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THERMODYNAMIC DESCRIPTION OF TERNARY Fe-B-X SYSTEMS. PART 2: Fe-B-Ni

OPIS TERMODYNAMICZNY TRÓJSKŁADNIKOWYCH UKŁADÓW Fe-B-X. CZĘŚĆ 2: Fe-B-Ni

A thermodynamic description of the ternary Fe-B-Ni system is presented in the context of a new Fe-B-X (X = Cr, Ni, Mn, Si, Ti, V, C) database. The thermodynamic parameters of the binary sub-systems, Fe-B, Fe-Ni and B-Ni, are taken from earlier assessments slightly modifying the B-Ni description. Those of the Fe-B-Ni system are optimized in this study using experimental thermodynamic and phase equilibrium data from the literature. The solution phases of the system are described using the substitutional solution model and the borides are treated as stoichiometric or semi-stoichiometric phases of the $(A,B)_pC_q$ type described with two-sublattice model.

Keywords: phase diagrams, thermodynamic modelling; Fe-based systems, Fe-B-X systems thermodynamic database, Fe-B-Ni system

Przedstawiono termodynamiczny opis trójskładnikowego układu Fe-B-Ni w kontekście nowej bazy danych dla układów Fe-B-X (X = Cr, Ni, Mn, Si, Ti, V, C). Parametry termodynamiczne dwuskładnikowych stopów Fe-B, Fe-Ni i B-Ni zostały są zaczerpnięte z wcześniejszych opracowań, przy tym opis B-Ni został nieznacznie zmodyfikowany. Parametry dla układu Fe-B-Ni zostały zoptymalizowane w tej pracy w oparciu o eksperymentalne równowagi fazowe i dane termodynamiczne zaczerpnięte z literatury. Roztwory stałe w układzie Fe-B-Ni opisano przy użyciu modelu roztworu substytucyjnego, a borki traktowane są jako fazy stechiometryczne lub półstechiometryczne typu (A,B)pCq opisane przy użyciu modelu dwu podsieci.

1. Introduction

We build upon our earlier work [1] regarding the development of Fe-B-X systems database, where boron is treated as a substitutional component. The first contribution (Fe-B-Cr system study [1]), is thereafter followed by the current Fe-B-Ni system assessment. The goal is to develop a simple and compatible thermodynamic database for steels, which provides important and practical input data for thermodynamic-kinetic models simulating their solidification.

In this second paper, a thermodynamic description of the Fe-B-Ni system is done, using experimental thermodynamic and phase equilibrium data. Although the ternary system has been recently assessed by Tokunga et al. [2], their description cannot be applied directly as the modeling of the binaries Fe-B and B-Ni differs from that of the current database. For that reason the binary thermodynamic data used in the current Fe-B-Ni description are taken from Miettinen and Vassilev [1] (Fe-B system), from Lee [3] (Fe-Ni system), and from Campbell and Kattner [4] (B-Ni system). However, the descriptions of the fcc and Ni_4B_3-m phases suggested by the latter authors [4], were slightly modified in this study. For the fcc phase, this was necessary due to the circumstance that boron had been treated [4] as an interstitial constituent. The modification of the Ni_4B_3-m phase was made in order to achieve a better agreement with some experimentally assessed reactions involving that phase.

2. Phases, modeling and data

TABLE 1 shows the phases and their modeling in the current Fe-B-Ni assessment. The solution phases (L, bcc_A2 (bcc), fcc_A1 (fcc)) are described using substitutional solution model and the borides (Fe_2B, FeB, Ni_3B, NiB) – with sublattice models taking into account the reciprocal solubility of the third constituent (Fe or Ni). A complete mutual solubility is assumed between Fe_2B and Ni_2B as proposed by Raghavan [5]. Two borides (Ni_4B_3-o and Ni_4B_3-m) are treated as stoichiometric phases. No solubility of neither Fe nor Ni in the rhombohedral boron phase (referred to as "bet" bellow) has been assumed. Detailed descriptions of the substitutional solution, the sublattice models and their parameters are available from Qiu [6].

Experimental studies on the Fe-B-Ni system up to 1992 have been reviewed by Raghavan [5]. TABLE 2 shows the experimental information selected in the current optimization. In addition, experimental data of B-Ni phase equilibria [7-11], mixing enthalpy in liquid B-Ni alloys [12, 13], activity of B

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in liquid B-Ni alloys [14, 15] and enthalpy of formation of Ni_2B and NiB [16], were used in the partial re-optimization of the B-Ni system.

