Thermodynamic Analysis of the Nb–Ti–B Ternary Phase Diagram

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A thermodynamic analysis of the Nb–Ti–B ternary system was carried out by estimating the unknown thermodynamic properties of binary and ternary borides by using a first-principles method. The calculated value for the binary TiB₂ phase was in reasonable agreement with those found by experiment. Due to a lack of experimental values concerning thermodynamic properties of the ternary system, the formation enthalpies for the Nb₃B₂–Ti₃B₂, NbB–TiB (*Cmcm*), NbB–TiB (*Pnma*), Nb₅B₆–Ti₅B₆, Nb₃B₄–Ti₃B₄, and NbB₂–TiB₂ pseudo-binary sections were also determined by constructing various kinds of superstructures for binary borides. The thermodynamic functions determined using these theoretical values, as well as the available experimental information on the phase fields, successfully revealed the phase equilibria in the Nb–Ti–B ternary system across the entire composition and all temperature ranges. [doi:10.2320/matertrans.MC200820]

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1. Introduction

The addition of small amounts of boron (B) to steels improves their strength and hardenability; therefore, this additive is used for various kinds of skinpass steel. This improvement in hardenability is generally explained by segregation of B on austenite grain boundaries, which suppresses the nucleation of ferrite on grain boundaries; however, this mechanism has not been clarified and is still controversial. On the other hand, the addition of Nb and Ti to steels improves their strength and grain refining by the formation of carbonitrides. Although the grain boundary segregation behavior of B is influenced by these additional elements, knowledge about the interaction with B is lacking. The objective of this study was to clarify the phase equilibria of the Nb–Ti–B ternary system across the entire range, using the Calculation of Phase Diagrams (CALPHAD) method.¹⁾ Some thermodynamic properties of borides that were not available experimentally were evaluated by incorporating first-principles calculations.

2. Computational Procedures

This section discusses the computational procedures used in the first-principles calculations and the expression for the Gibbs free energy.

2.1 First-principles calculations of the enthalpy of formation

The enthalpy of formation of the boride phases was calculated using the full potential linearized augmented plane wave (FLAPW) method.²⁾ The FLAPW method, as implemented in the WIEN2k software package,³⁾ is one of the most accurate schemes for electronic calculations and allows precise calculations of the total energies in solids. Therefore, this method is most appropriate for the evaluation of relative thermodynamic properties, such as the formation enthalpy. The exchange-correlation functional was described by the generalized gradient approximation (GGA) of the Perdew–Burke–Ernzerhof 96 form.⁴⁾ The plane-wave cutoff energy

was set to 270 eV throughout the calculation. For the integration we used a 12 × 12 × 12 k-points mesh in the whole first Brillouin zone.

2.2 Thermodynamic modeling

2.2.1 Liquid and terminal solution phases

The regular solution approximation was applied to the liquid phase, and to the (α Ti) and α solid solutions. The molar Gibbs energy, G_m^ϕ , was described as:

$$\begin{aligned} G_m^\phi = & x_{\text{Nb}} {}^\circ G_{\text{Nb}}^\phi + x_{\text{Ti}} {}^\circ G_{\text{Ti}}^\phi + x_{\text{B}} {}^\circ G_{\text{B}}^\phi \\ & + RT(x_{\text{Nb}} \ln x_{\text{Nb}} + x_{\text{Ti}} \ln x_{\text{Ti}} + x_{\text{B}} \ln x_{\text{B}}) \\ & + x_{\text{Nb}} x_{\text{Ti}} L_{\text{Nb,Ti}}^\phi + x_{\text{Nb}} x_{\text{B}} L_{\text{Nb,B}}^\phi \\ & + x_{\text{Ti}} x_{\text{B}} L_{\text{Ti,B}}^\phi + x_{\text{Nb}} x_{\text{Ti}} x_{\text{B}} L_{\text{Nb,Ti,B}}^\phi, \end{aligned} \quad (1)$$

where ${}^\circ G_i^\phi$ denotes the molar Gibbs energy of element i in the ϕ state. This quantity, called the lattice stability parameter, is described by the following formula:

$$\begin{aligned} {}^\circ G_i^\phi - {}^\circ H_i^{\text{ref}} = & A + BT + CT \ln T + DT^2 \\ & + ET^3 + FT^7 + IT^{-1} + JT^{-9}. \end{aligned} \quad (2)$$

In the above equation, ${}^\circ H_i^{\text{ref}}$ denotes the molar enthalpy of the pure element i in its stable state at $T = 298$ K. The parameter L_{ij}^ϕ denotes the interaction energy between i and j in the ϕ phase, and has a compositional dependency following the Redlich–Kister polynomial⁵⁾ as:

$$L_{ij}^\phi = {}^0 L_{ij}^\phi + {}^1 L_{ij}^\phi (x_i - x_j) + {}^2 L_{ij}^\phi (x_i - x_j)^2, \quad (3)$$

where the temperature dependency was introduced as ${}^n L_{ij}^\phi = a + bT$. The term $L_{\text{Nb,Ti,B}}^\phi$ is the ternary interaction parameter between the elements Nb, Ti, and B.

2.2.2 The (Nb,Ti)B₂ phase

The crystal structure of the (Nb,Ti)B₂ phase was illustrated in Fig. 1, where the metallic atoms occupy one sublattice as shown by open circles, while B atoms do another sublattice given by black circles. Furthermore, in our recent analysis,⁶⁾ we adopted a two-sublattice model to the binary NbB₂ phase, in which the Nb atoms and B atoms were substituted by vacancies in each sublattice, i.e., (Nb _{$\frac{1}{2}$} ⁽¹⁾ V _{$\frac{1}{2}$} ⁽¹⁾)₁ (B _{$\frac{1}{2}$} ⁽²⁾ V _{$\frac{1}{2}$} ⁽²⁾)₂. Therefore, for the ternary (Nb,Ti)B₂ phase, the same type

Fig. 1 Crystal structure of (Nb,Ti)B₂ phase.

