1. Introduction

Niobium and/or titanium added ultra-low carbon interstitial free (IF) steels are applied as steel sheets in automobile production, because of their good formability and drawability. In these steels, phosphorus is widely used as a solid solution strengthening element, because it causes relatively small reduction in ductility and zinc-coating adhesion in these steels. However, the retardation of recrystallization during annealing after cold rolling and the decrease in r-value could be caused by the formation of the ternary phosphides, FeTiP or possibly FeNbP. In addition, the formation of the ternary phosphide also influences the recrystallization behavior during hot rolling in high-purity ferritic stainless steels with Nb and/or Ti addition, in which P is present as a contaminant from the ferrochromium used as a raw material in stainless steelmaking. Therefore, it is useful to obtain information on the precipitation behavior of this ternary phosphide in these steels for microstructural control. The CALPHAD (Calculation of phase diagrams) approach provides a powerful tool for obtaining information on physical parameters, such as the amount and composition of constituent phases. Unfortunately, because of the high volatility of P, the thermodynamic properties as well as phase equilibria in the Fe–M–P (where M indicates an alloying element) ternary system have been limited to the Fe-rich region, and there is not enough experimental information for the determination of reliable thermodynamic parameters of the systems concerned. To overcome the above difficulty, our group carried out thermodynamic analyses of the Fe–Ti–P and Fe–Mn–P ternary systems by incorporating thermodynamic properties of various phosphides obtained from first-principles calculations into the CALPHAD approach, and has clarified phase equilibria in these systems over the entire composition range.

In this study, we initially evaluated the thermodynamic properties of various phosphides using first-principles calculations. Then, we carried out a thermodynamic analysis of the Fe–Nb–P ternary system using the thermodynamic properties obtained from first-principles calculations as well as the available experimental data.

2. Calculation Procedures

In this section we present details of procedures used to evaluate the enthalpy of formation of the phosphides using first-principles calculations, along with the thermodynamic descriptions of Gibbs energy of each phase.

2.1. First-principles Calculations for Evaluating Thermodynamic Properties

2.1.1. Enthalpy of Formation of Phosphides at Zero Temperature

To compensate for the lack of experimental information on the thermodynamic properties of the Fe–Nb–P ternary system, the energy of formation of the binary phosphides...
appearing in the Nb–P binary system and the ternary phosphides was evaluated using the WIEN2k software package,\textsuperscript{10} based on the Full Potential Linearized Augmented Plane Wave (FLAPW) method with a Generalized Gradient Approximation (GGA).\textsuperscript{11} We assumed Muffin radii of 2.0 au (0.106 nm) for Fe and Nb and 1.9 au (0.1005 nm) for P, and the plane wave basis set up to the cut-off energy of 20 Ry (270 eV) was utilized in our computations.

2.1.2. Free Energy of the bcc Solid Solution in the Nb–P Binary System

In addition to the formation energy of the various phosphides, the Gibbs energy of formation of the bcc solid solution (\(\alpha\)) of the Nb–P binary system was evaluated using first-principles calculations. The procedure for obtaining the Gibbs free energy of formation is explained in this section.

First, 36 types of bcc-based ordered superstructures, such as D0\(_2\), B2, and B32, were constructed by changing the stack of pure element planes along a given direction in the parent bcc structure lattice,\textsuperscript{12–14} and the total energies of those structures were calculated using the WIEN2k software package.\textsuperscript{10} Then, the energy of formation of the bcc-based ordered \(\phi\) phase, \(\Delta E_{\text{form}}^\phi\), was obtained from the total energy by subtracting the concentration-weighted averages from the total energy of the pure elements:

\[
\Delta E_{\text{form}}^\phi = E_{\text{total}}^\phi - c_{\text{Nb}} \cdot E_{\text{total}}^{\text{bcc-Nb}} - c_{\text{P}} \cdot E_{\text{total}}^{\text{P}} \tag{1}
\]

where \(c_i\) is the concentration of element \(i\). The term \(E_{\text{total}}^\phi\) denotes the total energy of the \(\phi\) superstructure, whereas the terms \(E_{\text{total}}^{\text{bcc-Nb}}\) and \(E_{\text{total}}^{\text{P}}\) refer to the total energy of bcc Nb and hypothetical bcc P, respectively. The energy of formation, \(\Delta E_{\text{form}}^\phi\), can be also expressed as the sum of effective interaction energies for clusters, such as a point, nearest and second nearest neighbor pairs, a triangle, a tetrahedron, etc., in the following equation:

\[
\Delta E_{\text{form}}^\phi = \sum_{j=0}^N v_j \cdot \xi_j^\phi \tag{2}
\]

where \(v_j\) is the effective cluster interaction energy for cluster \(i\), \(\xi_j^\phi\) is the correlation function that represents the atomic arrangement on cluster \(i\) in the \(\phi\) phase and can be obtained for bcc-based ordered structures.

