Abstract: Based on the available experimental data, the Bi-Ni binary system was optimized thermodynamically by the CALPHAD method. The solution phases, including liquid, fcc$_{\text{A1}}$(Ni) and rhombohedral$_{\text{A7}}$(Bi), were described as substitutional solution phases, of which the excess Gibbs energies were expressed with the Redlich-Kister polynomial. The intermetallic compound, BiNi, was modeled using three sublattices (Bi)(Ni,Va)(Ni,Va) considering its crystal structure (NiAs-type) and the compatibility of thermodynamic database in the multi-component systems, while Bi$_3$Ni was treated as a stoichiometric compound. Finally, a set of self-consistent thermodynamic parameters formulating the Gibbs energies of various phases in this binary system were obtained. The calculated results are in reasonable agreement with the reported experimental data.

Key words: Sn-based alloy; phase diagram; thermodynamics; CALPHAD; Bi-Ni binary system

1 Introduction

Increasing efforts have been conducted recently on the search for suitable Pb-free solders due to the harmful influence of Pb on both environment and human health[1–4]. Sn-based alloys with different additives, such as Ag, Bi, Cu, In, Sb and Zn, are potential candidates as Pb-free solders[5–7]. The Sn-Bi alloys with low melting point are developed for soldering the temperature-sensitive components in the step-by-step packaging process[7–9]. On the other hand, Ni is plated as an under bump metallurgy (UBM) layer on the substrate prior to soldering in modern microelectronic package[7–10]. Interfacial reactions between Sn-Bi solders and Ni play an important role on the reliability of the solder joints. Phase diagrams and thermodynamic properties of the related systems involving Sn-Bi solder and Ni are helpful to control interfacial microstructure during soldering[11–13]. In view of these, the phase relation of the Bi-Ni binary system as a binary sub-

The Bi-Ni binary system was reviewed critically by NASH[14] in 1985. The assessments of this binary system were performed by VASSILEV et al[15–17] and SEO et al[18]. However, there are still some problems in their assessments[15–18]. Firstly, the miscibility gap of liquid phase is stable at above 1630 K from the assessment by SEO et al[18], resulting in the inconsistence with the experimental phase diagram, but it was not noticed in the original publication. Secondly, the different thermodynamic models of intermetallic compound BiNi were used in their assessment[15–18], and they are thus not compatible with the extrapolation of the multi-component system. Finally, it is not reasonable that the heat capacity of BiNi measured by PERRING et al[19] was not employed to optimize its thermodynamic parameters. Therefore, the present work was to obtain a set of self-consistent and reliable thermodynamic description of the Bi-Ni binary system using the CALPHAD method[20–21] and Thermo-calc® software package[22].

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Corresponding author: WANG Jiang; E-mail: wangjiang158@gmail.com

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2 Experimental

2.1 Phase diagram data

The liquidus of the Bi-Ni binary system was measured by PORTEVIN[23] and VOSS[24] using thermal analysis. The experimental data on the liquidus are in good agreement with each other, while there is a discrepancy of the peritectic temperature of intermetallic compound BiNi. NASH[14] pointed out that the peritectic temperature (911 K) remarked by VOSS[24] is too low due to the supercooling effect of liquid alloys compared with the experimental data (927 K) obtained by PORTEVIN[23]. SHAVIN and al.[25] reported that the composition and temperature of the eutectic reaction, L=Bi(Ni)+rhombohedral(Bi), are 99.47% Bi (molar fraction) and 543 K, respectively. FESCHOTTE and ROSSET[26] investigated the Bi-Ni binary system and determined the eutectic and peritectic temperatures in this binary system. Their experimental results reveal that the intermetallic compound BiNi has a narrow homogeneity range and BiNi is a stoichiometric compound. Recently, VASSILEV et al.[15] determined the solidus of fcc_A1(Ni) phase as well as the compositions and temperatures of the invariant reactions by electron microprobe analyses, optical microscopy and differential scanning calorimetry. It was found that the narrow homogeneity region of BiNi is 50%–52% Bi and BiNi is a stoichiometric compound. Using the diffusion couple method, SEO et al.[18] measured accurately the homogeneity region of BiNi at different temperatures (473–873 K) through X-ray spectroscopy and electron microprobe analyzer. The experimental data mentioned above in Refs.[15, 18, 23–26] were taken into account in the present optimization.