TABLE 1

Phases and their modeling in the current Fe-B-Ni description

Phase	**Modeling**
liquid (L)	(B,Fe,Ni), substitutional, RKM^a
bcc_A2 (bcc)	(B,Fe,Ni), substitutional, RKM
fcc_A1 (fcc)	(B,Fe,Ni), substitutional, RKM
Fe_2B (extending to Ni_2B)	$(Fe,Ni)_2(B)$, sublattice, RKM
FeB (dissolving Ni)	(Fe,Ni)(B), sublattice, RKM
Ni_3B (dissolving Fe)	$(Fe,Ni)_3(B)$, sublattice, RKM
NiB (dissolving Fe)	(Fe,Ni)(B), sublattice, RKM
Ni_4B_3-o	$(Ni)_4(B)_3$, stoichiometric
Ni_4B_3-m	$(Ni)_4(B)_3$, stoichiometric
beta-rhombo-B (bet)	(B)

RKM^a = Redlich-Kister-Muggianu (excess energy model)

TABLE 2

Experimental data applied in the optimization for the Fe-B-Ni system

Experimental data	**Reference**
Liquidus projection	[5], [17]
2 isothermal sections, at 925 and 800°C	[18], [19], [20]
1 vertical section, at x_B =0.26	[2]
Enthalpy of mixing in liquid alloys, at 1600°C	[13]
Activity coefficient γ_B^{Ni} in liquid alloys, at 1600°C	[21]

3. Results

The thermodynamic description of the Fe-B-Ni system is presented in TABLE 3. The parameters marked with a reference code were taken from earlier assessments and those marked with O* or E* were optimized (O*) using experimental data (TABLE 2) or estimated (E*) since no experimental data is avaliable, respectively.

TABLE 3

Thermodynamic description of the Fe-B-Ni system. Thermodynamic data of the pure components are given by Dinsdale [22, 23] unless not shown in the table. Parameter values except for Tc and β are are in J/mol

liquid (1 sublattice, sites: 1, constituents: B,Fe,Ni)	**Ref.**
$L^L_{B,Fe}$ = (-133438+33.946T) + (+7771)(x_B-x_{Fe})+ (+29739)$(x_B-x_{Fe})^2$	[24]
$L^L_{B,Ni}$ = (-144934+36.84T) + (+85920-35.74T)(x_B-x_{Ni}) + (+62755-21.36T)$(x_B-x_{Ni})^2$+ (-10884)$(x_B-x_{Ni})^3$	[4]
$L^L_{Fe,Ni}$ = (-16911+5.162T) + (+10180-4.147T)(x_{Fe}-x_{Ni})	[3]
$L^L_{B,Fe,Ni}$ = (-70000)x_B+ (+120000-20T)x_{Fe}+ (+145000-80T)x_{Ni}	O*
bcc (1 sublattice, sites: 1, constituents: B,Fe,Ni)	
${}^oG^{bcc}_B$ =${}^oG^{bet}_B$+ (+43514-12.217T)	[23]
$L^{bcc}_{B,Fe}$ = (-50000+42T)	[1]
$L^{bcc}_{B,Ni}$ = $L^{fcc}_{B,Ni}$ (bcc not stable in binary B-Ni)	E*
$L^{bcc}_{Fe,Ni}$ = (-957-1.287T) + (+1789-1.929T)(x_{Fe}-x_{Ni})	[25]
Tc^{bcc} = 1043x_{Fe}+575x_{Ni}	[22]
β^{bcc} = 2.22x_{Fe}+0.85x_{Ni}	[22]
fcc (1 sublattice, sites: 1, constituents: B,Fe,Ni)	
${}^oG^{fcc}_B$ =${}^oG^{bet}_B$+ (+50208-13.478T)	[23]
$L^{fcc}_{B,Fe}$ = (-66000+50T)	[1]
$L^{fcc}_{B,Ni}$ = (-111000+50T)	O*
$L^{fcc}_{Fe,Ni}$ = (-12054+3.274T) + (+11082-4.45T)(x_{Fe}-x_{Ni})+ (-726)$(x_{Fe}-x_{Ni})^2$	[25]
$L^{fcc}_{B,Fe,Ni}$ = (0)x_B+ (-120000+50T)x_{Fe}+ (0)x_{Ni}	O*
Tc^{fcc} = -201x_{Fe}+633x_{Ni}+$x_{Fe}x_{Ni}$(2133-682(x_{Fe}-x_{Ni}))	[25]
β^{fcc} = -2.1x_{Fe}+0.52x_{Ni}+$x_{Fe}x_{Ni}$(9.55+7.23(x_{Fe}-x_{Ni})+5.93$(x_{Fe}-x_{Ni})^2$+6.18$(x_{Fe}-x_{Ni})^3$)	[25]
Fe_2B (Ni_2B) (2 sublattices, sites: 0.6667:0.3333, constituents: Fe,Ni:B)	
${}^oG^{Fe2B}_{Fe:B}$ = 0.6667${}^oG^{bcc}_{Fe}$+0.3333${}^oG^{bet}_B$+ (-26261+3.466T)	[24]
${}^oG^{Fe2B}_{Ni:B}$ = 0.6667${}^oG^{fcc}_{Ni}$+0.3333${}^oG^{bet}_B$+ (-26727+4.085T)	[4]
$L^{Fe2B}_{Fe,Ni:B}$ = (-2000)+(+3000)(y_{Fe}-y_{Ni})	O*

