Thermodynamic Study of Phase Equilibria in the Ni–Fe–B System

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The phase equilibria in the Ni–Fe–B ternary system have been studied experimentally and using thermodynamic calculations. The Gibbs energy of the individual phases was described by the regular solution approximation and the two-sublattice model. The thermodynamic parameters for each phase were evaluated using the experimental data on phase boundaries obtained from differential scanning calorimetry (DSC) and other available literature data. The evaluated parameters enabled us to obtain reproducible calculations of the isothermal section diagrams. The calculated isopleth at the 26 mol% B section agreed with the DSC data obtained in this study, whereas the calculated liquidus and solidus temperatures were higher than the reported values at the Ni₂B–Fe₂B pseudo-binary section.

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1. Introduction

A thermodynamic description for the Ni–Fe–B ternary system is of interest in several fields of materials engineering. For example, boron is a commonly known alloying element that enhances the hardenability of steels, and forms Ni- or Fe-based amorphous alloys. Recently, the effect of boron addition on the hardenability, mechanical properties, and workability of steels, stainless steels, and heat-resistant steels has been reviewed.¹⁾ In addition, in Ni-based brazing filler metals and Ni-based self-fluxing alloys, boron is added to reduce the melting temperatures and to improve fluidity. Furthermore, metallic composite materials comprised of various transition metal borides have attractive wear- or corrosion-resistant properties.^{2,3)} Therefore, information on the phase equilibria of the Ni–Fe–B ternary system is required to develop a wide variety of B-containing alloys.

The CALculation of PHase Diagrams (CALPHAD) approach⁴⁾ provides a powerful tool for obtaining information on physical parameters, such as the amount and composition of constituent phases, and the liquidus and solidus temperatures.

In the present study, a thermodynamic analysis of the Ni–Fe–B ternary system has been carried out by combining the experimental results obtained from differential scanning calorimetry with literature data on the phase relationships.

2. Experimental Procedures

The phase boundaries of the Ni–Fe–B ternary system were measured using differential scanning calorimetry (DSC) in the section with 26 mol% B. The starting materials used were Ni (99.9%), Fe (99.998%), and B (99%) powders. The nominal compositions of the prepared samples are listed in Table 1. The alloys for the DSC measurements were prepared by arc melting cold-pressed pellets, each of about 10 g in weight, in an argon atmosphere. A titanium button was melted to getter any residual oxygen in the chamber before melting the actual charges. The arc-melted alloys were re-melted under vacuum using an induction heater to ensure sample homogeneity. The as-cast alloys were then encapsulated in transparent quartz tubes under vacuum, and then annealed at 950°C for 7 d before being quenched in water. After the heat treatment, the actual compositions of samples were chemically analyzed. According to the results, the Ni/Fe ratios obtained by chemical analysis were consistent with the nominal ratios within the experimental uncertainties, whereas the losses of B were observed. Hence, the alloy compositions were corrected based on the results of chemical analysis. The corrected compositions are listed in Table 1. Thermal analysis was carried out using a Seiko EX-STAR6300 DSC (Seiko Instruments Inc., Chiba, Japan) on cylindrical samples heated and cooled in Al₂O₃ crucibles at a rate of 5°C/min under flowing purified argon using an α -

Table 1 Alloy compositions, experimental results from DSC on heating, and the calculated liquidus temperatures of Ni–Fe–B ternary alloys.

Alloy composition (mol%)						Peak temperature (°C)			Calculated liquidus temperature (°C)
Nominal			Corrected						
Ni	Fe	B	Ni	Fe	B				
60	12	28	62.2	11.4	26.4	1072	1096	1128	1137
50	22	28	52.0	23.2	24.8	1056	1095	1201	1192
40	32	28	40.8	34.3	24.9	1055	1090	1268	1260
30	42	28	28.1	45.6	26.3	1059	1091	1304	1331
20	52	28	17.4	57.4	25.2	1084	1088	1345	1350

Al₂O₃ reference standard. The peak temperature values during heating were adopted in our thermodynamic analysis to avoid any experimental errors caused by supercooling. The peak temperatures during heating are shown in Table 1.