2.2 Thermodynamic data

Up to now, no experimental enthalpy of mixing of liquid Bi-Ni alloys was reported in the published literature. Activities of Bi and Ni in liquid phase were investigated by IWASE and MCLEAN[27] and VASSILEV et al.[16]. IWASE and MCLEAN[27] determined the activities of Ni in liquid phase at 1 073 K and 1 773 K by electromotive force (EMF) method. Recently, VASSILEV et al.[16] measured the activities of Bi in liquid phase at different temperatures (1 723 K, 1 753 K and 1 773 K) using the modified isothermal isopiestic method. On the other hand, the enthalpy of formation of intermetallic compound BiNi was determined by PREDEL and RUGE[28] using calorimetric technique. PERRING et al.[19] measured the heat capacities of BiNi in the temperature range of 310–850 K by differential scanning calorimetry. The experimental data in Refs.[16, 19, 27–28] were used in the present optimization.

3 Thermodynamic model

3.1 Pure elements

The stable forms of the pure elements at 298.15 K and 100 kPa are chosen as the reference states. The Gibbs energy for the element i in status φi is given as

\[ \Theta G_i^\phi (T) = G_i^\phi (T) - \Theta H_i^{SER} = a + bT + cT \ln T + \]

\[ + dT^{-2} + eT^{-3} + fT^{-1} + gT^7 + hT^{-9} \]  

(1)

where \( \Theta H_i^{SER} \) is the enthalpy of the element i in its standard reference state (SER) at 298.15 K and 100 kPa; \( T \) is the temperature; \( G_i^\phi (T) \) is the Gibbs energy of the element i with structure \( \phi \); \( \Theta G_i^\phi (T) \) is the molar Gibbs energy of the element i with the structure of \( \phi \) referred to the enthalpy of its stable state at 298.15 K and 100 kPa. In the present work, \( \Theta G_i^\phi (T) \) and \( \Theta G_i^\phi (T) \) are taken from the SGTE (Scientific Group Thermodata Europe) database[29].

3.2 Solution phases

The solid solution phase \( \phi = \text{liquid, fcc or rhombohedral} \) is described with the substitutional solution model. The molar Gibbs energy of the solid solution with the Redlich-Kister polynomial[30] is expressed as follows:

\[ G_m^\phi = x_Bi \Theta G_{Bi}^\phi + x_Ni \Theta G_{Ni}^\phi + RT(x_Bi \ln x_Bi + x_Ni \ln x_Ni) + \]

\[ x_Bi x_Ni \sum_{i=0}^{n} L_i (x_Bi - x_Ni)^i \]  

(2)

where R is the gas constant; \( x_Bi \) and \( x_Ni \) are the mole fractions of Bi and Ni, respectively; and \( L_i \) is the interaction parameter dependent on temperature:

\[ L_i = A_i + B_i T \]  

(3)

where \( A_i \) and \( B_i \) are model parameters to be optimized in the present work.

3.3 Intermetallic compounds

On the basis of the experimental result in Ref. [31], the crystal structure of intermetallic compound BiNi is NiAs-type, as shown in Fig.1. The deviations from stoichiometric composition on both Bi-rich side and Ni-rich side are achieved by vacancies in the normal Ni atom sites and interstitial Ni atom in the normal vacancy sites, respectively. Therefore, the sublattice model \( (\text{Bi}_{0.3334}(\text{Ni},\text{Va})_{0.3333}(\text{Ni},\text{Va})_{0.3333} \text{Ni}_{0.3333}) \) is used in the present work. The second sublattice \( (\text{Ni},\text{Va})_{0.3333} \) means the normal Ni site with some vacancies, while the third one \( (\text{Ni},\text{Va})_{0.3333} \) means the normal interstitial site with some vacancies.
interstitial Ni atoms. Furthermore, the same model was employed to describe other intermetallic compounds with NiAs-type structure, CoSb and NiSb in the Co-Sb and Ni-Sb binary systems and Co-Ni-Sb ternary system by ZHANG et al[32–34]. The molar Gibbs energy of BiNi can be given as

