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Thermodynamic optimization of Bi-Ni binary system

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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_A1(Ni) and rhombohedral_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_3Ni 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

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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-system was considered here.

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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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]. SHAVINSKI et al[25] reported that the composition and temperature of the eutectic reaction, L↔Bi_3Ni+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 Bi_3Ni 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 Bi_3Ni 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 spectroscope 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 ϕ status is given as

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

$$dT^2+eT^3+fT^{-1}+gT^7+hT^{-9} \quad (1)$$

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

3.2 Solution phases

The solid solution phase ϕ (ϕ =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:

$$G_{\mathrm{m}}^{\phi}=x_{\mathrm{Bi}}\,{}^{\Theta}G_{\mathrm{Bi}}^{\phi}+x_{\mathrm{Ni}}\,{}^{\Theta}G_{\mathrm{Ni}}^{\phi}+RT(x_{\mathrm{Bi}}\ln x_{\mathrm{Bi}}+x_{\mathrm{Ni}}\ln x_{\mathrm{Ni}})+$$

$$x_{\mathrm{Bi}}x_{\mathrm{Ni}}\sum_{i=0}^{n}{}^{i}L^{\phi}(x_{\mathrm{Bi}}-x_{\mathrm{Ni}})^i \quad (2)$$

where R is the gas constant; x_{Bi} and x_{Ni} are the mole fractions of Bi and Ni, respectively; and ${}^{i}L^{\phi}$ is the interaction parameter dependent on temperature:

$${}^{i}L^{\phi}=A_i+B_iT \quad (3)$$

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 $(\mathrm{Bi})_{0.3334}(\mathrm{Ni,Va})_{0.3333}(\mathrm{Ni,Va})_{0.3333}$ is used in the present work. The second sublattice $(\mathrm{Ni,Va})_{0.3333}$ means the normal Ni site with some vacancies, while the third one $(\mathrm{Ni,Va})_{0.3333}$ means the normal interstitial site with some

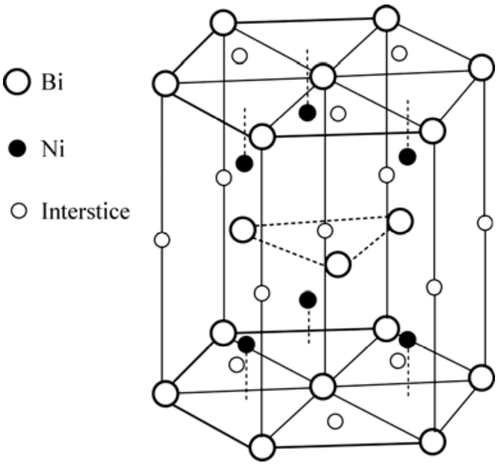

Fig.1 Schematic crystal structure of NiAs-type phase for intermetallic compound BiNi

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

$$\begin{aligned}G_{\rm m}^{\rm BiNi}={}&Y_{\rm Ni}^{\rm II}Y_{\rm Va}^{\rm III}G_{\rm Bi:Ni:Va}^{\rm BiNi}+Y_{\rm Ni}^{\rm II}Y_{\rm Ni}^{\rm III}G_{\rm Bi:Ni:Ni}^{\rm BiNi}+Y_{\rm Va}^{\rm II}Y_{\rm Ni}^{\rm III}G_{\rm Bi:Va:Ni}^{\rm BiNi}+\\&Y_{\rm Va}^{\rm II}Y_{\rm Va}^{\rm III}G_{\rm Bi:Va:Va}^{\rm BiNi}+0.3333RT(Y_{\rm Ni}^{\rm II}\ln Y_{\rm Ni}^{\rm II}+\\&Y_{\rm Va}^{\rm II}\ln Y_{\rm Va}^{\rm II}+Y_{\rm Va}^{\rm III}\ln Y_{\rm Va}^{\rm III}+Y_{\rm Ni}^{\rm III}\ln Y_{\rm Ni}^{\rm III})+\\&Y_{\rm Ni}^{\rm II}Y_{\rm Ni}^{\rm III}Y_{\rm Va}^{\rm III}\,{}^{0}L_{\rm Bi:Ni:Ni,Va}^{\rm BiNi}+Y_{\rm Va}^{\rm II}Y_{\rm Ni}^{\rm III}Y_{\rm Va}^{\rm III}\,{}^{0}L_{\rm Bi:Va:Ni,Va}^{\rm BiNi}+\\&Y_{\rm Ni}^{\rm II}Y_{\rm Va}^{\rm II}Y_{\rm Va}^{\rm III}\,{}^{0}L_{\rm Bi:Ni,Va:Va}^{\rm BiNi}+Y_{\rm Ni}^{\rm II}Y_{\rm Va}^{\rm II}Y_{\rm Ni}^{\rm III}\,{}^{0}L_{\rm Bi:Ni,Va:Ni}^{\rm BiNi}\end{aligned}\tag{4}$$