cd. TABLE 3

FeB (2 sublattices, sites: 0.5:0.5, constituents: Fe,Ni:B)	
${}^{o}G^{FeB}_{Fe:B} = 0.5{}^{o}G^{bcc}_{Fe}+0.5{}^{o}G^{bet}_{B}+ (-35150+6T)$	[1]
${}^{o}G^{FeB}_{Ni:B} = 0.5{}^{o}G^{fcc}_{Ni}+0.5{}^{o}G^{bet}_{B}+ (-15000+5T)$	O*
Ni_3B (2 sublattices, sites: 0.75:0.25, constituents: Fe,Ni:B)	
${}^{o}G^{Ni3B}_{Fe:B} = 0.75{}^{o}G^{bcc}_{Fe}+0.25{}^{o}G^{bet}_{B}+ (-15280+1.2T)$	O*
${}^{o}G^{Ni3B}_{Ni:B} = 0.75{}^{o}G^{fcc}_{Ni}+0.25{}^{o}G^{bet}_{B}+ (-30457+8.34T)$	[4]
$L^{Ni3B}_{Fe,Ni:B} = (+1000-3T)+(-4500)(y_{Fe}-y_{Ni})$	O*
NiB (2 sublattices, sites: 0.5:0.5, constituents: Fe,Ni:B)	
${}^{o}G^{NiB}_{Fe:B} = 0.5{}^{o}G^{bcc}_{Fe}+0.5{}^{o}G^{bet}_{B}+ (-24000+5T)$	O*
${}^{o}G^{NiB}_{Ni:B} = 0.5{}^{o}G^{fcc}_{Ni}+0.5{}^{o}G^{bet}_{B}+ (-25832+5.44T)$	[4]
Ni_4B_3-o (2 sublattices, sites: 0.586:0.414, constituents: Ni:B)	
${}^{o}G^{Ni4B3-o}_{Ni:B} = 0.586{}^{o}G^{fcc}_{Ni}+0.414{}^{o}G^{bet}_{B}+ (-26700+4.6T)$	[4]
Ni_4B_3-m (2 sublattices, sites: 0.564:0.436, constituents: Ni:B)	
${}^{o}G^{Ni4B3-m}_{Ni:B} = 0.564{}^{o}G^{fcc}_{Ni}+0.436{}^{o}G^{bet}_{B}+ (-26700+4.78T)$	O*

The calculated results are compared with the original experimental data to verify the optimization. All calculations were carried out using ThermoCalc software [26].

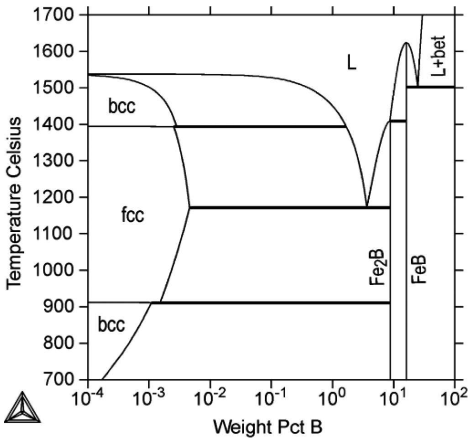

Fig. 1. Fe-B phase diagram calculated with the parameters of Miettinen, and Vassilev [1]