Thus, the effective interaction energy can be extracted using the cluster expansion method (CEM),\textsuperscript{15,16} by inversion of the matrix of Eq. (2), as follows:

\[
v_j = \sum_{i} (\xi_j^\phi)^{-1} \Delta E_{\text{form}}^\phi \tag{3}
\]

By using the effective interaction energy, the internal energy term of the free energy of formation can be written in the following form:

\[
\Delta E = \sum_{j=0}^N v_j \cdot \xi_j^\phi \tag{4}
\]

Finally, the free energy of formation at a finite temperature can be obtained by adding the configurational entropy term, \(\Delta S_{\text{conf}}\) using the cluster variation method (CVM)\textsuperscript{17} to the energy term as:

\[
\Delta F = \Delta E - T \cdot \Delta S_{\text{conf}} \tag{5}
\]

In this study, the tetrahedron-octahedron-pentuplet (TOP) maximal clusters\textsuperscript{18} were adopted to calculate the configurational entropy.

2.2. Thermodynamic Modeling of Each Phase

2.2.1. The Liquid (L), bcc (\(\alpha\)), and fcc (\(\gamma\)) Solution Phases

The regular solution approximation was applied to the liquid phase and terminal solid solution phases, bcc (\(\alpha\)) and fcc (\(\gamma\)), and the molar Gibbs energy of the \(\phi\) phase was described using the following equation:

\[
\phi^\phi = x_F e G_F e + x_N b G_N b + x_P G_P + RT (\ln x_F e + \ln x_N b + \ln x_P)
+ x_F e x_N b L_{F e-N b}^{\phi} + x_F e x_P L_{F e-P}^{\phi}
+ x_N b x_P L_{N b-P}^{\phi} + x_F e x_N b x_P L_{F e-N b-P}^{\phi} \tag{6}
\]

where \(x_i\) denotes the mole fraction of element \(i\), \(R\) is the universal gas constant, and \(T\) is temperature in Kelvin. The term \(\phi^\phi\) denotes the molar Gibbs energy of element \(i\) in the \(\phi\) phase and is called the lattice stability parameter. This parameter is described as a function of temperature by the formula:

\[
\phi^\phi = \phi^\phi_{\text{ref}} + A + B T + C T \ln T + D T^2 + E T^3 + F T^4 + G T^5 + H T^6 + I T^{-1} + J T^{-9} \tag{7}
\]

where \(\phi^\phi_{\text{ref}}\) denotes the molar enthalpy of the pure element \(i\) in its stable state at 298.15 K. The symbols \(A–J\) denote coefficients. The parameter \(L_{i,j}^{\phi}\) denotes the interaction energy between elements \(i\) and \(j\) in the \(\phi\) phase, and has a compositional dependency using an \(n\)-th degree Redlich–Kister polynomial, as follows:

\[
L_{i,j}^{\phi} = a_i + b_i T \tag{8}
\]

where the temperature dependency was introduced as:

\[
a_i + b_i T \tag{9}
\]

The term \(L_{F e-N b-P}^{\phi}\) is the ternary interaction parameter between Fe, Nb, and P, and the compositional dependency is expressed by the following equation:

\[
L_{F e-N b-P}^{\phi} = x_F e L_{F e-N b-P}^{\phi} + x_N b L_{N b-P}^{\phi} + x_P L_{P}^{\phi} \tag{10}
\]

The contribution to the Gibbs energy due to magnetic ordering was taken into account in the bcc and fcc solid solution phases of Fe by addition of the magnetic part to the nonmagnetic part of the Gibbs energy.\textsuperscript{19,20}