of two-sublattice model as $(\text{Nb}_{y_{\text{Nb}}^{(1)}}\text{Ti}_{y_{\text{Ti}}^{(1)}}\text{Va}_{y_{\text{Va}}^{(1)}})_1(\text{B}_{y_{\text{B}}^{(2)}}\text{Va}_{y_{\text{Va}}^{(2)}})_2$ was employed, assuming that Ti atoms were substituted by Nb atoms in the first sublattice. This model reproduces the actual atomic configurations in the (Nb,Ti)B₂ phase. The Gibbs energy per mole of formula unit of this phase is given by:

$$\begin{aligned}
 G_m^{(\text{Nb,Ti})\text{B}_2} = & y_{\text{Nb}}^{(1)} y_{\text{B}}^{(2)} G_{\text{Nb:B}}^{(\text{Nb,Ti})\text{B}_2} + y_{\text{Va}}^{(2)} G_{\text{Nb:Va}}^{(\text{Nb,Ti})\text{B}_2} \\
 & + y_{\text{Ti}}^{(1)} y_{\text{B}}^{(2)} G_{\text{Ti:B}}^{(\text{Nb,Ti})\text{B}_2} + y_{\text{Va}}^{(2)} G_{\text{Ti:Va}}^{(\text{Nb,Ti})\text{B}_2} \\
 & + y_{\text{Va}}^{(1)} y_{\text{B}}^{(2)} G_{\text{Va:B}}^{(\text{Nb,Ti})\text{B}_2} + y_{\text{Va}}^{(2)} G_{\text{Va:Va}}^{(\text{Nb,Ti})\text{B}_2} \\
 & + 0.333RT(y_{\text{Nb}}^{(1)} \ln y_{\text{Nb}}^{(1)} + y_{\text{Ti}}^{(1)} \ln y_{\text{Ti}}^{(1)} + y_{\text{Va}}^{(1)} \ln y_{\text{Va}}^{(1)}) \\
 & + 0.667RT(y_{\text{B}}^{(2)} \ln y_{\text{B}}^{(2)} + y_{\text{Va}}^{(2)} \ln y_{\text{Va}}^{(2)}) \\
 & + y_{\text{Nb}}^{(1)} y_{\text{Ti}}^{(1)} (y_{\text{B}}^{(2)} L_{\text{Nb,Ti:B}}^{(\text{Nb,Ti})\text{B}_2} + y_{\text{Va}}^{(2)} L_{\text{Nb,Ti:Va}}^{(\text{Nb,Ti})\text{B}_2}) \\
 & + y_{\text{Nb}}^{(1)} y_{\text{Va}}^{(1)} (y_{\text{B}}^{(2)} L_{\text{Nb,Va:B}}^{(\text{Nb,Ti})\text{B}_2} + y_{\text{Va}}^{(2)} L_{\text{Nb,Va:Va}}^{(\text{Nb,Ti})\text{B}_2}) \\
 & + y_{\text{Ti}}^{(1)} y_{\text{Va}}^{(1)} (y_{\text{B}}^{(2)} L_{\text{Ti,Va:B}}^{(\text{Nb,Ti})\text{B}_2} + y_{\text{Va}}^{(2)} L_{\text{Ti,Va:Va}}^{(\text{Nb,Ti})\text{B}_2}) \\
 & + y_{\text{B}}^{(2)} y_{\text{Va}}^{(2)} (y_{\text{Nb}}^{(1)} L_{\text{Nb:B, Va}}^{(\text{Nb,Ti})\text{B}_2} + y_{\text{Ti}}^{(1)} L_{\text{Ti:B, Va}}^{(\text{Nb,Ti})\text{B}_2} \\
 & + y_{\text{Va}}^{(1)} L_{\text{Va:B, Va}}^{(\text{Nb,Ti})\text{B}_2}) \\
 & + y_{\text{Nb}}^{(1)} y_{\text{Ti}}^{(1)} y_{\text{Va}}^{(2)} (y_{\text{B}}^{(2)} L_{\text{Nb,Ti, Va: B}}^{(\text{Nb,Ti})\text{B}_2} + y_{\text{Va}}^{(2)} L_{\text{Nb,Ti, Va: Va}}^{(\text{Nb,Ti})\text{B}_2}) \\
 & + y_{\text{B}}^{(2)} y_{\text{Va}}^{(2)} (y_{\text{Nb}}^{(1)} y_{\text{Ti}}^{(1)} L_{\text{Nb, Ti: B, Va}}^{(\text{Nb,Ti})\text{B}_2} + y_{\text{Nb}}^{(1)} y_{\text{Va}}^{(1)} L_{\text{Nb, Va: B, Va}}^{(\text{Nb,Ti})\text{B}_2} \\
 & + y_{\text{Ti}}^{(1)} y_{\text{Va}}^{(1)} L_{\text{Ti, Va: B, Va}}^{(\text{Nb,Ti})\text{B}_2}) \\
 & + y_{\text{Nb}}^{(1)} y_{\text{Ti}}^{(1)} y_{\text{Va}}^{(2)} y_{\text{Va}}^{(2)} L_{\text{Nb, Ti, Va: B, Va}}^{(\text{Nb,Ti})\text{B}_2} \quad (4)
 \end{aligned}$$

where $G_{\text{Nb:B}}^{(\text{Nb,Ti})\text{B}_2}$, for example, represents the Gibbs energy of a hypothetical compound, Nb₁B₂, and terms relating to the same stoichiometry are identical. The parameter $L_{i,j:k}^{(\text{Nb,Ti})\text{B}_2}$ denotes the interaction energy between unlike atoms on the first sublattice.