Figures 1 and 2 show the phase diagrams Fe-B and Fe-Ni calculated using the parameters from [1] and [3], respectively. The solid curves in Fig. 3 (B-Ni phase diagram) represent the calculations performed in this work while dotted lines refer to those of Campbell and Kattner [4]. The agreement with the experimental data is reasonable, as shown by the above mentioned authors. Nonetheless, the current B-Ni description results in a better agreement with the experimental data for the fcc solvus than [4]. In addition, the temperatures of the reactions L = Ni_4B_3-m and L = Ni_4B_3-m + NiB by [4] are 2 to 3 deg higher than those obtained in the current study and the agreement with the assessed values of [8] is worse. That is the main reason for the reassessment of the thermodynamic stability of the Ni_4B_3-m done in this study.

Additionally, a reasonable agreement was obtained between the calculated and experimental data for the mixing enthalpies and boron activity in liquid phase, as well as for the enthalpies of formation of Ni_2B and NiB (references for the experimental data are given in Section 2). In all cases, the results are identical to those of Campbell and Kattner [4].

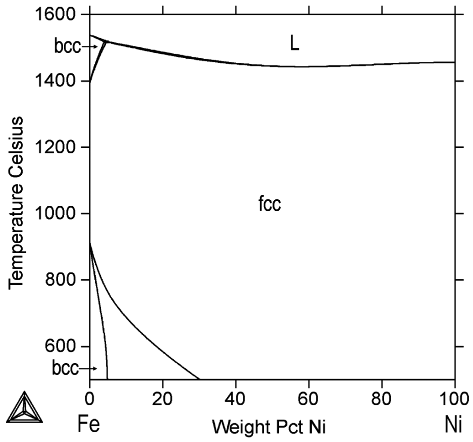

Fig. 2. Fe-Ni phase diagram calculated with the parameters of Lee [3]

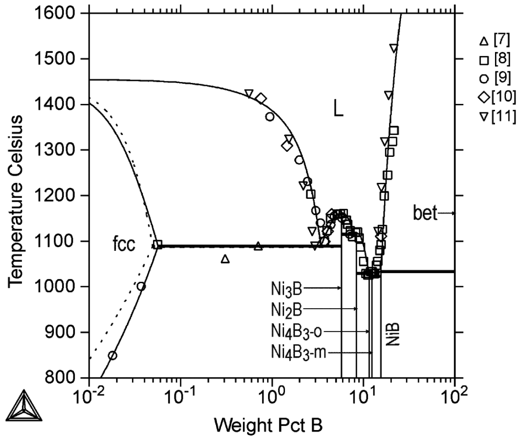

Fig. 3. B-Ni phase diagram calculated with the parameters obtained in this work, together with experimental data points [7-11]. Solid lines refer to the current calculations and dotted lines refer to those of Campbell and Kattner [4]

Figures 4-12 and TABLE 4 show the results from the current calculations and those of Tokunga et al. [2] for the Fe-B-Ni system, together with the experimental data (TABLE 2). Although a reasonable agreement between the calculated and experimental values in both cases is observed, it is slightly better when the results from the current optimization are used.

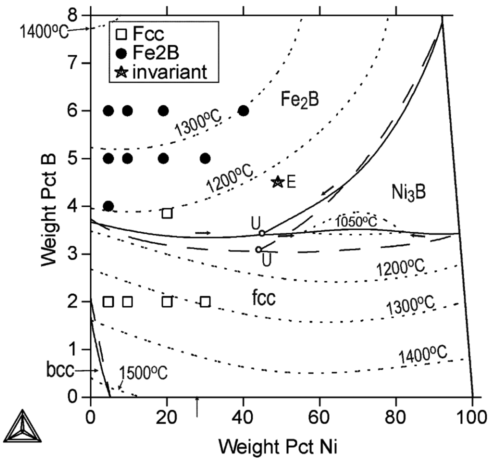

Fig. 4. Calculated liquidus projection of the Fe-B-Ni system, together with experimental data points [17, 5]. Solid lines refer to the current calculations and broken lines show those of [2]. Shown also are the calculated liquidus isotherms between 1050 and 1500°C, by dotted lines