$$G_{m}^{BiNi} = Y_{Ni}^{II} Y_{Va}^{II} G_{BiNi}^{BiNi} + Y_{Ni}^{III} Y_{Va}^{III} G_{BiNi}^{BiNi} + Y_{Va}^{II} Y_{Va}^{III} G_{BiNi}^{BiNi} +$$

$$+ Y_{Va}^{II} Y_{Va}^{III} G_{BiNi}^{BiNi} + 0.3333RT(y_{Ni}^{II} + y_{Ni}^{III}) +$$

$$Y_{Va}^{II} Y_{Va}^{II} Y_{Va}^{III} Y_{Va}^{III} G_{BiNi}^{BiNi} +$$

$$Y_{Ni}^{II} Y_{Ni}^{II} Y_{Ni}^{III} Y_{Ni}^{III} G_{NiNi}^{BiNi} +$$

$$Y_{Ni}^{II} Y_{Ni}^{II} Y_{Ni}^{III} Y_{Ni}^{III} G_{BiNi}^{BiNi} L_{BeNi}^{BiNi} +$$

$$Y_{Ni}^{II} Y_{Ni}^{II} Y_{Ni}^{III} Y_{Ni}^{III} G_{BiNi}^{BiNi} L_{BeNi}^{BiNi} +$$

$$+ Y_{Ni}^{II} Y_{Ni}^{II} Y_{Ni}^{III} Y_{Ni}^{III} G_{BiNi}^{BiNi} L_{BeNi}^{BiNi}$$

where

$$G_{BiNi}^{BiNi} = C_{0} + D_{0} T + E_{0} T \ln T + F_{0} T^{2} + G_{0} T^{3}$$

$$H_{0} T^{-1} + J_{0} T^{-2} + 0.3334 \theta_{G_{Bi}}^{ro} G_{Bi}^{ro} + 0.3334 \theta_{G_{Bi}}^{ro} G_{Bi}^{ro}$$

$$G_{BiNi}^{BeNi} = 0.3334 \theta_{G_{Bi}}^{ro} G_{Bi}^{ro} + 0.3334 \theta_{G_{Bi}}^{ro} G_{Bi}^{ro} + C_{1} + D_{1} T$$

$$G_{BiNi}^{BeNi} = 0.3334 \theta_{G_{Bi}}^{ro} G_{Bi}^{ro} + 0.3334 \theta_{G_{Bi}}^{ro} G_{Bi}^{ro} + C_{2} + D_{2} T$$

$$G_{BiNi}^{BeNi} = 0.3334 \theta_{G_{Bi}}^{ro} G_{Bi}^{ro} + C_{3} + D_{3} T$$

The enthalpies of mixing of liquid alloys at 1 773 K are calculated in the present work, as shown in Fig.6. It can be seen that, the calculated values are positive in Ni-rich side, but are negative in the Bi-rich side. The positive enthalpy of mixing of liquid phase in the Ni-rich side is corresponding with the smooth liquidus of the Bi-Ni phase diagram in Fig.2, which results in a possible metastable liquid miscibility gap at the low temperature. However, the calculated results need further experimental
Table 1 Thermodynamic parameters of Bi-Ni binary system