2.2.3 The Nb₃B₂, NbB, TiB, Nb₅B₆, and (Nb,Ti)₃B₄ phases

The binary compounds, Nb₃B₂, NbB (*Cmcm*), TiB (*Pnma*), Nb₅B₆, isostructural Nb₃B₄ and Ti₃B₄, dissolve the third metallic component to some extent, and therefore, the two-sublattice model denoted by $(\text{Nb}_{y_{\text{Nb}}^{(1)}}\text{Ti}_{y_{\text{Ti}}^{(1)}})_m(\text{B}_{y_{\text{B}}^{(2)}}\text{Va}_{y_{\text{Va}}^{(2)}})_n$ was applied to these phases. The Gibbs energy per mole of formula unit of, for example, (Nb,Ti)₃B₄ is given by:

$$\begin{aligned}
 G_m^{(\text{Nb,Ti})\text{B}_4} = & y_{\text{Nb}}^{(1)} G_{\text{Nb:B}}^{(\text{Nb,Ti})\text{B}_4} + y_{\text{Ti}}^{(1)} G_{\text{Ti:B}}^{(\text{Nb,Ti})\text{B}_4} \\
 & + 0.429RT(y_{\text{Nb}}^{(1)} \ln y_{\text{Nb}}^{(1)} + y_{\text{Ti}}^{(1)} \ln y_{\text{Ti}}^{(1)}) \\
 & + y_{\text{Nb}}^{(1)} y_{\text{Ti}}^{(1)} L_{\text{Nb, Ti: B}}^{(\text{Nb,Ti})\text{B}_4} \quad (5)
 \end{aligned}$$

2.2.4 Stoichiometric compounds

The binary compound phase Nb₂B₃ with a zero homogeneity range was treated as being a stoichiometric compound, and the Gibbs energy for the phase is described as in eq. (6):

$$\begin{aligned}
 G_{\text{Nb:B}_3}^{(\text{Nb,Ti})\text{B}_3} = & 0.4 G_{\text{Nb}}^{\alpha} - 0.6 G_{\text{B}}^{\beta\text{B}} \\
 = & a + bT + cT \ln T + dT^2. \quad (6)
 \end{aligned}$$

3. Thermodynamic Analysis and Calculation of the Phase Diagram

A brief outline of the thermodynamic analysis and the calculated results are presented in this section. Most of the descriptions of lattice stability parameters for each pure element were obtained from the SGTE (Scientific Group Thermodata Europe) data set,⁷⁾ and are shown in Table 1.

3.1 The Nb–Ti binary system

The equilibrium phases of the Nb–Ti binary system are the liquid (L) phase, a continuous series of bcc solid solution α , and the Ti terminal solution (αTi). Thermodynamic analysis of this binary system was performed by several researchers,^{8,9)} and agreement with experimental data is almost equal. The description by Kumar *et al.*¹⁰⁾ is accepted in the present work. The calculated Nb–Ti binary phase diagram is shown in Fig. 2.

3.2 The Nb–B binary system

The equilibrium phase diagram of the Nb–B binary system contains the liquid (L) phase, the terminal solutions of Nb (α) and B (βB), and six intermetallic compounds: Nb₃B₂, NbB, Nb₅B₆, Nb₃B₄, Nb₂B₃, and NbB₂. The thermodynamic analysis concerning this binary system has already been done by our group.⁶⁾ However, to retain consistency with the Fe–Zr–B ternary system,¹¹⁾ some thermodynamic parameters of the NbB₂ phase were slightly modified. These parameters are summarized in Table 2, and the calculated phase diagram is compared with the experimental results in Fig. 3.

3.3 The Ti–B binary system

According to the critical assessment by Murray *et al.*,¹²⁾ the equilibrium phase diagram of the Ti–B binary system contains the liquid (L) phase, terminal solutions of Ti (αTi) and α and B (βB), and three intermetallic compounds, namely the TiB, Ti₃B₄, and TiB₂ phases. The TiB phase has an orthorhombic FeB-type structure (*Pnma*), and its homogeneity range is narrow with a range of about 49 to 50 mol% B. The structure of the diboride TiB₂ is well established by several experimental studies,^{13–17)} having the AlB₂ structure (*P6/mmm*). The Ti₃B₄ phase was absent from the phase diagram of Rudy *et al.*,¹⁷⁾ which may be due to its narrow composition; however, Spear *et al.*¹⁸⁾ confirmed the existence of this phase through arc-melting and annealing studies. The crystal structure of Ti₃B₄ was reported as isomorphous with that of Nb₃B₄ (*Immm*),^{16,18,19)} and the homogeneity range is rather small. The Ti₃B₄ phase was said to transform to a high-temperature form at about 2283 K, but the transformation is not reversible, and these allotropic forms were not considered in the present study.

The solubility of B in the α phase is less than 1 mol% at the eutectic temperature 1813 K,¹⁷⁾ where solidification occurs by the eutectic reaction as $L \rightleftharpoons \alpha + \text{TiB}$.¹⁷⁾ The peritectic-type reaction between the α , αTi and TiB phases occurs at around 1157 K.^{12,15,17)} The TiB phase forms from the melt by

Table 1 Lattice stability parameters for B, Nb, and Ti.