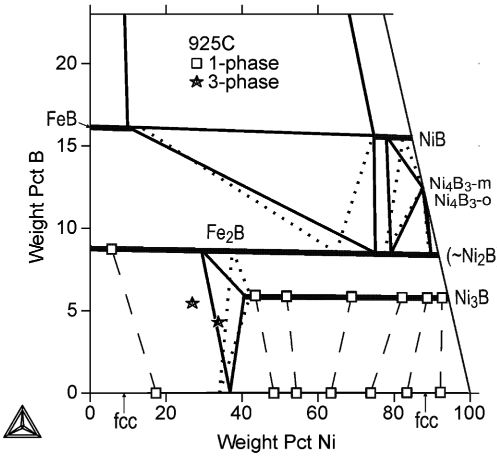

Fig. 5. Calculated isotherm at 925°C in the Fe-B-Ni system, together with experimental data points [20]. Solid lines refer to the current calculations and dotted lines show those of [2]

We would like to denote that somewhat different locations of the calculated invariant points U and the experimental invariant point E suggested by Raghavan [5] are observed (Fig. 4 and TABLE 4). The calculations of Tokunga et al. [2] agree better with the suggestion by Raghavan [5] for the invariant points' (U and E) temperatures, but not for their chemical compositions. Note that both calculations (i.e. the current one and that in [2]) result in the following invariant reaction, L + Fe_2B = fcc + Ni_3B, whereas [5] suggested an eutectic reaction: L = fcc + Fe_2B + Ni_3B. The latter, however, should be regarded as tentative only, due to the lack of experimental data in that region. Better agreement might be obtained by introducing stronger composition dependence for the ternary interaction parameter of the liquid phase, but this would lead to a worse agreement for the calculated vertical section at x_B = 0.26 (Fig. 7) (x_B is the molar fraction of boron) and the calculated enthalpy of mixing at 1600°C (Fig. 8).

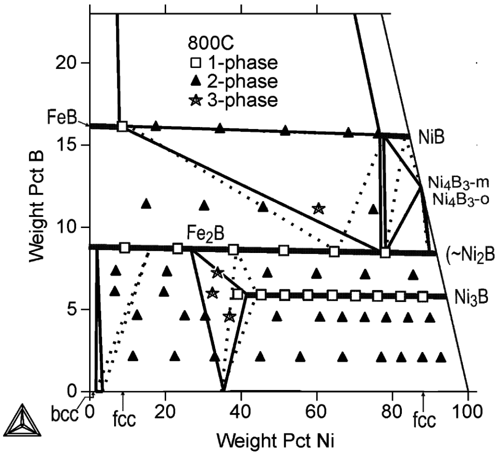

Fig. 6. Calculated isotherm at 800°C in the Fe-B-Ni system, together with experimental data points [18, 19]. Solid lines refer to the current calculations and dotted lines show those of [2]

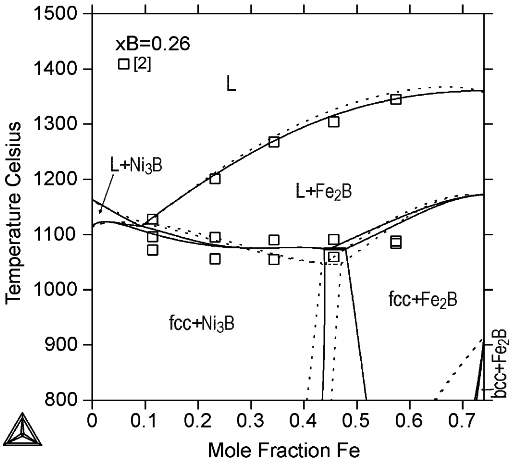

Fig. 7. Calculated vertical section at x_B = 0.26 in the Fe-B-Ni system, together with experimental data points [2]. Solid lines refer to the current calculations and dotted lines show those of [2]. x_B is the molar fraction of boron

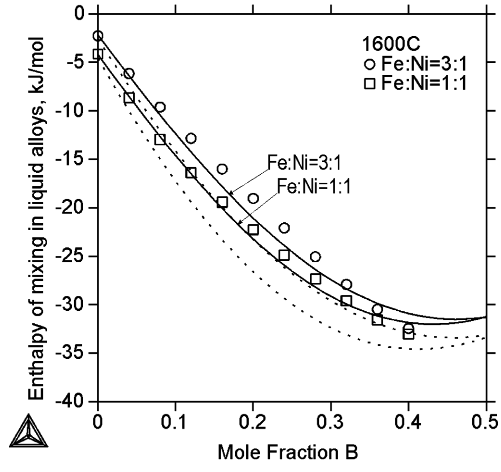

Fig. 8. Calculated enthalpy of mixing in liquid Fe-B-Ni alloys at 1600°C, together with experimental data points [13]. Solid lines refer to the current calculations and dotted lines show the enthalpy values assessed by Tokunga et al. [2]. The reference states used are pure liquid components