<table>
<thead>
<tr>
<th>Phase</th>
<th>Thermodynamic parameters*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid(Bi,Ni)</td>
<td>(L_{\text{liq}}^{(0)} = 46943.96 + 1.819T)</td>
</tr>
<tr>
<td></td>
<td>(L_{\text{liq}}^{(1)} = -13225.22 - 1.155T)</td>
</tr>
<tr>
<td>fcc(Ni)(Bi,Ni)</td>
<td>(E_{\text{fcc}} = 40000)</td>
</tr>
<tr>
<td>Rhombohedral(Bi)</td>
<td>[\theta ] (G_{\text{Bi}}^{\text{rho}}) cited from SGTE database[29]\</td>
</tr>
</tbody>
</table>

\[
G_{\text{Bi}_{x}\text{Ni}_{1-x}}^{\text{fliq}} = -4000 + 10T - 1.3057\ln T - 0.0021957T^2 + 1.8436 \times 10^{-6} T^3 + 46523.937T^{-1} + \]
\[
9.50315 \times 10^{-21} T^7 + 0.3334G_{\text{Bi}}^{\text{rho}} + 0.3333G_{\text{Ni}}^{\text{fliq}}
\]

\[
G_{\text{Bi}_{x}\text{Ni}_{1-x}}^{\text{fliq}} = 0.3334G_{\text{Bi}}^{\text{rho}} + 0.6666G_{\text{Ni}}^{\text{fliq}} + 5000
\]

\[
G_{\text{Bi}_{x}\text{Ni}_{1-x}}^{\text{fliq}} = 0.3334^\theta G_{\text{Bi}}^{\text{rho}} + 0.3333^\theta G_{\text{Ni}}^{\text{fliq}} + 3000
\]

\[
G_{\text{Bi}_{x}\text{Ni}_{1-x}}^{\text{fliq}} = 0.3334^\theta G_{\text{Bi}}^{\text{rho}} + 1500 + 1.87T
\]

\[
G_{\text{Bi}_{x}\text{Ni}_{1-x}}^{\text{fliq}} = 0.3334^\theta G_{\text{Bi}}^{\text{rho}} + G_{\text{Bi}_{x}\text{Ni}_{1-x}}^{\text{fliq}} - 2.453.42 + 8.187T
\]

\[
G_{\text{Bi}_{x}\text{Ni}_{1-x}}^{\text{fliq}} = -2.822.58 + 6.465T
\]

\[
G_{\text{Bi}_{x}\text{Ni}_{1-x}}^{\text{fliq}} = 0.75G_{\text{Bi}}^{\text{rho}} + 0.25G_{\text{Ni}}^{\text{fliq}} - 5000 + 4.87T
\]

* Note: Gibbs energies are expressed in J/mol and temperatures in Kelvin. The lattice stabilities of Bi and Ni are given by DINSDALE[29].

Table 2 Invariant reactions in Ni-Bi binary system

<table>
<thead>
<tr>
<th>Invariant reaction</th>
<th>Type</th>
<th>(T/K)</th>
<th>(x_{\text{Bi}}^L)</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>L + fcc(Ni) ↔ BiNi</td>
<td>Peritectic</td>
<td>927</td>
<td>–</td>
<td>Ref[23]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>911</td>
<td>0.760</td>
<td>Ref[24]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>919</td>
<td>0.814</td>
<td>Ref[15]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>919</td>
<td>0.762</td>
<td>Ref[16]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>921</td>
<td>0.759</td>
<td>Ref[17]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>925</td>
<td>0.799</td>
<td>Ref[19]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>927</td>
<td>0.784</td>
<td>This work</td>
</tr>
<tr>
<td>L + BiNi ↔ Bi3Ni</td>
<td>Peritectic</td>
<td>735</td>
<td>–</td>
<td>Ref[23]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>748</td>
<td>–</td>
<td>Ref[24]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>738</td>
<td>0.860</td>
<td>Ref[26]</td>
</tr>
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<td></td>
<td>738</td>
<td>0.913</td>
<td>Ref[15]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>737</td>
<td>0.877</td>
<td>Ref[16]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>741</td>
<td>0.881</td>
<td>Ref[17]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>741</td>
<td>0.920</td>
<td>Ref[18]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>744</td>
<td>0.905</td>
<td>This work</td>
</tr>
<tr>
<td>L ↔ Bi3Ni + rhombohedral (Bi)</td>
<td>Eutectic</td>
<td>542</td>
<td>–</td>
<td>Ref[23]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>543</td>
<td>0.9947</td>
<td>Ref[25]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>543</td>
<td>1.000</td>
<td>Ref[15]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>543</td>
<td>1.000</td>
<td>Ref[16]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>543</td>
<td>0.993</td>
<td>Ref[17]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>544</td>
<td>1.000</td>
<td>Ref[18]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>544</td>
<td>0.977</td>
<td>This work</td>
</tr>
</tbody>
</table>