Element	Phase	Lattice stability parameter (J/mol)	Temperature (K)	Reference
B	βB	$= -7735.284 + 107.111864T - 15.6641T \ln T$ $-6.864515 \times 10^{-3}T^2 + 6.18878 \times 10^{-7}T^3 + 370843T^{-1}$	$298.15 < T < 1100$	7)
		$= -16649.474 + 184.801744T - 26.6047T \ln T$ $-7.9809 \times 10^{-4}T^2 - 2.556 \times 10^{-8}T^3 + 1748270T^{-1}$	$1100 < T < 2348$	
		$= -36667.582 + 231.336244T - 31.5957527T \ln T$ $-1.59488 \times 10^{-3}T^2 + 1.34719 \times 10^{-7}T^3 + 11205883T^{-1}$	$2348 < T < 3000$	
	L	$= -21530.653 + 222.396264T - 31.4T \ln T$	$3000 < T < 6000$	
		$= +40723.275 + 86.843839T - 15.6641T \ln T$ $-6.864515 \times 10^{-3}T^2 + 6.18878 \times 10^{-7}T^3 + 370843T^{-1}$	$298.15 < T < 500$	
		$= +41119.703 + 82.101722T - 14.9827763T \ln T$ $-7.095669 \times 10^{-3}T^2 + 5.07347 \times 10^{-7}T^3 + 335484T^{-1}$	$500 < T < 2348$	
		$= +28842.012 + 200.94731T - 31.4T \ln T$	$2348 < T < 6000$	
	α	$= +43514 - 12.217T$	$298.15 < T < 6000$	
	αTi	$= +50208 - 9.706T$	$298.15 < T < 6000$	
Nb	α	$= -8519.353 + 142.045475T - 26.4711T \ln T$ $+2.03475 \times 10^{-4}T^2 - 3.5012 \times 10^{-7}T^3 + 93399T^{-1}$	$298.15 < T < 2750$	7)
		$= -37669.3 + 271.720843T - 41.77T \ln T$ $+1.528238 \times 10^{32}T^{-9}$	$2750 < T < 6000$	
		$= +29781.555 - 10.816418T - 3.06098 \times 10^{-23}T^7$	$298.15 < T < 2750$	
	L	$= +30169.902 - 10.964695T - 1.528238 \times 10^{32}T^{-9}$	$2750 < T < 6000$	
		$= +1480.65 + 144.448T - 26.4711T \ln T$ $+2.03475 \times 10^{-4}T^2 - 3.50119 \times 10^{-7}T^3 + 93398.8T^{-1}$	$298.15 < T < 6000$	
	αTi	$= +1480.65 + 144.448T - 26.4711T \ln T$ $+2.03475 \times 10^{-4}T^2 - 3.50119 \times 10^{-7}T^3 + 93398.8T^{-1}$	$298.15 < T < 6000$	
Ti	αTi	$= -8059.921 + 133.615208T - 23.9933T \ln T$ $-4.777975 \times 10^{-3}T^2 + 1.06716 \times 10^{-7}T^3 + 72636T^{-1}$	$298.15 < T < 900$	7)
		$= -7811.815 + 132.988068T - 23.9887T \ln T$ $-4.2033 \times 10^{-3}T^2 - 9.0876 \times 10^{-8}T^3 + 42680T^{-1}$	$900 < T < 1155$	
		$= +908.837 + 66.976538T - 14.9466T \ln T$ $-8.1465 \times 10^{-3}T^2 + 2.02715 \times 10^{-7}T^3 - 1477660T^{-1}$	$1155 < T < 1941$	
		$= -124526.786 + 638.806871T$ $-87.2182461T \ln T + 8.204849 \times 10^{-3}T^2$ $-3.04747 \times 10^{-7}T^3 + 36699805T^{-1}$	$1941 < T < 4000$	
		$= +4134.494 + 126.63427T - 23.9933T \ln T$ $-4.777975 \times 10^{-3}T^2 + 1.06716 \times 10^{-7}T^3 + 72636T^{-1}$	$298.15 < T < 900$	
		$= +4382.601 + 126.00713T - 23.9887T \ln T$ $-4.2033 \times 10^{-3}T^2 - 9.0876 \times 10^{-8}T^3 + 42680T^{-1}$	$900 < T < 1155$	
	L	$= +13103.253 + 59.9956T - 14.9466T \ln T$ $-8.1465 \times 10^{-3}T^2 + 2.02715 \times 10^{-7}T^3 - 1477660T^{-1}$	$1155 < T < 1300$	
		$= +369519.198 - 2556.0225T - 342.059267T \ln T$ $-0.163409355T^2 + 1.2457117 \times 10^{-5}T^3$ $-67034516T^{-1}$	$1300 < T < 1941$	
		$= -19887.066 + 298.7367T - 46.29T \ln T$	$1941 < T < 4000$	
		$= -1272.064 + 134.71418T - 25.5768T \ln T$ $-6.63845 \times 10^{-4}T^2 - 2.78803 \times 10^{-7}T^3 + 7208T^{-1}$	$298.15 < T < 1155$	
	α	$= +6667.385 + 105.366379T - 22.3771T \ln T$ $+1.21707 \times 10^{-3}T^2 - 8.4534 \times 10^{-7}T^3 - 2002750T^{-1}$	$1155 < T < 1941$	
		$= +26483.26 - 182.426471T + 19.0900905T \ln T$ $-2.200832 \times 10^{-2}T^2 + 1.228863 \times 10^{-6}T^3 + 1400501T^{-1}$	$1941 < T < 4000$	

a peritectic reaction with Ti_3B_4 at 2453 K. The peritectic reaction, $\text{L} + \text{TiB}_2 \rightleftharpoons \text{Ti}_3\text{B}_4$, takes place at the slightly higher temperature of 2473 K,¹²⁾ and the two peritectic reactions are separated by 20 K. The TiB_2 phase melts congruently; however, the experimental melting points

showed some scattering in the range 3063–3498 K, possibly caused by vaporization.¹⁶⁾ Murray *et al.*¹²⁾ pointed out that the major difficulty of determining the melting temperature was due to the reaction with the crucible material, which results in the detection of a ternary eutectic temperature

Fig. 2 The calculated Nb–Ti binary phase diagram.

Fig. 3 The calculated Nb–B binary phase diagram.

Table 2 Optimized thermodynamic parameters for the binary and ternary systems.