2.2.2. The Fe\(_2\)Nb Laves Phase

To describe the Gibbs energy of the C14 Laves phase, Fe\(_2\)Nb, with some homogeneity range, a three-sublattice
The ternary phosphide, FeNbP, showed a range of some homogeneity,\textsuperscript{24} and thus a three-sublattice model with the formula (Fe,Nb)\textsubscript{2}(Fe,Nb)\textsubscript{2}(P)\textsubscript{1} was applied to this phosphide, based on the crystallographic information.\textsuperscript{25}

3. Results and Discussion

3.1. Calculation of Enthalpy of Formation of Phosphides

The enthalpy of formation of the various phosphides appearing in the Nb–P binary and Fe–Nb–P ternary systems was evaluated using first-principles calculations. Information on the crystallographic data was obtained from Villar’s compilation.\textsuperscript{26} In his compilation, information on the atomic positions for Nb\textsubscript{2}P\textsubscript{2}, FeNbP, and FeNbP\textsubscript{2} was not available, and therefore, these phosphides referred to the atomic positions of VP\textsubscript{2}, FeZrP, and FeTa\textsubscript{2}P, respectively. The calculated results are shown in Table 1, together with the equilibrium lattice constants. Each listed value is referred to as bcc Fe, bcc Nb, and black P. In the SGTE (Scientific Group Thermodata Europe) data file,\textsuperscript{27} white P was adopted as the stable element reference for P, and thus black P is not the most stable state for P. However, in this study, the total energy of pure P was calculated using the crystallographic data of black P (space group \textit{Cnca})\textsuperscript{28} because of the lack of information on the internal atomic positions for both white and red P, and we assumed that the phase stability of black P did not differ much from that of white P, following a previous study.\textsuperscript{5} Thus, in our thermodynamic analysis, we regarded the calculated values listed in Table 1 as the formation enthalpy relative to bcc Fe, bcc Nb, and white P. Unfortunately, although there is no experimental information on the thermodynamic properties of Nb–P binary phosphides and ternary phosphides to be compared with the calculated values, the enthalpy of formation obtained from first-principles calculations seems to be reasonable after considering that agreement between calculated values and experimental results for the Fe–P binary phosphides was almost satisfactory.\textsuperscript{5}

3.2. The Electronic Structure and Phase Stability of the FeNbP Phase

The total density of states (DOS) and the angular momentum-resolved density of states (p-DOS) for each element of the FeNbP are shown in Figs. 1(a)–1(d). The term $E_F$ shown in Fig. 1 denotes the Fermi energy, which represents the highest energy of occupied states and is taken as the zero of energy. From Figs. 1(a)–1(d), it is found that the total DOS is composed of the 3s states of P, located more than 10 eV below the Fermi level, the 3p states of P and the 3d states of Fe and Nb just below $E_F$, and the 3d states of Nb above $E_F$. The calculations also showed a significant hybridization between the 3d states of Fe and Nb and the 3p
states of P, and a pseudogap in the metal d-band complex. In the orthorhombic anti-PbCl₂-type structure of FeNbP with the space group \(Pnma\), the Fe, Nb, and P atoms occupy three of the 4c internal positions of the Wyckoff-letter multiplicity. In our previous study,\(^8\) we performed the electronic band energy calculations for the hypothetical anti-PbCl₂-type Fe₂P (space group \(Pnma\)) by replacing the unlike atoms at the 4c sites by the same type of atoms. The calculated formation energies for these structures, including the hypothetical anti-PbCl₂-type NbP₂ with the space group \(Pnma\), correspond to the thermodynamic parameters required for formulating the Gibbs energy of the FeNbP phase, and the values are listed in Table 1.