In Figure 9, better agreement between the experimental activity coefficient values of γ_B^{Ni} in liquid alloys, and the calculated data is observed. Finally, Figure 10 shows the calculated B solubility in the fcc phase of the system. The Ni content increase results in an increase of the B content in the fcc phase. Decreasing the temperature from 1150 to 1000°C replaces the fcc+L equilibrium with that of fcc+Fe$_2$B, but at both temperatures the B solubility is relatively high.

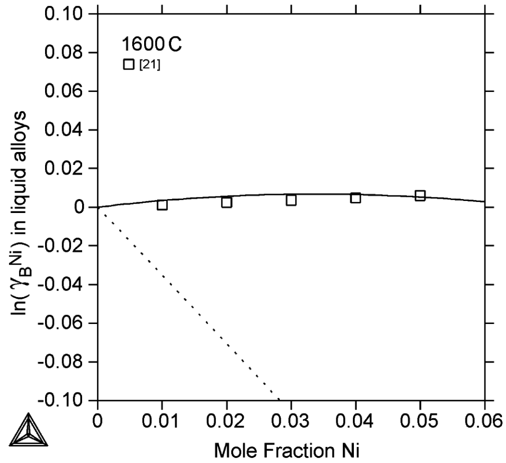

Fig. 9. Calculated activity coefficient γ_B^{Ni} in liquid Fe-B-Ni alloys at 1600°C, together with smoothed experimental data points [21]. Solid lines refer to the current calculations and dotted lines show those of [2]

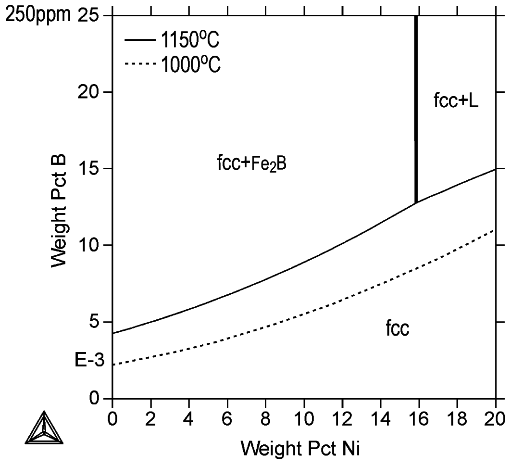

Fig. 10. Calculated in this work B solubility in the fcc phase of the Fe-B-Ni system, at 1150 and 1000°C

TABLE 4

Calculated (calc) and experimental (exp) invariant points in the Fe-B-Ni system. Code – reaction type, U – unknown, E – eutectic; t – temperature, °C

Reaction	Code	t °C	wt% Ni in L	wt% B in L	Reference
L+Fe$_2$B = fcc+Ni$_3$B	U	1074	44.84	3.41	calc This work
	U	1048	43.48	3.06	calc [2]
L = fcc+Fe$_2$B +Ni$_3$B	E*	1040	49.0	4.5	exp [5]

* – Tentative estimation

4. Summary

A partial reoptimization of the B-Ni system was done (descriptions of the fcc- and Ni$_4$B$_3$-m phases) thus achieving a better agreement with the experimental data for the fcc solvus and with the temperatures of some invariant reactions. A thermodynamic optimization of the ternary Fe-B-Ni system was performed using experimental thermodynamic and phase equilibrium data. In this description, ten phases, i.e., liquid, bcc, fcc, Fe$_2$B (extending to Ni$_2$B), FeB (dissolving Ni), Ni$_3$B (dissolving Fe), NiB (dissolving Fe), Ni$_4$B$_3$-o, Ni$_4$B$_3$-m and beta-rhombo-B, were considered. Good or reasonable correlation was obtained between the calculated and the experimental thermodynamic and phase equilibrium data. Moreover, the current description agrees better with the experimental results than the previous one reported in the literature, particularly regarding the ternary liquid phase molar enthalpy of mixing and the nickel activity coefficients values.

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