System	Phase	Thermodynamic parameter (J/mol)	Reference
Nb–Ti	L	${}^0L_{\text{Nb,Ti}}^{\text{L}} = +3000$	9)
	α	${}^0L_{\text{Nb,Ti}}^{\alpha} = +8900$	
	αTi	${}^0L_{\text{Nb,Ti}}^{\alpha\text{Ti}} = +13150$	
Nb–B	L	${}^0L_{\text{Nb,B}}^{\text{L}} = -182310 + 5.02T$	Present work
		${}^1L_{\text{Nb,B}}^{\text{L}} = +13710 - 27.64T$	
		${}^2L_{\text{Nb,B}}^{\text{L}} = +8840$	
	α	${}^0L_{\text{Nb,B}}^{\alpha} = -85000 + 28.48T$	
		${}^1L_{\text{Nb,B}}^{\alpha} = -5000$	
		${}^2L_{\text{Nb,B}}^{\alpha} = -68000$	
	Nb ₃ B ₂	${}^{\circ}G_{\text{Nb}_3\text{B}_2}^{\text{Nb}_3\text{B}_2} - 0.6^{\circ}G_{\text{Nb}}^{\alpha} - 0.4^{\circ}G_{\text{B}}^{\beta\text{B}} = -64430 - 12.81T + 2.02T \ln T - 3 \times 10^{-4}T^2$	
	NbB	${}^{\circ}G_{\text{NbB}}^{\text{NbB}} - 0.5^{\circ}G_{\text{Nb}}^{\alpha} - 0.5^{\circ}G_{\text{B}}^{\beta\text{B}} = -78710 - 11.01T + 1.7T \ln T - 9.8 \times 10^{-5}T^2$	
	Nb ₅ B ₆	${}^{\circ}G_{\text{Nb}_5\text{B}_6}^{\text{Nb}_5\text{B}_6} - 0.455^{\circ}G_{\text{Nb}}^{\alpha} - 0.545^{\circ}G_{\text{B}}^{\beta\text{B}} = -78740 - 14.33T + 2T \ln T$	
	Nb ₃ B ₄	${}^{\circ}G_{\text{Nb}_3\text{B}_4}^{\text{Nb}_3\text{B}_4} - 0.429^{\circ}G_{\text{Nb}}^{\alpha} - 0.571^{\circ}G_{\text{B}}^{\beta\text{B}} = -78780 - 14.66T + 2T \ln T$	
	Nb ₂ B ₃	${}^{\circ}G_{\text{Nb}_2\text{B}_3}^{\text{Nb}_2\text{B}_3} - 0.4^{\circ}G_{\text{Nb}}^{\alpha} - 0.6^{\circ}G_{\text{B}}^{\beta\text{B}} = -77350 - 15.33T + 2T \ln T$	
	NbB ₂	${}^{\circ}G_{\text{NbB}_2}^{\text{NbB}_2} - 0.333^{\circ}G_{\text{Nb}}^{\alpha} - 0.667^{\circ}G_{\text{B}}^{\beta\text{B}} = -72700 + 5.3T - 1.1T \ln T + 9 \times 10^{-4}T^2$	
		${}^{\circ}G_{\text{NbB}_2}^{\text{NbB}_2} - 0.333^{\circ}G_{\text{Nb}}^{\alpha} = +19693$	
		${}^{\circ}G_{\text{Va:B}}^{\text{NbB}_2} - 0.667^{\circ}G_{\text{B}}^{\beta\text{B}} = +49554$	
		${}^{\circ}G_{\text{Va:Va}}^{\text{NbB}_2} = +100T$	
		${}^0L_{\text{NbB}_2}^{\text{NbB}_2} = -84572 + 18T$	
		${}^1L_{\text{NbB}_2}^{\text{NbB}_2} = -7644 - 10T$	
		${}^0L_{\text{NbB}_2}^{\text{NbB}_2} = -80000 + 23T$	
		${}^1L_{\text{NbB}_2}^{\text{NbB}_2} = +10000$	

Continued on next page.

lower than the melting point of the binary boride. Thus, they employed the highest reported congruent temperature as $3498 \pm 25 \text{ K}^{17)}$ in the assessed diagram.

Experimental thermodynamic data are available only for TiB₂. The enthalpy of phase formation varies, ranging from -134 to $-324 \text{ kJ/mol}^{20-29)}$ The most recent paper by Yurick *et al.*³⁰⁾ presented experimental measurements of equilibrium reactions of TiB₂ with nitrogen, yielding the enthalpy of formation for TiB₂ of $-304.2 \pm 3.8 \text{ kJ/mol}$ at 298 K. The heat capacity values for the diboride have been measured in

several studies.³¹⁻³⁶⁾ Assessments of these data by Stull and Prophet²⁷⁾ and Hultgren *et al.*²⁸⁾ are in good agreement.

The thermodynamic analysis of this binary system was performed based on the experimental information above, as well as the calculated enthalpy of formation for the three types of Ti borides, using first-principles calculations. Information on the crystallographic data was obtained from Ref. 37). The calculated results are listed in Table 3. The listed values denote the enthalpy of formation based on hcp Ti, and rhombohedral αB with the *hR12*-type structure.

Continued.