with

$$\begin{aligned}G_{\rm Bi:Ni:Va}^{\rm BiNi}={}&C_0+D_0T+E_0T\ln T+F_0T^2+G_0T^3+\\&H_0T^{-1}+J_0T^7+0.333\,4\,{}^{\Theta}G_{\rm Bi}^{\rm rho}+0.333\,3\,{}^{\Theta}G_{\rm Ni}^{\rm fcc}\end{aligned}\tag{5}$$

$$G_{\rm Bi:Ni:Ni}^{\rm BiNi}=0.333\,4\,{}^{\Theta}G_{\rm Bi}^{\rm roh}+0.666\,6\,{}^{\Theta}G_{\rm Ni}^{\rm fcc}+C_1+D_1T\tag{6}$$

$$G_{\rm Bi:Va:Ni}^{\rm BiNi}=0.333\,4\,{}^{\Theta}G_{\rm Bi}^{\rm rho}+0.333\,3\,{}^{\Theta}G_{\rm Ni}^{\rm fcc}+C_2+D_2T\tag{7}$$

$$G_{\rm Bi:Va:Va}^{\rm BiNi}=0.333\,4\,{}^{\Theta}G_{\rm Bi}^{\rm rho}+C_3+D_3T\tag{8}$$

where ${}^{\Theta}G_{\rm Bi}^{\rm rho}$ and ${}^{\Theta}G_{\rm Ni}^{\rm fcc}$ are the Gibbs energies of elements Bi and Ni at their respective standard states, and are taken from Ref.[29]; $Y_i^{\rm II}$ and $Y_i^{\rm III}$ denote mole fraction of i in the second and third sublattices, respectively; ${}^{0}L_{\rm Bi:Ni:Va,Ni}^{\rm BiNi}$, ${}^{0}L_{\rm Bi:Va:Va,Ni}^{\rm BiNi}$, ${}^{0}L_{\rm Bi:Ni,Va:Va}^{\rm BiNi}$, ${}^{0}L_{\rm Bi:Ni,Va:Ni}^{\rm BiNi}$ are the interactive parameters, and optimized as dependent temperature. The parameters from C_0 to J_0 as well as C_i and D_i are assessed in the present work.

On the other hand, intermetallic compound $\rm Bi_3Ni$ is treated as a stoichiometric compound because of its limited homogeneity range. The molar Gibbs energy of $\rm Bi_3Ni$ is given as follows:

$$G_{\rm m}^{\rm Bi_3Ni}=0.25\,{}^{\Theta}G_{\rm Ni}^{\rm fcc}+0.75\,{}^{\Theta}G_{\rm Bi}^{\rm rho}+C_4+D_4T\tag{9}$$

where the parameters C_4 and D_4 are to be optimized.

4 Results and discussion

Using the lattice stabilities of Bi and Ni cited from Ref.[29], the optimization of the model parameters was performed using the PARROT module in the Thermo-calc® software package developed by SUNDMAN et al[22]. This module works by minimizing the square sum of the differences between the experimental data and calculated values. In the optimization procedure, each set of the experimental data is given a certain weight according to the reliability and compatibility of the experimental data. Thermodynamic parameters for all condensed phases in the Bi-Ni binary system are summarized in Table 1. The calculated temperatures and composition of all invariant reactions in this binary system are compared with the experimental data and listed in Table 2.

Fig.2 shows the calculated phase diagram of the Bi-Ni binary system in the present work. The comparison of the calculated phase diagram with the experimental data[15, 18, 23−24] is given in Fig. 3. In combination with Table 2, it can be seen that the calculated liquidus, sodidus, the homogeneity region of intermetallic compound BiNi, as well as temperatures and compositions of the invariant reactions are in good agreement with the experimental data[23−24] and the previous results assessed by Refs.[15−18].