3. Thermodynamic Description

In the present modeling of the Ni–Fe–B system, the thermodynamic parameters in the Ni–Fe and Fe–B systems were taken from Dinsdale and Chart⁵⁾ and Pan,⁶⁾ respectively. For the Ni–B system, the parameters assessed by Tokunaga *et al.*,⁷⁾ based on the results of Campbell and Kattner,⁸⁾ were adopted. In the latter two modelings, boron was treated as a substitutional element in the bcc or fcc phases, and the solubility of Ni or Fe in β -rhombohedral B was not taken into account because of the negligible solubility.

For the liquid and terminal solid solution phases, the Gibbs energy was expressed using the regular solution approximation as follows:

$$G_m^\phi = x_B {}^\circ G_B^\phi + x_{Fe} {}^\circ G_{Fe}^\phi + x_{Ni} {}^\circ G_{Ni}^\phi + RT(x_B \ln x_B + x_{Fe} \ln x_{Fe} + x_{Ni} \ln x_{Ni})$$

$$+ x_B x_{Fe} L_{B,Fe}^\phi + x_{Fe} x_{Ni} L_{Fe,Ni}^\phi + x_B x_{Ni} L_{B,Ni}^\phi + x_B x_{Fe} x_{Ni} L_{B,Fe,Ni}^\phi, \quad (1)$$

where ${}^\circ G_i^\phi$ is the lattice stability, and denotes the Gibbs energy of element i in the ϕ phase state. The descriptions of the lattice stability parameters were taken from the Scientific Group Thermodata Europe (SGTE) data file,⁹⁾ where the Gibbs energy of each element is defined with respect to its stable state at 25°C and 101325 Pa, and are listed in Table 2. R is the gas constant, and x_B , x_{Fe} and x_{Ni} denote the mole fractions of B, Fe, and Ni, respectively. The parameter $L_{i,j}^\phi$ denotes the interaction energy between elements i and j in the ϕ phase. The term $L_{B,Fe,Ni}^\phi$ is the ternary interaction parameter between elements B, Fe, and Ni. The composition dependency of the interaction parameters $L_{i,j}^\phi$ and $L_{B,Fe,Ni}^\phi$ is expressed by eqs. (2) and (3), respectively.

$$L_{i,j}^\phi = \sum_n (x_i - x_j)^n \cdot {}^n L_{i,j}^\phi, \quad (2)$$

$$L_{B,Fe,Ni}^\phi = x_B \cdot {}^0 L_{B,Fe,Ni}^\phi + x_{Fe} \cdot {}^1 L_{B,Fe,Ni}^\phi + x_{Ni} \cdot {}^2 L_{B,Fe,Ni}^\phi. \quad (3)$$

Table 2 The lattice stability parameters for Ni, Fe, and B.

