8b) can be obtained directly from $G^{Excess,L}$ in Eq. (3) by using Eqs. (9a) and (9b).

$$G_A^E(T,N_B^L) = G^{Excess,L} - N_B \frac{\partial G^{Excess,L}}{\partial N_B} \quad (9a)$$

$$G_B^E(T,N_B) = G^{Excess,L} + (1 - N_B) \frac{\partial G^{Excess,L}}{\partial N_B} \quad (9b)$$

For the excess Gibbs energy in the surface, we derived the following equations [97Tan1, 98Tan1, 98Tan2, 98Tan3, 99Tan1, 99Tan2, 99Tan3, 99Ued] based on the model proposed by Yeum et al. [89Yeu].

$$G_X^S(T,N_B^L) = \beta^{Mix} \cdot G_X^E(T,N_B^L) \quad (10)$$

with $\beta^{Mix} = 0.83$ for liquid metallic alloys and $\beta^{Mix} = 1.1$ for molten ionic mixtures and molten slags.

Equation (10) means that $G_X^S(T,N_B^L)$, which has the same formula as $G_X^E(T,N_B^L)$, is obtained by replacing $N_B$ by $N_B^L$ in $G_X^E(T,N_B^L)$ ($X = A$ or $B$) and then multiplying $\beta^{Mix}$ to $G_X^E(T,N_B^L)$. $\beta^{Mix}$ is a parameter corresponding to the ratio of the coordination number in the surface to that in the bulk considering the surface relaxation [97Tan1, 98Tan1, 98Tan2, 98Tan3, 99Tan1, 99Tan2, 99Tans3, 99Ued].

The surface tension, $\sigma^L$, of liquid alloys can be calculated from Eqs. (8)–(10) as follows:

1. Setting temperature $T$ and composition $N_B^L$ of a solution.
2. Inserting the values for surface tension $\sigma_X^L$ and molar volume $V_X$ of pure liquid substances at the above temperature in Eqs. (8a) and (8b).
3. Determining excess Gibbs energies in the bulk phase at the above temperature and composition, and substituting them in Eqs. (8a) and (8b).

In the present work, we have evaluated the phase diagrams of Cu–Pb, Cu–Bi, and Au–Si binary systems, of which phase diagrams consist of liquid phase and pure solid phases. The data which are used for the calculations are summarized in Tables 1–3 [72Wit, 86Hay, 88Nie, 91Din, 00Spe]. Figs. 2a–c show the calculated results of the surface tension of the liquid alloys for a given temperature with the activity curves in the bulk of the liquid phase. As described in previous works [94Tan, 96Tan, 98Tan1, 99Tan1, 99Tan2], the calculated surface tension of liquid alloys obtained from Eqs. (8)–(10) agrees well with the experimental results although only the Cu–Pb alloy in Fig. 2a shows the comparison of the calculated values with the experimental results [59Met, 73Jou] in the present work. It is well known that when the alloy, such as Cu–Pb or Cu–Bi, has a large difference between $\sigma_X^L$ and $\sigma_X^L$ of the pure liquid components, the composition dependence of $\sigma^L$ shows a large downward deviation from the linearity between $\sigma_X^L$ and $\sigma_X^L$. In addition, we found from these calculations that in alloys with a positive deviation of the activity from the
ideal solution in the bulk (Cu–Pb and Cu–Bi alloys), the surface tension deviates negatively from the ideal solution. On the other hand, in alloys with a negative deviation of the activity from the ideal solution in the bulk (Au–Si alloy), the surface tension has the tendency to show a positive deviation from the ideal solution. It is found that this rule can be applied generally to liquid alloys [96Tan, 98Tan1, 98Tan2, 98Tan3, 99Tan1, 99Tan2, 99Tan3, 99ued]. Thus, as shown in Figs. 2a–c, Cu–Pb and Cu–Bi liquid alloys indicate the large downward curvature of the composition dependence of the surface tension. On the other hand, the surface tension of the liquid phase changes smoothly with the composition in Au–Si alloys.