Fig.4 presents the calculated activities of Bi in liquid phase at 1753 K with the limited experimental data[16]. The calculated activities of Ni at 1 073 K and 1 773 K are compared respectively with the experimental data[27] and shown in Fig.5. It is evident that the calculated results are in good agreement with the experimental results[16, 27].

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

Phase	Thermodynamic parameters*
Liquid(Bi,Ni)	${}^{(0)}L^{\mathrm{Liq}}=+6\,943.96+1.819T$
	${}^{(1)}L^{\mathrm{Liq}}=-13\,225.22-1.155T$
fcc(Ni)(Bi,Ni)	${}^{(0)}L^{\mathrm{fcc}}=+40\,000$
Rhombohedral(Bi)	${}^{\Theta}G_{\mathrm{Bi}}^{\mathrm{rho}}$ cited from SGTE database[29]
BiNi(Bi)$_{0.3334}$(Ni,Va)$_{0.3333}$(Ni,Va)$_{0.3333}$	$G_{\mathrm{Bi:Ni:Va}}^{\mathrm{BiNi}}=-4\,000+10T-1.305T\ln T-0.002\ 195T^2+1.843\,6\times10^{-6}T^3+46\,523.93T^{-1}+$ $9.503\,515\times10^{-21}T^7+0.333\,4{}^{\Theta}G_{\mathrm{Bi}}^{\mathrm{rho}}+0.333\,3{}^{\Theta}G_{\mathrm{Ni}}^{\mathrm{fcc}}$
	$G_{\mathrm{Bi:Ni:Ni}}^{\mathrm{BiNi}}=0.333\,4{}^{\Theta}G_{\mathrm{Bi}}^{\mathrm{rh.}}+0.666\,6{}^{\Theta}G_{\mathrm{Ni}}^{\mathrm{fcc}}+5\,000$
	$G_{\mathrm{Bi:Va:Ni}}^{\mathrm{BiNi}}=0.333\,4{}^{\Theta}G_{\mathrm{Bi}}^{\mathrm{rho}}+0.333\,3{}^{\Theta}G_{\mathrm{Ni}}^{\mathrm{fcc}}+3\,000$
	$G_{\mathrm{Bi:Va:Va}}^{\mathrm{BiNi}}=0.333\,4{}^{\Theta}G_{\mathrm{Bi}}^{\mathrm{rho}}+1\,500+1.8T$
	${}^{(0)}L_{\mathrm{Bi:Ni:Va,Ni}}^{\mathrm{BiNi}}={}^{(0)}L_{\mathrm{Bi:Va:Va,Ni}}^{\mathrm{BiNi}}=-2\,453.42+8.187T$
	${}^{(0)}L_{\mathrm{Bi:Ni,Va:Va}}^{\mathrm{BiNi}}={}^{(0)}L_{\mathrm{Bi:Ni,Va:Ni}}^{\mathrm{BiNi}}=-2\,822.58+6.465T$
Bi$_3$Ni(Bi)$_{0.75}$(Ni)$_{0.25}$	$G_{\mathrm{m}}^{\mathrm{Bi_3Ni}}=0.75G_{\mathrm{Bi}}^{\mathrm{rho.}}+0.25G_{\mathrm{Ni}}^{\mathrm{fcc}}-5\,500+4.8T$

* 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

Invariant reaction	Type	T/K	$x_{\mathrm{Bi}}^{\mathrm{L}}$	Literature
L + fcc(Ni)↔ BiNi	Peritectic	927	−	Ref.[23]
		911	−	Ref.[24]
		919	0.760	Ref.[26]
		919	0.814	Ref.[15]
		919	0.762	Ref.[16]
		921	0.759	Ref.[17]
		925	0.799	Ref.[19]
		927	0.784	This work
L +BiNi↔ Bi$_3$Ni	Peritectic	735	−	Ref.[23]
		748	−	Ref.[24]
		738	0.860	Ref.[26]
		738	0.913	Ref.[15]
		738	0.877	Ref.[16]
		737	0.881	Ref.[17]
		741	0.920	Ref.[18]
		744	0.905	This work
L ↔ Bi$_3$Ni + rhombohedral (Bi)	Eutectic	542	−	Ref.[23]
		543	−	Ref.[24]
		544	−	Ref.[26]
		543	0.9947	Ref.[25]
		543	1.000	Ref.[15]
		543	1.000	Ref.[16]
		543	0.993	Ref.[17]
		544	1.000	Ref.[18]
		544	0.997	This work