System	Phase	Thermodynamic parameter (J/mol)	Reference
Ti–B	L	${}^0L_{\text{Ti,B}}^{\text{L}} = -265410 + 15.54T$	Present work
		${}^1L_{\text{Ti,B}}^{\text{L}} = -134300 + 17.71T$	
		${}^2L_{\text{Nb,B}}^{\text{L}} = +61690$	
		${}^3L_{\text{Nb,B}}^{\text{L}} = +52660$	
	α	${}^0L_{\text{Ti,B}}^{\alpha} = -75000 + 4T$	
		${}^1L_{\text{Ti,B}}^{\alpha} = +44000 + 2T$	
	αTi	${}^0L_{\text{Ti,B}}^{\alpha\text{Ti}} = -80000$	
		${}^1L_{\text{Ti,B}}^{\alpha\text{Ti}} = +55000 + 3T$	
	TiB	${}^\circ G_{\text{Ti,B}}^{\text{TiB}} - 0.5^\circ G_{\text{Ti}}^{\alpha\text{Ti}} - 0.5^\circ G_{\text{B}}^{\beta\text{B}} = -83020 + 1.62T$	
	Ti ₃ B ₄	${}^\circ G_{\text{Ti,B}}^{\text{Ti}_3\text{B}_4} - 0.429^\circ G_{\text{Ti}}^{\alpha\text{Ti}} - 0.571^\circ G_{\text{B}}^{\beta\text{B}} = -94390 + 3.05T$	
	TiB ₂	${}^\circ G_{\text{Ti,B}}^{\text{TiB}_2} - 0.333^\circ G_{\text{Ti}}^{\alpha\text{Ti}} - 0.667^\circ G_{\text{B}}^{\beta\text{B}} = -105210 + 2.2T - 0.118T \ln T$ $+1.26 \times 10^{-3}T^2 - 9.71 \times 10^{-8}T^3 + 22089T^{-1}$	
		${}^\circ G_{\text{Ti,Va}}^{\text{TiB}_2} - 0.333^\circ G_{\text{Ti}}^{\alpha\text{Ti}} = +11668$	
		${}^\circ G_{\text{Va,B}}^{\text{TiB}_2} - 0.667^\circ G_{\text{B}}^{\beta\text{B}} = +49554$	
		${}^\circ G_{\text{Va,Va}}^{\text{TiB}_2} = +100T$	
		${}^0L_{\text{Ti,Va,B}}^{\text{TiB}_2} = -29300 + T$	
		${}^0L_{\text{Ti,B,Va}}^{\text{TiB}_2} = +6610 + 2.5T$	
Nb–Ti–B	L	${}^0L_{\text{Nb,Ti,B}}^{\text{L}} = +5.61T$	Present work
		${}^1L_{\text{Nb,Ti,B}}^{\text{L}} = +187620 - 27T$	
		${}^2L_{\text{Nb,Ti,B}}^{\text{L}} = +152940 + 7.09T$	
	Nb ₃ B ₂	${}^\circ G_{\text{Ti,B}}^{\text{Nb}_3\text{B}_2} - 0.6^\circ G_{\text{Ti}}^{\alpha\text{Ti}} - 0.4^\circ G_{\text{B}}^{\beta\text{B}} = -57760 + 7.21T$	
		${}^0L_{\text{Nb,Ti,B}}^{\text{Nb}_3\text{B}_2} = -13910 + 0.13T$	
		${}^1L_{\text{Nb,Ti,B}}^{\text{Nb}_3\text{B}_2} = -9500 - 1.16T$	
	NbB (Cmcm)	${}^\circ G_{\text{Ti,B}}^{\text{NbB}} - 0.5^\circ G_{\text{Ti}}^{\alpha\text{Ti}} - 0.5^\circ G_{\text{B}}^{\beta\text{B}} = -82630 + 2.82T$	
		${}^0L_{\text{Nb,Ti,B}}^{\text{NbB}} = -5070 + 0.25T$	
		${}^1L_{\text{Nb,Ti,B}}^{\text{NbB}} = -2540 - 1.9T$	
	TiB (Pnma)	${}^\circ G_{\text{Nb,B}}^{\text{TiB}} - 0.5^\circ G_{\text{Nb}}^{\alpha\text{Nb}} - 0.5^\circ G_{\text{B}}^{\beta\text{B}} = -78700 + 3.17T$	
		${}^0L_{\text{Nb,Ti,B}}^{\text{TiB}} = -7110 - 0.14T$	
		${}^1L_{\text{Nb,Ti,B}}^{\text{TiB}} = -2260 - 1.29T$	
	Nb ₅ B ₆	${}^\circ G_{\text{Ti,B}}^{\text{Nb}_5\text{B}_6} - 0.455^\circ G_{\text{Ti}}^{\alpha\text{Ti}} - 0.545^\circ G_{\text{B}}^{\beta\text{B}} = -89030 + 5.19T$	
		${}^0L_{\text{Nb,Ti,B}}^{\text{Nb}_5\text{B}_6} = -16000 + 4.15T$	
		${}^1L_{\text{Nb,Ti,B}}^{\text{Nb}_5\text{B}_6} = -8840 - 3.78T$	
	(Nb,Ti) ₃ B ₄	${}^0L_{\text{Nb,Ti,B}}^{(\text{Nb,Ti})_3\text{B}_4} = -15960 + 8.12T$	
		${}^1L_{\text{Nb,Ti,B}}^{(\text{Nb,Ti})_3\text{B}_4} = -9810 - 7.74T$	
		${}^2L_{\text{Nb,Ti,B}}^{(\text{Nb,Ti})_3\text{B}_4} = +11000 + 1.97T$	
	(Nb,Ti)B ₂	${}^0L_{\text{Nb,Ti,B}}^{(\text{Nb,Ti})\text{B}_2} = -8570 + 3.21T$	
		${}^1L_{\text{Nb,Ti,B}}^{(\text{Nb,Ti})\text{B}_2} = +1610$	

The formation energy calculated for the Ti₃B₄ phase by the first-principles calculation did not make this boride stable at absolute zero temperature, and the value was then evaluated using the CALPHAD method. The calculated enthalpy of formation of TiB₂ has been determined to be -315.6 kJ/mol, which agrees well with the experimental value of -304.2 ± 3.8 kJ/mol at 298 K.³⁰⁾ In addition, the structure of the diboride TiB₂ is isomorphous with the NbB₂ phase with a large homogeneity range, extending from 61 to 70 mol% B. We carried out a ground state analysis on the TiB₂ phase by constructing superstructures based on the $P6/mmm$ space group,⁶⁾ as given in Table 3. The calculated results are shown in Fig. 4. Thus, the thermodynamic

parameters required for the $(\text{Ti}_{y_{\text{Ti}}^{(1)}}\text{Va}_{y_{\text{Va}}^{(1)}})_1(\text{B}_{y_{\text{B}}^{(2)}}\text{Va}_{y_{\text{Va}}^{(2)}})_2$ -type sublattice model were evaluated based on these results, as shown by the solid line in Fig. 4. Moreover, the heat capacity data at constant pressure by Chase³⁸⁾ were also considered in the thermodynamic analysis to evaluate the temperature dependency of the formation energy for the stoichiometric TiB₂. The calculated values for the heat capacity were compared with the experimental data in Fig. 5. Figure 6 shows a comparison of the calculated and experimental data of the Ti–B binary phase diagram by Rudy *et al.*¹⁷⁾ It can be seen that the evaluated parameters show a good agreement with the corresponding experimental data on the phase boundaries.

Table 3 Calculated enthalpy of formation for the compounds at the ground state in the Ti–B binary system.

Phase	Space group	Composition (mol% B)	Enthalpy of formation (kJ/mol)	
			First principles	Assessed
TiB	<i>Pnma</i>	50.0	−83.0	−82.5 ⁴⁵⁾
Ti ₃ B ₄	<i>Immm</i>	57.1	−85.5	−94.3 ⁴⁵⁾
	<i>P6/mmm</i>	0.0	+35.0	—
	<i>Imm2</i>	33.3	−32.1	—
	<i>P6/mmm</i>	50.0	−68.2	—
	<i>P6/mmm</i>	57.1	−83.1	—
TiB ₂	<i>P6/mmm</i>	66.7	−105.2	−109.7 ⁴⁵⁾
	<i>P6/mmm</i>	72.7	−78.9	—
	<i>P6/mmm</i>	75.0	−68.7	—
	<i>P6/mmm</i>	77.8	−56.6	—
	<i>P6/mmm</i>	80.0	−46.4	—
	<i>Fmmm</i>	84.2	−21.7	—
	<i>P6/mmm</i>	100.0	+68.1	—

Fig. 4 Variation of the enthalpy of formation of TiB₂ with composition.