Element	Phase	Lattice stability parameters (J/mol)	Temperature (K)
Ni	L	${}^\circ G_{Ni}^L = 11235.527 + 108.457T - 22.096T \ln T - 0.00484077T^2$ $- 3.82318 \times 10^{-21} T^7$ $= -9549.775 + 268.598T - 43.1T \ln T$	$298 < T < 1728$ $1728 < T < 3000$
		${}^\circ G_{Ni}^{fcc} = -5179.159 + 117.854T - 22.096T \ln T - 0.00484077T^2$ $= -27840.655 + 279.135T - 43.1T \ln T + 1.12754 \times 10^{31} T^{-9}$ $T_{C(Ni)}^{fcc} = 633, \beta_{Ni}^{fcc} = 0.52$	$298 < T < 1728$ $1728 < T < 3000$ $298 < T < 6000$
		${}^\circ G_{Ni}^{bcc} = 8715.084 - 3.556T + {}^\circ G_{Ni}^{fcc}$ $T_{C(Ni)}^{bcc} = 575, \beta_{Ni}^{bcc} = 0.85$	$298 < T < 6000$
	bcc	${}^\circ G_{Fe}^L = 12040.17 - 6.55843T - 3.6751551 \times 10^{-21} T^7 + {}^\circ G_{Fe}^{bcc}$ $= -10839.7 + 291.302T - 46T \ln T$	$298 < T < 1811$ $1811 < T < 6000$
		${}^\circ G_{Fe}^{bcc} = 1225.7 + 124.134T - 23.5143T \ln T - 0.00439752T^2$ $- 5.8927 \times 10^{-8} T^3 + 77359T^{-1}$ $= -25383.581 + 299.31255T - 46T \ln T + 2.29603 \times 10^{31} T^{-9}$ $T_{C(Fe)}^{bcc} = 1043, \beta_{Fe}^{bcc} = 2.22$	$298 < T < 1811$ $1811 < T < 6000$ $298 < T < 6000$
		${}^\circ G_{Fe}^{fcc} = -1462.4 + 8.282T - 1.15T \ln T + 6.4 \times 10^{-4} T^2 + {}^\circ G_{Fe}^{bcc}$ $= -27098.266 + 300.25256T - 46T \ln T + 2.78854 \times 10^{31} T^{-9}$ $T_{C(Fe)}^{fcc} = -201, \beta_{Fe}^{fcc} = -2.1$	$298 < T < 1811$ $1811 < T < 6000$ $298 < T < 6000$
Fe	L	${}^\circ G_B^L = 40723.275 + 86.843839T - 15.6641T \ln T - 0.006864515T^2$ $+ 6.18878 \times 10^{-7} T^3 + 370843T^{-1}$ $= 41119.703 + 82.101722T - 14.9827763T \ln T$ $- 0.007095669T^2 + 5.07347 \times 10^{-7} T^3 + 335484T^{-1}$ $= 28842.012 + 200.94731T - 31.4T \ln T$	$298 < T < 500$ $500 < T < 2348$ $2348 < T < 6000$
		$G_B^{\beta\text{-rhombohedral}} = -7735.284 + 107.111864T - 15.6641T \ln T$ $- 0.006864515T^2 + 6.18878 \times 10^{-7} T^3 + 370843T^{-1}$ $= -16649.474 + 184.801744T - 26.6047T \ln T$ $- 7.9809 \times 10^{-4} T^2 - 2.556 \times 10^{-8} T^3 + 1748270T^{-1}$ $= -36667.582 + 231.336244T - 31.5957527T \ln T$ $- 0.00159488T^2 + 1.34719 \times 10^{-7} T^3 + 11205883T^{-1}$ $= -21530.653 + 222.396264T - 31.4T \ln T$	$298 < T < 1100$ $1100 < T < 2348$ $2348 < T < 3000$ $3000 < T < 6000$
		${}^\circ G_B^{bcc} = 43514 - 12.217T + {}^\circ G_B^{\beta\text{-rhombohedral}}$	$298 < T < 6000$
	β -rhombohedral	${}^\circ G_B^{fcc} = 50208 - 13.472T + {}^\circ G_B^{\beta\text{-rhombohedral}}$	$298 < T < 6000$
B	bcc		

The Gibbs energy contributions due to the ferromagnetic ordering of a phase, such as the bcc phase, were described using the model of Hillert and Jarl¹⁰⁾

$${}^{\text{mag}}G_m^\phi = RT \ln(\beta^\phi + 1)f(\tau), \quad (4)$$

where ${}^{\text{mag}}G_m^\phi$ is the Gibbs energy of magnetic ordering, β^ϕ is the average magnetic moment per atom in the ϕ phase (expressed in Bohr magnetons), and $f(\tau)$ is a polynomial function of τ . The term τ is defined as T/T_C^ϕ , where T_C^ϕ is the critical temperature of the magnetic transition in the ϕ phase. Both β^ϕ and T_C^ϕ can be concentration-dependent, and are represented by an equation similar to that of eq. (2).

Except for Ni_3B , Ni_2B , Fe_2B , FeB , and NiB , the other binary compound phases were treated as being pure binary phases based on the experimental results, as described in the next section. Borides that can dissolve a different metallic element are considered to be stoichiometric with respect to the boron content, and the Gibbs energy of φ boride having the formula M_mB_n (where M represents Fe or Ni) was described using the two-sublattice model,¹¹⁾ assuming one sublattice was occupied by Fe and Ni atoms, and the other sublattice was occupied by B atoms as follows:

$$G = y_{\text{Fe}} \cdot {}^\circ G_{\text{Fe:B}}^\varphi + y_{\text{Ni}} \cdot {}^\circ G_{\text{Ni:B}}^\varphi + mRT(y_{\text{Fe}} \ln y_{\text{Fe}} + y_{\text{Ni}} \ln y_{\text{Ni}}) + y_{\text{Fe}}y_{\text{Ni}} \cdot L_{\text{Fe,Ni:B}}^\varphi, \quad (5)$$

where ${}^\circ G_{\text{Fe:B}}^\varphi$ and ${}^\circ G_{\text{Ni:B}}^\varphi$ represent the Gibbs energies of pure Fe_mB_n and Ni_mB_n , respectively. The term $L_{\text{Fe,Ni:B}}^\varphi$ is the interaction parameter between Fe and Ni in the metallic sublattice, and is described by an equation similar to eq. (2). The term y_i is the site fraction of element i in the metallic sublattice.

