Thermodynamics and thermophysical properties of liquid Bi - Sn alloys

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What kind of input data are necessary for modelling?

1. Phase diagram information

2. Thermodynamic data

3. Thermophysical data

4. Structural data

5. Experimental property data for a comparison with theoretical results
1. The Bi-Sn phase diagram
Results of calculations

$G_M/RT \approx 0.6$

Bi-Sn is segregating alloy system
Results of calculations
Surface tension measurements
IENI-HTTLabs Equipments
Surface Tension Measurements

Preparation of samples
- High purity Tin and Bi (99.9998%)
- $P_{\text{tot}} \leq 10^{-2}$ Pa + Ta-getter
- Alloy sample of about $2.5 \div 3$ g
- Check of alloy composition by EDS
- Etching + chemical

Experimental procedure
- Measurements by Large drop method
- Sapphire crucible
- Atmosphere: Ar-5%H$_2$ Flow rate = 0.25 l/m
- Temperature range: 573-1123 K step 50°
- $P_{O_2} \leq 10^{-20}$ (“oxygen free”) Pa average value in the temperature range
- Real time acquisition of the drop profile by ASTRAview
- 10/15 min after the temperature stabilization (~ 800 acq /T)
- SEM/EDS analyses on the surface of solidified drop
Effect of temperature on surface tension of Bi, Sn and some of their alloys; the symbols (□) refer to the experimental data of the present work (T = 773, 873, 973, 1073 and 1173 K).

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Table 1: Surface tension together with the corresponding temperature coefficients of binary liquid alloys of the Bi-Sn system. The own surface tension experimental data of liquid Bi and Sn are taken as the reference data.

<table>
<thead>
<tr>
<th>Composition [at.%]</th>
<th>Melting temp. $T_M$ [K]</th>
<th>Surface tension $\sigma_0$ at $T_M$ [mN.m$^{-1}$]</th>
<th>Surface tension temp. coeff. $\frac{d\sigma}{dT}$ [mN.m$^{-1}$.K$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>Sn</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>-</td>
<td>544</td>
<td>379.82</td>
</tr>
<tr>
<td>85</td>
<td>15</td>
<td>510</td>
<td>393.69</td>
</tr>
<tr>
<td>70</td>
<td>30</td>
<td>475</td>
<td>400.25</td>
</tr>
<tr>
<td>55</td>
<td>45</td>
<td>440</td>
<td>422.42</td>
</tr>
<tr>
<td>43</td>
<td>57</td>
<td>412</td>
<td>429.16</td>
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<tr>
<td>30</td>
<td>70</td>
<td>440</td>
<td>439.54</td>
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<td>20</td>
<td>80</td>
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<td>90</td>
<td>482</td>
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<tr>
<td>5</td>
<td>95</td>
<td>494</td>
<td>522.23</td>
</tr>
<tr>
<td>-</td>
<td>100</td>
<td>505</td>
<td>560.77</td>
</tr>
</tbody>
</table>
Surface properties of liquid binary alloys: surface tension & surface segregation

Butler (1932):

\[ \sigma = \sigma_i + \frac{k_B T}{\alpha_i} \ln \frac{a_i^s}{a_i^b} \]

gives the relation between the surface tension and thermodynamics of liquids in which the bulk and surface phases are in equilibrium.

& Different solution model
Surface tension reference data of Bi

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Surface tension reference data of Sn
Results of calculations

Surface tension of liquid Bi-Sn alloys at T=873K

- present work
- [09Ple]
- [01Mos]

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Results of calculations

Surface composition of liquid Bi-Sn alloys at T=873K

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Microscopic functions (B-T) & Thermodynamics

\[ S_{cc}(0) = RT \left( \frac{\partial^2 G_M}{\partial C_A^2} \right)_{T,P,N}^{-1} = C_B a_A \left( \frac{\partial a_A}{\partial C_A} \right)_{T,P,N}^{-1} = C_A a_B \left( \frac{\partial a_B}{\partial C_B} \right)_{T,P,N}^{-1} \]

For ideal solution the \( S_{cc}(0) \) becomes

\[ S^{id}_{cc}(0) = c_A c_B \]

The CSRO parameter and \( S_{cc}(0) \) are related to each other by

\[ \frac{S_{cc}(0)}{c_A c_B} = \frac{1 + \alpha_1}{1 - (Z - 1)\alpha_1} \]

where \( Z \) is the coordination number.
Results of calculations

Microscopic functions of liquid Bi-Sn alloys at T=700K

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The interdiffusion coefficient \((D_m)\) can be given in terms of the \(S_{CC}(0)\) by

\[
D_m = (c_A D_B^* + c_B D_A^*) \frac{S_{id}^{cc}(0)}{S_{cc}(0)}
\]

For “ideal” alloys, \(S_{cc}(0) = S_{cc}(0, id) = c_A c_B\), then

\[
D_m = c_A D_B + c_B D_A = (c_A D_B^* + c_B D_A^*) = D_{id}
\]

and finally combining the last two eqs. it is obtained,

\[
\frac{D_m}{D_{id}} = \frac{S_{id}^{cc}(0)}{S_{cc}(0)}
\]

The criteria for mixing behaviour:

\(S_{cc}(0) > S_{cc}(0, id)\) segregation \(\Rightarrow D_m < D_{id}\)

\(S_{cc}(0) < S_{cc}(0, id)\) presence of chem. order \(\Rightarrow D_m > D_{id}\)
Results of calculations

Diffusivity of liquid Bi-Sn alloys at T=700K

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Work in progress

Calculation of the viscosity and electrical resistivity of Bi-Sn melts and comparison with literature data ([0Ple] *****)
Thank you for your attention!