**Table 1.** Calculated energy of formation and lattice parameters for various phosphides.

<table>
<thead>
<tr>
<th>System</th>
<th>Phase</th>
<th>Structure phase diagrams</th>
<th>Space group</th>
<th>Calculated lattice parameter (\text{a} ) ((\text{nm}))</th>
<th>Calculated lattice parameter (\text{c} ) ((\text{nm}))</th>
<th>Calculated formation energy(%Gibbs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NbP</td>
<td>stable</td>
<td>(P4_1/2/m)</td>
<td>(a = 0.986)</td>
<td>(c = 0.3017)</td>
<td>(a = 1.0328)</td>
<td>(c = 0.2299)</td>
</tr>
<tr>
<td>NbP(Fe,Nb)</td>
<td>metastable</td>
<td>(P52m)</td>
<td>(a = 1.003)</td>
<td>(c = 0.302)</td>
<td>(a = 1.030)</td>
<td>(c = 0.2305)</td>
</tr>
<tr>
<td>NbP(Fe,Nb)</td>
<td>metastable</td>
<td>(Pnma)</td>
<td>(a = 0.978)</td>
<td>(b = 0.894)</td>
<td>(c = 0.702)</td>
<td>(a = 1.060)</td>
</tr>
<tr>
<td>NbP(Fe,Nb)</td>
<td>metastable</td>
<td>(Pbnm)</td>
<td>(a = 2.0675)</td>
<td>(b = 0.984)</td>
<td>(c = 0.343)</td>
<td>(a = 2.030)</td>
</tr>
<tr>
<td>NbP(Fe,Nb)</td>
<td>metastable</td>
<td>(I4_1/md)</td>
<td>(a = 0.331)</td>
<td>(c = 1.130)</td>
<td>(a = 0.334)</td>
<td>(c = 1.132)</td>
</tr>
<tr>
<td>NbP</td>
<td>stable</td>
<td>(C2/m)</td>
<td>(a = 0.770)</td>
<td>(b = 0.753)</td>
<td>(c = 0.375)</td>
<td>(a = 0.766)</td>
</tr>
<tr>
<td>Fe-NbP</td>
<td>stable</td>
<td>(Pnma)</td>
<td>(a = 0.6347)</td>
<td>(b = 0.570)</td>
<td>(c = 0.203)</td>
<td>(a = 0.619)</td>
</tr>
<tr>
<td>Fe-NbP</td>
<td>stable</td>
<td>(P4/mnc)</td>
<td>(a = 0.6340)</td>
<td>(c = 0.530)</td>
<td>(a = 0.634)</td>
<td>(c = 0.526)</td>
</tr>
</tbody>
</table>

![Fig. 1](image1)

Fig. 1. (a) The total density of states, and the angular momentum-resolved density of states of the FeNbP structure for (b) Fe, (c) Nb, and (d) P.

The total DOS of the anti-PbCl₂-type Fe₁P\(^9\) and the distribution of this DOS is similar to that of FeNbP shown in Fig. 1(a). However, we can see that the Fermi level for the Fe₁P structure is located in the hybridization band of the Fe d-states and the P p-states, whereas the Fermi level is located close to the pseudogap for the FeNbP structure. Therefore, from an energetic point of view, the FeNbP structure forms a stable structure by dissolving Nb in the anti-PbCl₂-type Fe₁P. The above interpretation of the electronic structure of the FeNbP phase is the same as that for the FeTiP phase with the anti-PbCl₂-type structure.\(^5,\(^2\)\)
3.3. Thermodynamic Analysis and Calculation of Phase Diagrams

In our thermodynamic analysis, the descriptions of the lattice stability parameters for each element were mostly taken from the SGTE data set\cite{27,29} and are summarized in Table 2.

3.3.1. The Fe–Nb Binary System

The Fe–Nb binary system is composed of a liquid (L) phase, terminal solutions ($\alpha$, $\gamma$, and $\delta$), and two intermetallic compounds, Fe$_2$Nb and FeNb.\cite{30,31} Thermodynamic analyses of this binary system have been performed by several researchers,\cite{32–34} with different sublattice models for analyses of this binary system have been performed by several researchers,\cite{32–34} with different sublattice models for the two intermetallic compounds. The most recent work of Toffolon and Servant\cite{34} adopted two types of description for the two intermetallic compounds. The most recent work of Toffolon and Servant\cite{34} adopted two types of description for Fe$_2$Nb with a C14 Laves-type structure using the three-sublattice and four-sublattice models. In our previous study,\cite{22} Toffolon’s thermodynamic description for Fe$_2$Nb was modified by applying the three-sublattice model given in Eq. (11), to maintain consistency with the three-sublattice model used for the thermodynamic description of Fe$_2$Ti with the same C14 Laves-type structure.\cite{22} The thermodynamic parameters adopted in this study are listed in Table 3, and the calculated Fe–Nb binary phase diagram is shown in Fig. 3.