For the pure binary compound phases, M_aB_b , the Gibbs energy per mole of atoms was expressed using following equation:

$$G_m^{\text{M}_a\text{B}_b} = \frac{a}{a+b} \cdot {}^\circ G_M^{\text{ref}} + \frac{b}{a+b} \cdot {}^\circ G_B^{\beta\text{-rhombohedral}} + \Delta G_{\text{M}_a\text{B}_b}^f, \quad (6)$$

where ${}^\circ G_M^{\text{ref}}$ denotes the reference state of the metallic elements. The term $\Delta G_{\text{M}_a\text{B}_b}^f$ is the Gibbs energy of formation per mole of atoms of the boride. It can be expressed using the following equation:

$$\Delta G_{\text{M}_a\text{B}_b}^f = A + B \cdot T. \quad (7)$$

4. Thermodynamic Analysis and Calculation of the Phase Diagrams

In the Ni-Fe-B ternary system, Kaneko *et al.*¹²⁾ and Stadelmaier and Pollock¹³⁾ have investigated the phase relationships at 700 and 800°C, respectively, at the Ni-Fe side using microscopy and X-ray diffraction techniques, where Kaneko *et al.* did not identify a stable Ni_3B phase in the Ni-B system. Kuz'ma and Koval¹⁴⁾ have provided the isothermal section diagrams at 800°C over the entire composition range using both microscopy and X-ray diffraction. According to the experimental results,¹²⁻¹⁴⁾ a continuous series of solid solutions is formed between the tetragonal borides Fe_2B and Ni_2B , where both borides have

the same crystal structure (CuAl₂-type). Hereafter, these are denoted as the $\text{M}_2\text{B}_{\text{tet}}$ phase. For the Ni_3B phase, the solubility of Fe reaches about 45 mol% Fe.^{13,14)} Although Kuz'ma and Koval¹⁴⁾ could not determine the solubility limit accurately, the FeB phase dissolves not less than 5 mol% Ni, whereas NiB does not dissolve any appreciable amounts of Fe (less than 5 mol% Fe).¹⁴⁾ Tavadze *et al.*^{15,16)} have studied the phase equilibria in the Fe_2B - Ni_2B section of the pseudo-binary system. They also confirmed the existence of a complete solid solution existing between both borides, and they provided the liquidus and solidus temperatures in this pseudo-binary system. Gianoglio and Badini¹⁷⁾ have studied the variation in lattice parameter at 800°C at the Fe_2B - Ni_2B and FeB - NiB sections. They reported that a complete solid solution exists between the Fe_2B and Ni_2B , and that Ni atoms can substitute for Fe in the FeB phase up to 70 mol%, whereas Fe atoms can substitute for Ni in the NiB phase up to 15 mol%. The results on the solubility of metallic elements in both the FeB and NiB phases are different from those obtained by Stadelmaier and Pollock¹³⁾ and Kuz'ma and Koval.¹⁴⁾ It seems that these discrepancies are due to differences in the duration of a heat treatment, as Gianoglio and Badini heated the alloys to 800°C for 20 h at most, while on the other hand, Kuz'ma and Koval annealed their samples at 800°C for 600 h. Therefore, the experimental diagram described by Gianoglio and Badini may not have reached equilibrium state. Loo and Beek¹⁸⁾ have reported on the isothermal section diagram at 925°C at the Ni-Fe side, and their results are almost the same as those of Stadelmaier and Pollock,¹³⁾ and Kuz'ma and Koval.¹⁴⁾

Although no stable ternary compound phase has been reported in the Ni-Fe-B ternary system, a metastable $\text{Ni}_{20}\text{Fe}_3\text{B}_6$ phase with a Cr_{23}C_6 -type structure has been reported.¹³⁾ There are no experimental data available on the thermodynamic properties of the Ni-Fe-B system.