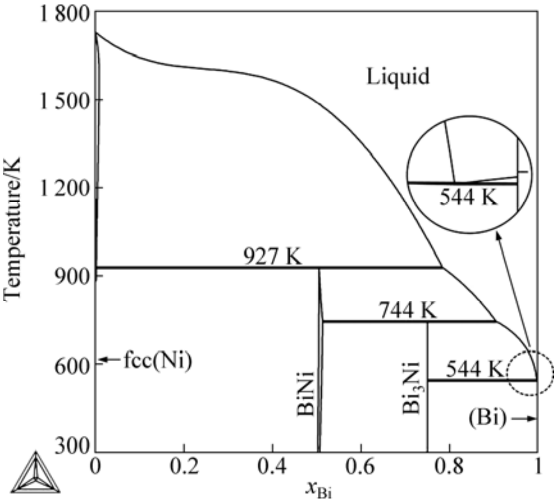

Fig.2 Calculated phase diagram of Bi-Ni binary system in present work

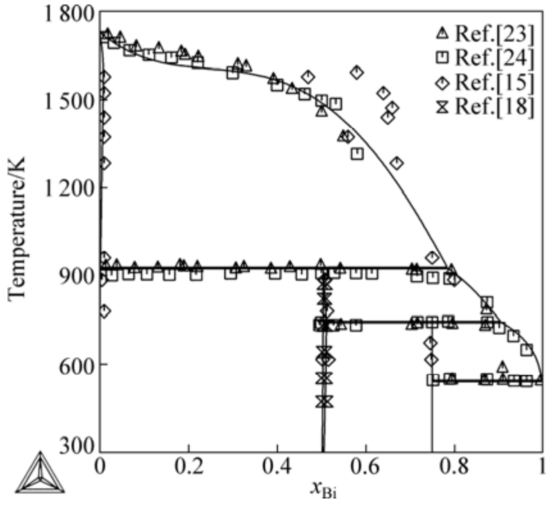

Fig.3 Calculated phase diagram of Bi-Ni binary system in present work compared with experimental data[15, 18, 23−24]

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

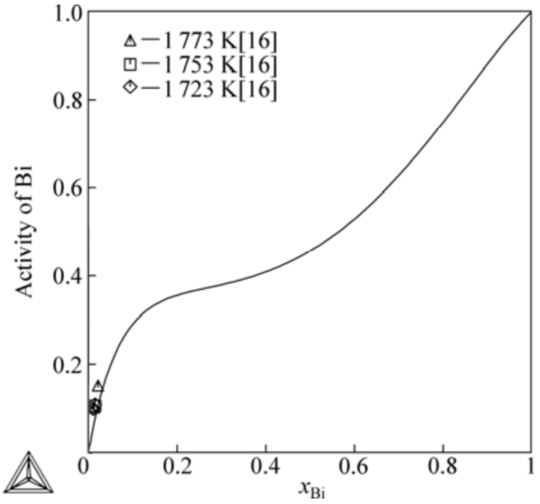

Fig.4 Calculated activity of Bi at 1 753 K with experimental data in Ref.[16] (Referred state: liquid Bi)