3.3.2. The Fe–P Binary System

The Fe–P binary system is composed of a liquid (L) phase, bcc ($\alpha$), fcc ($\gamma$), Fe$_3$P, Fe$_2$P, Fe$_2$P$_2$, FeP$_5$, and P (red and white) phases.\cite{35} However, the phase equilibria in the P-rich portion (P $>$ 50 at%) are not known because of the experimental difficulty of the high volatility of P. The thermodynamic description for the Fe–rich region of the binary system has been presented in the literature.\cite{36,37} More recently, a thermodynamic analysis has been carried out by combining first-principles and CALPHAD methods, and the evaluated thermodynamic parameters enabled us to calculate the phase diagram in a whole composition range by the authors’ group.\cite{38,39} Later, we made a slight modification by considering additional sources of experimental data.\cite{39} In this study, we adopted the modified parameters, and those are listed in Table 3. The calculated Fe–P binary phase diagram is shown in Fig. 4.

3.3.3. The Nb–P Binary System

As regards the Nb–P binary system, no phase diagram has ever been proposed; however, six phosphides were identified in this binary system: Nb$_3$P,\cite{39} Nb$_7$P$_4$,\cite{40} Nb$_5$P$_3$,\cite{41} NbP,\cite{42,43} and NbP$_2$.\cite{44} Among these phosphides, NbP was estimated to decompose at 1730°C.\cite{45} In addition, the existence of a eutectic reaction was reported to occur between bcc Nb and NbP at $\sim$16 at% P.\cite{23}

In this thermodynamic analysis of the Nb–P binary system, in addition to the enthalpy of formation of the phosphides obtained from first-principles calculations, the thermodynamic properties of the liquid phase were estimated by assuming that the liquid phase has almost the same Gibbs energy of formation as the bcc phase in the temperature range at which the liquid and the bcc phase are in equilibrium. This assumption was based on the idea that the chemical short-range ordering due to the clustering of constituent elements exits in the liquid alloy just above the liquidus temperatures. Indeed, Pasturel et al.\cite{46} have approximated the liquid phase of the Ni–Ti binary system as a chemical short-range ordered phase, and successfully reproduced the thermodynamic property of the liquid phase as well as the liquid–solid phase equilibrium by combining total energy linear-muffin-tin-orbital (LMTO) calculations with the tetrahedron CVM approximation. Thus, in this study, the thermodynamic parameters of the liquid phase were determined in such a way that the Gibbs energy of formation of the liquid phase would fit that of the bcc phase at the temperature of 2000°C obtained from our first-principles calculations. It should be noted that, although six phosphides for the Nb–P binary system have been reported in the literature\cite{39,44} as shown in Table 1, only four phosphides, namely Nb$_3$P, Nb$_7$P$_4$, NbP, and NbP$_2$, were considered in the thermodynamic analysis since the other phosphides, Nb$_5$P$_3$ and NbP$_5$, have higher energy relative to the convex hull that represents the set of tie lines connecting the formation energy of the ground states. The temperature dependency of the formation energy of NbP was evaluated based on the estimated melting temperature.\cite{45} As regards the Nb$_3$P, Nb$_7$P$_4$, and NbP$_2$ phases, the experimental results on the Fe–Nb–P ternary system indicated that these Nb–P binary phosphides did not participate in phase equilibria in the Fe-rich corner;\cite{23} however, there is not enough experimental information for the determination of reliable thermodynamic parameters, and thus almost the same temperature dependency of the formation enthalpy for NbP was ascribed.

The evaluated thermodynamic parameters are listed in Table 3, and the calculated Nb–P binary phase diagram is shown in Fig. 5. The calculations show no occurrence of the eutectic reaction between bcc Nb and NbP since we assumed that the temperature dependency of the formation enthalpy of Nb$_7$P$_4$ is almost the same as that of NbP. To elucidate phase equilibria in the Nb–P binary system, further experimental work is needed.

3.3.4. The Fe–Nb–P Ternary System

In the Fe–Nb–P ternary system, Vogel and Bleichroth\cite{23} investigated the phase equilibria in the Fe–FeP–Nb region using thermal analysis, metallography, and X-ray diffraction.

Fig. 2. The total density of states for a hypothetical anti-PbCl$_2$ type Fe$_2$P.
Table 2. Lattice stability parameters for Fe, Nb, and P.