In the present study, the thermodynamic parameters of the Ni-Fe-B system have been evaluated based on the experimental data of Stadelmaier and Pollock,¹³⁾ Kuz'ma and Koval,¹⁴⁾ and Loo and Beek¹⁸⁾ as well as the present DSC results. It is noted that, since we could not obtain ternary parameters to fit to the experimental data of Tavadze *et al.*^{15,16)} with other experimental data as well as the DSC data in our preliminary analysis, the data of Tavadze *et al.* were not adopted finally. Because of the lack of experimental information on the phase stability of the nonstable NiB phase with the same structure as that of the stable FeB phase, the parameter ${}^\circ G_{\text{Ni:B}}^{\text{FeB}}$ was determined in accordance with the following equation:

$${}^\circ G_{\text{Ni:B}}^{\text{FeB}} - {}^\circ G_{\text{Ni:B}}^{\text{NiB}} = E_{\text{total}}^{\text{FeB(Ni:B)}} - E_{\text{total}}^{\text{NiB(Ni:B)}}, \quad (8)$$

where $E_{\text{total}}^{\text{FeB(Ni:B)}}$ and $E_{\text{total}}^{\text{NiB(Ni:B)}}$ represent the total energies of the nonstable NiB phase with the same structure as that of the stable FeB phase and the stable NiB phase, respectively. The total energies were obtained from *ab initio* energetic calculations using the WIEN2k software package,¹⁹⁾ based on the Full Potential Linearized Augmented Plane Wave (FLAPW) method within the generalized gradient approximation (GGA),²⁰⁾ and calculations of the total energy as a function of the cell volume were performed around the equilibrium cell volumes. Since there is no information

available on the atomic positions for both the stable and nonstable NiB phases, both phases referred to the atomic positions of their prototype structures, CrB (Pearson Symbol *oC8*, Space Group *Cmcm*) and FeB (Pearson Symbol *hI12*, Space Group *I4/mcm*),²¹⁾ respectively. In our calculations, we assumed muffin-tin radii of 2.0 a.u. (0.106 nm) for Ni, and 1.4 a.u. (0.074 nm) for B, and the value of $RK_{\max}$ was fixed at 6.26 for B atom, which almost corresponds to the cut-off energy of 20 Ry. It is noteworthy that the parameters $^{\circ}G_{\text{Fe:B}}^{\text{NiB}}$ and $^{\circ}G_{\text{Fe:B}}^{\text{NiB}}$ were taken from the data of the Fe–B–C–Cr–Ti system obtained by Furukawa.²²⁾ The thermodynamic parameters obtained for the Ni–Fe–B ternary system are listed in Table 3.

The calculated isothermal section diagrams at 800 and

925°C are shown in Figs. 1 and 2, respectively, together with the experimental isothermal sections.^{14,18)} The experimental isothermal section of Kuz'ma and Koval¹⁴⁾ includes NiB₆. However, this phase is not reported as being a stable phase.²³⁾ In the three-phase equilibria occurring between the fcc, Ni₃B, and M₂B_{tetr} phases at both 800 and 925°C, the calculated Fe content in the M₂B_{tetr} phase was lower than that in the results of Kuz'ma and Koval¹⁴⁾ and Loo and Beek.¹⁸⁾ In addition, for the tie triangle between the NiB, *m*-Ni₄B₃, and M₂B_{tetr} phases, the calculated Fe content in the M₂B_{tetr} phase was higher than that of Kuz'ma and Koval,¹⁴⁾ where this tie triangle was presented as a tentative construction. Although there are several discrepancies in the equilibrium compositions, the calculated results reproduce the exper-

Table 3 The thermodynamic parameters in the Ni–Fe–B ternary system.