3.4 The Nb–Ti–B ternary system

Concerning the Nb–Ti–B ternary system, there is some experimental information on phase equilibria by Kuz'ma³⁹⁾ and Borisov *et al.*⁴⁰⁾ A thermodynamic analysis of the entire ternary system was carried out by Witusiewicz *et al.*⁴¹⁾

Kuz'ma³⁹⁾ reported an isothermal section at 1673 K examined using the X-ray diffraction method. The isothermal section is composed of the Nb₃B₂, NbB, TiB, Nb₃B₄, and (Nb,Ti)B₂ phases, and no ternary compound exists. The solubility of Ti in the Nb₃B₄ phase attains 5 mol%, and TiB dissolves up to 5 mol% Nb. The solubility of Ti in Nb₃B₂ is also small at less than 5 mol%. In contrast, the NbB phase dissolves up to 30 mol% Ti. The isostructural borides NbB₂ and TiB₂ form a continuous solid solution (Nb,Ti)B₂ in this ternary system. Borisov *et al.*⁴⁰⁾ also examined a partial isothermal section diagram at 1673 K, a vertical section at 7.5 mol% B, and projections of the solidus and liquidus surfaces with X-ray diffraction, metallography, electron probe microanalysis (EPMA), and differential thermal analysis. They showed that NbB (*Cmcm*) and TiB (*Pnma*) yield a

Fig. 5 Heat capacity of TiB₂ in the Ti–B system.

Fig. 6 The calculated Ti–B binary phase diagram.

narrow three-phase triangle for the α , NbB, and TiB phases, which is due to a difference in structure between the Nb- and Ti-based monoboride phases. According to the measurement of the Nb partition using EPMA, the mutual solubility values of Nb in TiB and of Ti in NbB are no less than 23 and 15 mol%, respectively. The solubility of Ti in Nb₃B₄ is approximately 7 mol%, whereas that of Nb in Ti₃B₄ is approximately 2 mol%.⁴⁰⁾ These results are somewhat different from those by Kuz'ma; however, the former data might be more accurate and preferable for optimization, because the solubility values were checked using several different experimental methods. The solidus and liquidus projections using EPMA and microstructure analysis were also constructed in the experimental study.

To cover the lack of the experimental values concerning the thermodynamic properties of the Nb–Ti–B ternary system, variation of formation energies for the binary borides with dissolving third component was evaluated in the present study using first-principles calculations. Superstructures for computing the formation energies were constructed by changing the stack of atoms along a given direction of the parent structure lattices.^{6,42,43)} Sixty types of superstructure for the Nb₃B₂–Ti₃B₂, for example, were used during the

analysis and the nine structures having the lowest energies at the corresponding compositions were selected, as given in Table 4. Volume optimization was performed by varying total volume with constant axes ratio of a superstructure, and the total energy was expressed as a function of the volume using the Murnaghan equation of state.⁴⁴⁾ The corresponding results are summarized in Table 4 for the Nb₃B₂–Ti₃B₂, NbB–TiB (*Cmcm*), NbB–TiB (*Pnma*), Nb₅B₆–Ti₅B₆, Nb₃B₄–Ti₃B₄, and NbB₂–TiB₂ pseudo-binary sections. These calculated values were used as a kind of experimental information to evaluate our thermodynamic parameters by fitting eqs. (4) and (5).

Our thermodynamic analysis was performed using the abovementioned experimental phase diagrams of Kuz'ma³⁹⁾ and Borisov *et al.*,⁴⁰⁾ and the energies of formation of the six pseudo-binary sections determined using first-principles calculations. In addition to the information on the solid phases, the experimental liquidus surface was also considered to estimate the ternary interaction parameters in the melt. The optimized thermodynamic parameters are summarized in Table 2. In Fig. 7(a) to (f), the calculated energies of formation of the six pseudo-binary sections were compared with those obtained using the conventional CALPHAD approach⁴¹⁾ depicted by the dashed lines. The solid lines in these figures represent the results obtained by the present thermodynamic analysis. We can observe considerable difference between the calculated values and those obtained using the conventional CALPHAD approach. A shortcoming of the CALPHAD approach is that it is hard to obtain information on metastable equilibria, because the thermodynamic parameters from this method can only be evaluated from experimental data. Thus, the deduced thermodynamic behavior of the pseudo-binary borides in their metastable regions is quite controversial, mainly because of difficulties in experimental verification. Such serious problems, which are intrinsic to the CALPHAD approach, can be solved with the assistance of the first-principles energy calculations. From this viewpoint, the first-principles values are regarded more reliable than those obtained by the conventional CALPHAD method. Figure 8 shows the calculated Nb partition between the matrix phase and the ternary monoboride phases. The Nb content in the phases, as well as the directions and positions of the tie-lines, agree satisfactorily well with the experimental data obtained by Borisov *et al.*⁴⁰⁾ The calculated isothermal sections at 1673 K are shown in Fig. 9(a) and (b), in comparison with the data obtained by Kuz'ma³⁹⁾ and Borisov *et al.*,⁴⁰⁾ respectively. The calculated vertical section for the alloys at 7.5 at% B is shown in Fig. 10. Here the agreement is also satisfactory. Figure 11 shows the projections of the liquidus surface, and the details of the five invariant reactions are summarized in Table 5, comparing the data with the experimental work⁴⁰⁾ and the previous calculation.⁴¹⁾

4. Conclusions

A thermodynamic analysis of the Nb–Ti–B ternary system was performed by incorporating first-principles calculations into the CALPHAD approach, yielding the following results.

Table 4 Calculated enthalpy of formation for the compounds at the ground state in the Nb–Ti–B ternary system.