From Eqs. (1)–(4), the Gibbs energy of the pure component X including the surface is obtained as follows:

\[ \Delta G^{Total} = \Delta G^{Bulk} + \Delta G^{Surface} \]

\[ = \Delta G^{LS}_X + \frac{2\sigma^L_{X,V}V^L_X}{r} - \frac{2\sigma^S_{X,V}V^S_X}{r} \]

\[ = \Delta G^{LS}_X + \frac{2}{r} \times \left[ \sigma^L_{X,V}V^L_X - \left\{ 1.25\sigma_{X,mp}^L \frac{\partial \sigma_{X,V}^L}{\partial T} (T - T_{X,mp}) \right\} \frac{V^L_X}{1 + \sigma_{X}} \right] \]

(11)

Fig. 2. Surface tension of liquid alloys and activity of the second component in the bulk of the liquid phase. (a) Cu–Pb alloys: • [59Met], ○ [73ou]; (b) Cu–Bi alloys; (c) Au–Si alloys.

Fig. 3. Change in the melting point of the pure metals as a function of the particle radius. (a) Au [71sam]; (b) Pb [72Coo]; (c) Cu; (d) Bi; (e) Si.
The temperature $T$ which gives $\Delta G^{\text{Total}} = 0$ in Eq. (11) is the melting point of pure X at a given radius $r$ of a particle. Figures 3a--c show the change in the melting point of pure Pb, Au, Cu, Bi and Si with the radius of the particle. As shown in these figures, the effect of the size on the melting point becomes remarkable under 50 nm. In addition, the calculated results for Au and Pb agree with the experimental data [71Sum, 72Coo].

The Gibbs energy curves of the liquid phase in Cu–Pb, Cu–Bi and Au–Si alloys at 1000 K are shown in Figs. 4a–c for three particle radii. Figures 5a–c show the phase diagrams of the Cu–Pb, Cu–Bi and Au–Si systems for $r = 20$ nm, 10 nm and 5 nm as well as the bulk. Since the value of the surface tension $\sigma^s$, $\sigma^L$ etc. is influenced by the curvature of the surface in a small particle below $r = 5$ nm [49Tol, 79Mor, 89Gla], the present approach cannot be extended to the evaluation of the phase diagrams in small particle systems with $r < 5$ nm.

Our results show the following.

1. The liquid phase region in the phase diagrams is enlarged as the size of the particle becomes smaller.
2. The two-liquid phase region spreads as the size of the particle becomes smaller.
3. In alloys, of which composition dependence of the surface tension of the liquid phase shows large downward curvature, such as Cu–Pb and Cu–Bi alloys, the size of the particle influences largely on the phase relations. On the other hand, in Au–Si alloy, of which the surface tension of the liquid phase changes smoothly with composition, the effect of the size on the phase relations is not so large.

As described above, the phase diagrams of binary alloys with small particles, which consist of a liquid phase with pure solid phases, can be evaluated from the information on the Gibbs energy in the bulk and the surface tension of the liquid phase, although the following rough approximations have been used in the present work:

1. The mass balance of atoms between the bulk and the surface is not considered though the surface segregation occurs in alloys.
2. The effect of the crystal faces on the surface properties of the solid phases is ignored.
3. The temperature dependence of the surface tension of the pure solid phase is assumed to be the same as that of the pure liquid phase.

### 4 Concluding Remarks

In the present work, binary phase diagrams of small particle systems, which consist of a liquid phase with pure solid phases, can be evaluated from the information on the Gibbs energy in the bulk and the surface tension of the liquid phase. If the effect of the crystal faces on $\sigma^L$ can be considered, the dependence of the phase relation upon the crystal faces, for example, the change in the melting point on each crystal surface can be evaluated on the basis of the present approach. In addition, if the surface tensions of the solid solution and compound phases are evaluated, we can extend the present approach to the evaluation of phase diagrams of any kind of binary systems with small particles.

The authors wish to express their hearty thanks to Emeritus Prof. K. Ogiso from Osaka University for his valuable information on the melting points of pure metals in small particle systems.
References

00Sp Spencer, P.J.: Personal communication (2000).

(Rceived August 28, 2000)

Correspondence Address

T. Tanaka, S. Hara
Department of Materials Science and Processing, Osaka University
2–1 Yamadaoka, Suita, Osaka 565–0871, Japan
Fax: +81 6 6879 7466
E-mail: tanaka@mat.eng.osaka-u.ac.jp