<table>
<thead>
<tr>
<th>Element</th>
<th>Phase</th>
<th>Lattice stability parameters (J/mol)</th>
<th>Temperature range (K)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>( G_{Fe}^{\alpha} - G_{FeVa}^{\alpha} )</td>
<td>( 12040.17 - 6.55843T - 3.675155 \times 10^{-21} T^{-1} )</td>
<td>298.15&lt;T&lt;1811</td>
<td>27)</td>
</tr>
<tr>
<td></td>
<td>( G_{Fe}^{\gamma} - H_{Fe}^{\gamma} )</td>
<td>( -10859.7 + 291.3027 - 467 \ln T )</td>
<td>1811&lt;T&lt;76000</td>
<td>27)</td>
</tr>
<tr>
<td></td>
<td>( T_{Fe}^{E} )</td>
<td>( 1043 ), ( T_{Fe}^{E} = 2.22 )</td>
<td>2200&lt;T&lt;76000</td>
<td>29)</td>
</tr>
<tr>
<td>Nb</td>
<td>( G_{Nb}^{\alpha} - G_{NbVa}^{\alpha} )</td>
<td>( 29781.555 - 10.8164187T - 3.06098 \times 10^{-23} T^{-1} )</td>
<td>298.15&lt;T&lt;2750</td>
<td>27)</td>
</tr>
<tr>
<td></td>
<td>( G_{Nb}^{\gamma} - H_{Nb}^{\gamma} )</td>
<td>( -8519.353 + 60.0344757T - 1.24711 \ln T )</td>
<td>298.15&lt;T&lt;76000</td>
<td>27)</td>
</tr>
<tr>
<td></td>
<td>( T_{Nb}^{E} )</td>
<td>( 980 ), ( T_{Nb}^{E} = 2.1 )</td>
<td>2200&lt;T&lt;76000</td>
<td>29)</td>
</tr>
<tr>
<td>Fe-Nb</td>
<td>( G_{FeNb}^{\alpha} - 8G_{Fe}^{\alpha} + 4G_{Nb}^{\alpha} )</td>
<td>( 69869 )</td>
<td>298.15&lt;T&lt;76000</td>
<td>34)</td>
</tr>
<tr>
<td></td>
<td>( G_{FeNb}^{\gamma} - 6G_{Fe}^{\gamma} + 4G_{Nb}^{\gamma} )</td>
<td>( 60724 )</td>
<td>298.15&lt;T&lt;76000</td>
<td>34)</td>
</tr>
<tr>
<td>P</td>
<td>( G_{P}^{\alpha} - H_{P}^{\alpha} )</td>
<td>( 26316.11 + 439.49317T - 7.04405847 \ln T )</td>
<td>298.15&lt;T&lt;2750</td>
<td>27)</td>
</tr>
<tr>
<td></td>
<td>( G_{P}^{\gamma} - H_{P}^{\gamma} )</td>
<td>( -7232.449 + 133.3048737T - 26.3267T \ln T )</td>
<td>317&lt;T&lt;76000</td>
<td>27)</td>
</tr>
<tr>
<td></td>
<td>( T_{P}^{E} )</td>
<td>( 522 ), ( T_{P}^{E} = 1.0 )</td>
<td>2200&lt;T&lt;76000</td>
<td>29)</td>
</tr>
<tr>
<td>Red</td>
<td>( G_{P}^{\alpha} - H_{P}^{\alpha} )</td>
<td>( 36819 + 13.1387 )</td>
<td>298.15&lt;T&lt;76000</td>
<td>28)</td>
</tr>
<tr>
<td>White</td>
<td>( G_{P}^{\alpha} - H_{P}^{\alpha} )</td>
<td>( 25976.559 + 148.6850027T - 25.557 \ln T )</td>
<td>298.15&lt;T&lt;76000</td>
<td>28)</td>
</tr>
<tr>
<td></td>
<td>( 0.0341243 )</td>
<td>( -2.418867 \times 10^{-10} T^{-1} + 160095 )</td>
<td>2200&lt;T&lt;76000</td>
<td>28)</td>
</tr>
<tr>
<td>Red</td>
<td>( G_{P}^{\alpha} - H_{P}^{\alpha} )</td>
<td>( -21723.721 + 77.6847377 - 14.3687 \ln T )</td>
<td>500&lt;T&lt;552.15</td>
<td>27)</td>
</tr>
<tr>
<td></td>
<td>( -0.0957665 )</td>
<td>( + 3.95117 \times 10^{-7} T + 141373 )</td>
<td>500&lt;T&lt;552.15</td>
<td>27)</td>
</tr>
<tr>
<td></td>
<td>( -11940.413 + 1026.04267T - 149.499567 \ln T )</td>
<td>( + 0.067227364 )</td>
<td>500&lt;T&lt;552.15</td>
<td>27)</td>
</tr>
<tr>
<td></td>
<td>( -24524.119 + 153.8521817 - 26.3267 \ln T )</td>
<td>( + 1.53852 )</td>
<td>500&lt;T&lt;552.15</td>
<td>27)</td>
</tr>
<tr>
<td>White</td>
<td>( G_{P}^{\alpha} - H_{P}^{\alpha} )</td>
<td>( -3821.799 + 1026.706897 - 178.4267 \ln T )</td>
<td>298.15&lt;T&lt;76000</td>
<td>27)</td>
</tr>
<tr>
<td></td>
<td>( + 0.2907087 )</td>
<td>( + 1.04022667 \times 10^{-7} T + 1632695 )</td>
<td>298.15&lt;T&lt;76000</td>
<td>27)</td>
</tr>
<tr>
<td></td>
<td>( + 0.001715669 )</td>
<td>( - 2.2829 \times 10^{-7} T + 1729668 )</td>
<td>298.15&lt;T&lt;76000</td>
<td>27)</td>
</tr>
<tr>
<td></td>
<td>( -893.075 + 135.8898317 - 26.3267 \ln T )</td>
<td>( + 0.001715669 )</td>
<td>298.15&lt;T&lt;76000</td>
<td>27)</td>
</tr>
</tbody>
</table>
Table 3. Optimized thermodynamic parameters of the binary and ternary systems.