Phase	Space group	Site fraction of Ti	Enthalpy of formation (kJ/mol)	
			First principles	Assessed
(Nb,Ti) ₃ B ₂	<i>P4/mbm</i>	0.000	–64.4	–74.5 ⁴⁵⁾
	<i>I4/m</i>	0.083	–65.8	—
	<i>Imma</i>	0.167	–66.6	—
	<i>I4/m</i>	0.250	–66.8	—
	<i>P4/mbm</i>	0.333	–66.7	—
	<i>Amm2</i>	0.417	–65.7	—
	<i>Amm2</i>	0.500	–64.5	—
	<i>C2/m</i>	0.667	–62.7	—
	<i>P4/mbm</i>	1.000	–57.8	–60.0 ⁴¹⁾
NbB	<i>Cmcm</i>	0.000	–78.7	–78.7 ⁴⁵⁾
	<i>C2</i>	0.125	–79.2	—
	<i>C2</i>	0.167	–79.4	—
	<i>C2/m</i>	0.500	–82.2	—
	<i>Cmcm</i>	0.667	–82.4	—
	<i>Amm2</i>	0.833	–82.6	—
	<i>Cmcm</i>	1.000	–82.6	–67.9 ⁴¹⁾
TiB	<i>Pnma</i>	0.000	–78.7	–69.3 ⁴¹⁾
	<i>Cm</i>	0.125	–80.1	—
	<i>Pnma</i>	0.333	–82.0	—
	<i>P2₁/c</i>	0.500	–82.7	—
	<i>Pnma</i>	0.667	–82.9	—
	<i>Pm</i>	0.875	–83.0	—
	<i>Pnma</i>	1.000	–83.0	–82.5 ⁴⁵⁾
(Nb,Ti) ₅ B ₆	<i>Cmmm</i>	0.000	–78.7	–80.6 ⁴⁵⁾
	<i>Immm</i>	0.100	–82.2	—
	<i>Cmmm</i>	0.200	–84.9	—
	<i>Amm2</i>	0.300	–86.2	—
	<i>Amm2</i>	0.600	–88.2	—
	<i>Amm2</i>	0.800	–88.8	—
	<i>Cmmm</i>	1.000	–89.0	+2.3 ⁴¹⁾
(Nb,Ti) ₃ B ₄	<i>Immm</i>	0.000	–78.8	–81.7 ⁴⁵⁾
	<i>C2/m</i>	0.222	–85.5	—
	<i>Immm</i>	0.333	–88.7	—
	<i>Imm2</i>	0.444	–90.6	—
	<i>C2/m</i>	0.556	–90.8	—
	<i>Immm</i>	0.778	–92.5	—
	<i>Immm</i>	1.000	–85.5	–94.3 ⁴⁵⁾
(Nb,Ti) ₂	<i>P6/mmm</i>	0.000	–72.7	–84.4 ⁴⁵⁾
	<i>Cmmm</i>	0.200	–80.1	—
	<i>R$\bar{3}m$</i>	0.333	–85.3	—
	<i>P6/mmm</i>	0.500	–90.9	—
	<i>P6/mmm</i>	0.667	–96.2	—
	<i>P6/mmm</i>	0.833	–101.1	—
	<i>P6/mmm</i>	1.000	–105.2	–109.7 ⁴⁵⁾

- (1) The thermodynamic analysis of the Ti–B binary system was carried out based on experimental information concerning phase boundaries and thermody-

Fig. 7 Variation of the enthalpy of formation of (a) Nb_3B_2 , (b) NbB (c) TiB (d) Nb_5B_6 (e) $(\text{Nb,Ti})_3\text{B}_4$ (f) $(\text{Nb,Ti})\text{B}_2$ with composition.

dynamic properties, as well as the calculated enthalpy of formation for the TiB , Ti_3B_4 , and TiB_2 phases, using first-principles calculations. The calculated enthalpy of formation of TiB_2 was -315.6 kJ/mol , which agrees well with the corresponding experimental value.

However, the formation energy of the Ti_3B_4 phase calculated using first-principles calculations did not make this boride stable at absolute zero temperature, and the value was then evaluated using the CALPHAD method.

Fig. 8 Nb content in the α , TiB and NbB phases.

Fig. 10 The calculated vertical at 7.5 mol%B for the Nb-Ti-B system.

Fig. 9 Calculated isothermal section diagrams of the Nb-Ti-B system at 1673 K compared (a) with Kuz'ma; (b) with Borisov *et al.*

Fig. 11 The calculated liquidus projection of the Nb-Ti-B system.

- (2) Due to a lack of experimental information on the thermodynamic properties of the Nb-Ti-B ternary system, the variation in the formation energies for the binary borides with a dissolving third component was evaluated for the Nb_3B_2 , NbB, TiB, Nb_5B_6 , $(\text{Nb,Ti})_3\text{B}_4$, and $(\text{Nb,Ti})\text{B}_2$ phases using first-principles calculations. Comparison of the calculated values with those obtained using the conventional CALPHAD approach showed considerable difference. The phase equilibria of the Fe-Nb-B ternary system were elucidated across the entire composition range by determining the thermodynamic functions based on the theoretical values as well as any available experimental information.

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Table 5 Invariant reaction points of the Nb–Ti–B ternary system.

Type	Invariant reaction	Liquid composition		Temperature (K)	Reference
		(mol% Ti)	(mol% B)		
U ₁	$L + Nb_5B_6 \rightleftharpoons Nb_3B_4 + NbB$	16.1	47.9	3068	Present work
		10.8	50.2	3070	41)
		~4	~53	3068 ± 16	40)
U ₂	$L + Nb_3B_4 \rightleftharpoons (Nb,Ti)B_2 + NbB$	24.2	46.8	2978	Present work
		19.0	47.8	2966	41)
		~11	~53	2965 ± 17	40)
P ₁	$L + (Nb,Ti)B_2 + NbB \rightleftharpoons TiB$	28.1	45.3	2920	Present work
		22.0	46.4	2920	41)
		~33	~42	2923 ± 15	40)
P ₂	$L + (Nb,Ti)B_2 + TiB \rightleftharpoons Ti_3B_4$	62.1	37.5	2464	Present work
		35.4	39.9	2683	41)
		~52	~41	2683 ± 36	40)
U ₃	$L + NbB \rightleftharpoons TiB + \alpha$	39.5	16.1	2061	Present work
		49.6	14.9	2063	41)
		~39	~13	2063 ± 10	40)

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