Thermodynamic parameters, J/mol	Reference
Liquid: model (B, Fe, Ni) ₁	
$L_{\text{B,Fe}}^{\text{L}} = -140000 + 42.834T + (x_{\text{B}} - x_{\text{Fe}}) \cdot (-1500) + (x_{\text{B}} - x_{\text{Fe}})^2 \cdot (20000)$	6)
$L_{\text{B,Ni}}^{\text{L}} = -144934.43 + 36.84T + (x_{\text{B}} - x_{\text{Ni}}) \cdot (85920.44 - 35.74T) + (x_{\text{B}} - x_{\text{Ni}})^2 \cdot (62755.14 - 21.36T) + (x_{\text{B}} - x_{\text{Ni}})^3 \cdot (-10883.87)$	8)
$L_{\text{Fe,Ni}}^{\text{L}} = -18378.86 + 6.03912T + (x_{\text{Fe}} - x_{\text{Ni}}) \cdot (9228.1 - 3.54642T)$	5)
$L_{\text{B,Fe,Ni}}^{\text{L}} = x_{\text{Fe}} \cdot (56000 - 20T) + x_{\text{Ni}} \cdot (-40000)$	This work
Fcc: model (B, Fe, Ni) ₁	
$L_{\text{B,Fe}}^{\text{fcc}} = -21000 - 15T$	6)
$L_{\text{B,Ni}}^{\text{fcc}} = -41420$	7)
$L_{\text{Fe,Ni}}^{\text{fcc}} = -12054.355 + 3.27413T + (x_{\text{Fe}} - x_{\text{Ni}}) \cdot (11082.1315 - 4.45077T) + (x_{\text{Fe}} - x_{\text{Ni}})^2 \cdot (-725.805174)$	5)
$T_{\text{C(Fe,Ni)}}^{\text{fcc}} = 2133 + (x_{\text{Fe}} - x_{\text{Ni}}) \cdot (-682)$	5)
$\beta_{\text{Fe,Ni}}^{\text{fcc}} = 9.55 + (x_{\text{Fe}} - x_{\text{Ni}}) \cdot (7.23) + (x_{\text{Fe}} - x_{\text{Ni}})^2 \cdot (5.93) + (x_{\text{Fe}} - x_{\text{Ni}})^3 \cdot (6.18)$	
Bcc: model (B, Fe, Ni) ₁	
$L_{\text{B,Fe}}^{\text{bcc}} = -1000 - 5T$	6)
$L_{\text{Fe,Ni}}^{\text{bcc}} = -956.63 - 1.28726T + (x_{\text{Fe}} - x_{\text{Ni}}) \cdot (1789.03 - 1.92912T)$	5)
M₂B_{tetr}: model (Fe, Ni) _{0.667} B _{0.333}	
$G_{\text{Fe:B}}^{\text{M}_2\text{B}_{\text{tetr}}} = -24175 + 3.62T + 0.667 \cdot G_{\text{Fe}}^{\text{bcc}} + 0.333 \cdot G_{\text{B}}^{\beta\text{-rhombohedral}}$	6)
$T_{\text{C(Fe:B)}}^{\text{M}_2\text{B}_{\text{tetr}}} = 1018, \beta_{\text{Fe:B}}^{\text{M}_2\text{B}_{\text{tetr}}} = 1.91$	
$G_{\text{Ni:B}}^{\text{M}_2\text{B}_{\text{tetr}}} = -26702.78 + 4.07298T + 0.667 \cdot G_{\text{Ni}}^{\text{fcc}} + 0.333 \cdot G_{\text{B}}^{\beta\text{-rhombohedral}}$	7)
$L_{\text{Fe,Ni:B}}^{\text{M}_2\text{B}_{\text{tetr}}} = -36800 + 19.4T$	This work
FeB: model (Fe, Ni) _{0.5} B _{0.5}	
$G_{\text{Fe:B}}^{\text{FeB}} = -33000 + 6.35T + 0.5 \cdot G_{\text{Fe}}^{\text{bcc}} + 0.5 \cdot G_{\text{B}}^{\beta\text{-rhombohedral}}$	6)
$T_{\text{C(Fe:B)}}^{\text{FeB}} = 600, \beta_{\text{Fe:B}}^{\text{FeB}} = 1.03$	
$G_{\text{Ni:B}}^{\text{FeB}} = 4500 + G_{\text{Ni:B}}^{\text{NiB}}$	This work
$L_{\text{Fe,B}}^{\text{FeB}} = 6000$	
Ni₃B: model (Fe, Ni) _{0.75} B _{0.25}	
$G_{\text{Fe:B}}^{\text{Ni}_3\text{B}} = 1/4 \cdot (-79170 + 17.98T + 3 \cdot G_{\text{Fe}}^{\text{fcc}} + G_{\text{B}}^{\beta\text{-rhombohedral}})$	22)
$G_{\text{Ni:B}}^{\text{Ni}_3\text{B}} = 1/4 \cdot (-121828.96 + 33.36T + 3 \cdot G_{\text{Ni}}^{\text{fcc}} + G_{\text{B}}^{\beta\text{-rhombohedral}})$	8)
$L_{\text{Fe,Ni:B}}^{\text{Ni}_3\text{B}} = -5850$	This work
o-Ni₄B₃: model Ni _{0.586} B _{0.414}	
$G_{\text{Ni:B}}^{\text{o-Ni}_4\text{B}_3} = -23747.78 + 2.35549T + 0.586 \cdot G_{\text{Ni}}^{\text{fcc}} + 0.414 \cdot G_{\text{B}}^{\beta\text{-rhombohedral}}$	7)
m-Ni₄B₃: model Ni _{0.564} B _{0.436}	
$G_{\text{Ni:B}}^{\text{m-Ni}_4\text{B}_3} = -22952.21 + 1.93373T + 0.564 \cdot G_{\text{Ni}}^{\text{fcc}} + 0.436 \cdot G_{\text{B}}^{\beta\text{-rhombohedral}}$	7)
NiB: model (Fe, Ni) _{0.5} B _{0.5}	
$G_{\text{Fe:B}}^{\text{NiB}} = -24432 + 2.84T + 0.5 \cdot G_{\text{Fe}}^{\text{bcc}} + 0.5 \cdot G_{\text{B}}^{\beta\text{-rhombohedral}}$	22)
$G_{\text{Ni:B}}^{\text{NiB}} = -20865.7 + 1.67458T + 0.5 \cdot G_{\text{Ni}}^{\text{fcc}} + 0.5 \cdot G_{\text{B}}^{\beta\text{-rhombohedral}}$	7)
$L_{\text{Fe,Ni:B}}^{\text{NiB}} = 7000$	This work