Fig. 2 Calculated phase diagram of Bi-Ni binary system in present work compared with experimental data[15, 18, 23–24].

Fig. 3 Calculated phase diagram of Bi-Ni binary system in present work compared with experimental data[15, 18, 23–24].
verification because there is no reported experimental data on the mixing enthalpy of liquid phase in published literature.

Fig. 7 shows the calculated enthalpies of formation of the intermetallic compounds and the experimental data[28]. The calculated heat capacities of BiNi are compared with the experimental data[19] and shown in Fig. 8. Obviously, the calculated results are in good agreement with the experimental data.

![Fig.4](image1) Calculated activity of Bi at 1753 K with experimental data in Ref.[16] (Referred state: liquid Bi)

![Fig.5](image2) Calculated activities of Ni at 1073 K (a) and 1773 (b) with experimental data in Ref.[27] (Referred state: liquid Ni)

![Fig.6](image3) Calculated enthalpies of mixing of liquid alloys at 1773 K in present work (Referred states: liquid Bi and liquid Ni)

![Fig.7](image4) Calculated enthalpies of formation of intermetallic compounds in comparison with experimental data in Ref.[28] at 298 K (Referred states: solid Bi and solid Ni)

![Fig.8](image5) Calculated heat capacity of intermetallic compound BiNi with experimental data in Ref.[19]
agreement with the experimental data.

5 Conclusions

1) The present work reviewed critically the experimental information on phase diagram and thermodynamic properties of the Bi-Ni binary system in published literature.

2) Using the CALPHAD method, thermodynamic modelling of the Bi-Ni binary system was performed through the Thermo-calc® software package.

3) A set of self-consistent thermodynamic parameters formulating the Gibbs energies of various phases in the Bi-Ni binary system were obtained, which can reproduce well most of the experimental data on thermodynamic properties and phase diagram.

References

热力学优化 Bi-Ni 二元系

王江, 孟凡桂, 刘立斌, 金展鹏

1. 桂林电子科技大学 材料科学与工程学院，桂林 541004；
2. 中南大学 材料科学与工程学院，长沙 410083；
3. 瑞士联邦材料测试与研究实验室 焊接与界面技术实验室，苏黎世 CH-8600；
4. 中南林业科技大学 材料科学与工程学院，长沙 410004

摘 要: 基于文献报导的实验数据，采用相图计算（CALPHAD）方法，热力学优化了 Bi-Ni 二元系相图。该二元系的液相、fcc_A1(Ni) 相和 rhombohedral_A7(Bi) 相用替换溶液模型来描述，其过剩吉布斯自由能用 Redlich-Kister 多项式来表达。考虑到晶体结构(NiAs 型)以及与多组元体系热力学数据库的兼容性，中间化合物 BiNi 相采用亚点阵模型: (Bi)(Ni,Va)(Ni,Va); Bi3Ni 相处理为化学计量比化合物。最后，通过优化该二元系实测的相图和热力学数据，获得一组能够表达各相吉布斯自由能的自洽的热力学参数。根据这些热力学参数计算的相图和热力学数据与报导的实验数据吻合良好。

关键词: 锡基合金; 相图; 热力学; 相图计算; Bi-Ni 二元系

(Edited by YANG Hua)