<table>
<thead>
<tr>
<th>System</th>
<th>Phase</th>
<th>Thermodynamic parameters (J/mol)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-Nb</td>
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<td>$\Delta_{\text{f,Fe-Nb}} = -48231.518 + 11.22257T$</td>
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<td>$\Delta_{\text{f,Fe-Nb}}' = 9786.6216 + 5.14457T$</td>
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<td>$\Delta_{\text{f,Fe-Nb}}'' = 2981.806 - 14.60367T$</td>
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<td>$\Delta_{\text{f,Fe-Nb}}''' = 16016.944 + 0.009957T$</td>
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<td>$\Delta_{\text{f,Fe-Nb}}'''' = -9737.8048 + 1.9117T$</td>
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<td>$\Delta_{\text{f,Fe-Nb}}''''' = -8392.8109 - 0.02137T$</td>
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<td>$G^0_{\text{Fe-Nb}} = -300000 + 79T$</td>
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<td>Fe-Nb</td>
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<td>$G^0_{\text{Fe-Nb}} = -57408 - 26.78T$</td>
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<td>$G^0_{\text{Fe-Nb}} = -305500 + 81.653T$</td>
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<td>$G^0_{\text{Fe-Nb}} = -248092 + 54.873T$</td>
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<tr>
<td>Fe-P</td>
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<td>$\Delta_{\text{f,Fe-P}} = 89500 - 43.927T$</td>
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<td>$\Delta_{\text{f,Fe-P}} = -167900$</td>
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<td>$\Delta_{\text{f,Fe-P}} = -149900$</td>
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<td>Fe-Nb-P</td>
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<td>$G^0_{\text{Fe-Nb-P}} = 3G^0_{\text{Fe-P}} - G^0_{\text{White}} = -193600 + 30.4T$</td>
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<tr>
<td>(Fe, Nb)P</td>
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<td>$G^0_{\text{Fe-Nb-P}} = 2G^0_{\text{Fe-P}} - G^0_{\text{White}} = -184550 + 28.91T$</td>
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<tr>
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<td>$\Delta_{\text{f,Nb-P}} = -328900 + 12.49T$</td>
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<td>$\Delta_{\text{f,Nb-P}} = 128100 - 16.36T$</td>
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<td>(Fe, Nb)P</td>
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<tr>
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<td>$G^0_{\text{Np-P}} = -314800 + 80T$</td>
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<td>$G^0_{\text{Fe-Nb-P}} = 2G^0_{\text{Fe-Nb-P}} - G^0_{\text{White}} = -215400 + 65T$</td>
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<td>$G^0_{\text{Fe-Nb-P}} = -336000 + 487T$</td>
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tion analysis. The pseudobinary sections for Fe–FeNbP, Fe–FeNb4P, Fe2–FeNbP, Fe3–FeNbP, Fe–FeNb4P, Fe–FeNbP, 2mass%Nb–P, and 2mass%P–Nb, as well as the liquidus surface projection, were presented. Kaneko et al.24) have proposed the isothermal section diagram in the Fe-rich corner at 800°C. We evaluated the thermodynamic parameters using the formation energy of the FeNbP and FeNb4P phases obtained from first-principles calculations as well as the above experimental information. The assessed thermodynamic parameters are listed in Table 3.