Fig. 1 (a) Calculated and (b) experimental isothermal sections of the Ni–Fe–B system at 800°C.

Fig. 2 (a) Calculated and (b) experimental isothermal sections of the Ni–Fe–B system at 925°C.

imental phase relationships satisfactorily.

Figure 3(a) shows the calculated isopleth at the 26 mol% B section together with the experimental data obtained from DSC measurements for comparison with the calculated phase boundaries, where the experimental data are not accurately present in this section, and hence, the data are plotted based on the Ni/Fe ratios determined by chemical analysis. The calculated liquidus temperatures for each alloy composition are also shown in Table 1. From such a comparison, the calculated phase boundaries agree well with the experimental results. Figure 3(b) shows the calculated isopleth at the Ni_2B – Fe_2B pseudo-binary section compared with the experimental liquidus and solidus temperatures.^{15,16} As regards the liquidus and solidus temperatures, the calculated values are higher than the experimental values. It is noteworthy that the experimental melting temperature of Ni_2B is higher than the calculated value by about 100°C, whereas the experimental melting temperature of Fe_2B is lower than the

calculated value by about 50°C. The assessed congruent melting temperature for the Ni_2B phase is 1125°C,²³⁾ while on the other hand, the Fe_2B phase melts by peritectic reaction at 1389°C,²⁴⁾ rather than by congruent reaction. Above the peritectic temperature, FeB coexists with the liquid phase. In the present description, both the congruent melting and the peritectic reaction temperatures are in good agreement with the assessed values within the experimental uncertainties. We could not obtain a copy of the original paper of Tavazde *et al.*¹⁵⁾ cited by Bannykh *et al.*,¹⁶⁾ and so its contents are not known. However, by considering the agreement between the calculated and experimental results on the isothermal sections and 26 mol% B section, the experimental liquidus and solidus temperatures^{15,16)} at the Ni_2B – Fe_2B pseudo-binary section seem to be rather low. Therefore, to clarify these discrepancies, further experimental re-investigation might be needed.

Fig. 3 Calculated isopleths of the Ni-Fe-B system at: (a) the 26 mol% B and (b) 33.3 mol% B sections.

5. Conclusions

A thermodynamic analysis of the Ni-Fe-B ternary system has been carried out based on the DSC results obtained in this study and available experimental data on the phase equilibria. The results obtained are summarized as follows:

- (1) The assessed parameters in the Ni-Fe-B system reproduced the experimental isothermal section diagrams well.
- (2) The calculated phase boundaries at the 26 mol% B section agreed well with the DSC data. In contrast, for

the Ni₂B-Fe₂B pseudo-binary section, there were discrepancies between the calculated and the reported values of the liquidus and solidus temperatures.

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