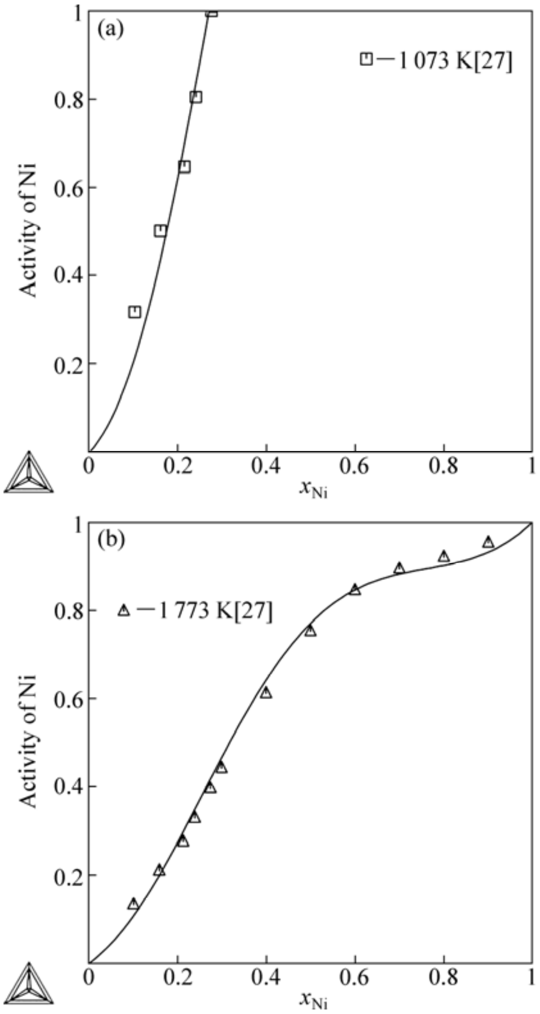

Fig.5 Calculated activities of Ni at 1 073 K (a) and 1 773 (b) with experimental data in Ref.[27] (Referred state: liquid Ni)

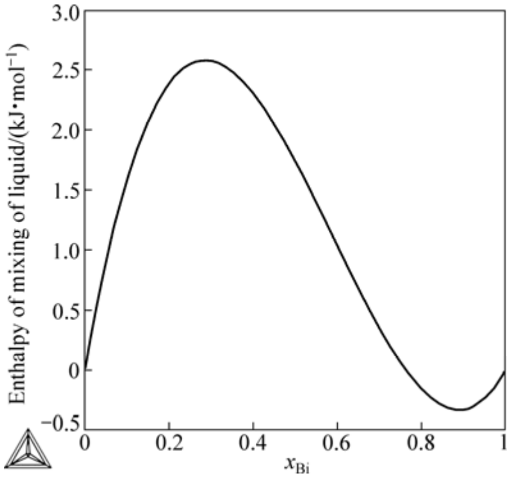

Fig.6 Calculated enthalpies of mixing of liquid alloys at 1 773 K in present work (Referred states: liquid Bi and liquid Ni)

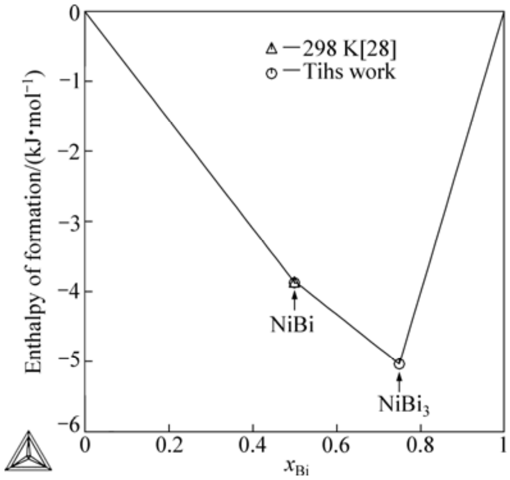

Fig.7 Calculated enthalpies of formation of intermetallic compounds in comparison with experimental data in Ref.[28] at 298 K (Referred states: solid Bi and solid Ni)

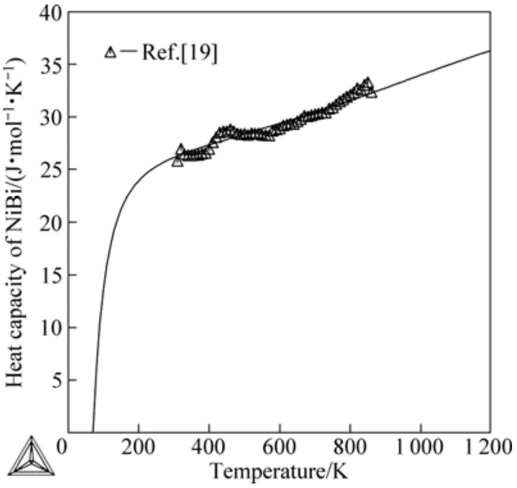

Fig.8 Calculated heat capacity of intermetallic compound BiNi with experimental data in Ref.[19]

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.

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热力学优化 Bi-Ni 二元系

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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)；Bi_3Ni 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

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