The calculated isothermal section diagram at 800°C is shown in Fig. 6, together with the experimental phase diagram.23,24) Figures 7(a)–7(d) shows the calculated vertical section diagrams along the Fe3–FeNbP, Fe–FeNbP, 2mass%Nb–P, and 2mass%P–Nb, as well as the liquidus surface projection, for comparison with the experimental data determined using thermal analysis.23) The calculated phase boundaries are almost consistent with the experimental data. The calculated liquidus surface projection is compared with the proposed diagram23) in Fig. 8. The FeNbP phase was found to be dominant in the primary crystallization region. Some invariant reactions appearing in the Fe-rich region were calculated as follows:

\[ E_1: \ \text{L} \leftrightarrow \text{FeP} + \text{Fe}_2\text{P} + \text{FeNbP} \text{ at } 1257^\circ\text{C}, 4.8 \text{ mass}\% \text{ Nb, and } 28.2 \text{ mass}\% \text{ P.} \]

\[ U_2: \ \text{L} + \text{Fe}_2\text{P} \leftrightarrow \text{FeNbP} + \text{FeP} \text{ at } 1149^\circ\text{C}, 0.39 \text{ mass}\% \text{ Nb, and } 13.2 \text{ mass}\% \text{ P.} \]

\[ E_3: \ \text{L} \leftrightarrow \text{Fe}_3\text{P} + \text{FeNbP} + \text{FeP} \text{ at } 1049^\circ\text{C}, 0.25 \text{ mass}\% \text{ Nb, and } 9.75 \text{ mass}\% \text{ P.} \]

\[ E_4: \ \text{L} \leftrightarrow \text{Fe}_2\text{Nb} + \text{FeNbP} + \text{FeP} \text{ at } 1283^\circ\text{C}, 17.6 \text{ mass}\% \text{ Nb, and } 3.50 \text{ mass}\% \text{ P.} \]

\[ U_5: \ \text{L} + \text{FeNbP} \leftrightarrow \text{FeNb}_2\text{P} + \text{FeNb}_2\text{P} \text{ at } 1382^\circ\text{C}, 64.1 \text{ mass}\% \text{ Nb, and } 6.40 \text{ mass}\% \text{ P.} \]

\[ E_5: \ \text{L} \leftrightarrow \text{FeNb}_2\text{P} + \text{FeNb}_2\text{P} + \text{FeNb} \text{ at } 1383^\circ\text{C}, 75.3 \text{ mass}\% \text{ Nb, and } 3.66 \text{ mass}\% \text{ P.} \]

\[ E_6: \ \text{L} \leftrightarrow \text{FeNb}_2\text{P} + \text{FeNb}_2\text{P} + \text{FeNb} \text{ at } 1363^\circ\text{C}, 67.9 \]
4. Conclusions

The phase equilibria in the Fe–Nb–P ternary system were investigated by incorporating first-principles calculations into the CALPHAD approach, and the following results were obtained:

1. The formation energy of the Nb–P binary and the Fe–Nb–P ternary phosphides were obtained from first-principles calculations, and the free energy of formation of the bcc phase in the Nb–P binary system was calculated using cluster expansion of the superstructures. By introducing the above thermodynamic properties into the CALPHAD approach, we proposed a highly plausible Nb–P binary phase diagram.

2. The enthalpy of formation of FeNbP was calculated to be about $107 \text{ kJ/mol}$. According to the electronic structure calculations, the Fermi level for the FeNbP structure is located close to the pseudogap formed in the metal d-band complex, and this leads to a high phase stability of FeNbP.

3. The phase equilibria in the Fe–Nb–P ternary system over the entire composition range were established from our thermodynamic calculations, and the calculated results agreed with the available experimental data. The thermodynam-
namic calculations confirmed that FeNbP was in equilib-
rium with most of the binary phosphides, and that FeNbP
was also dominant in the liquidus surface.

Acknowledgement

Financial support from Nippon Steel Co., Japan is grate-
fully acknowledged for carrying out a part of this work.

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