Calculation of Phase Equilibria between Austenite and (Nb, Ti, V)(C, N) in Microalloyed Steels

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Thermodynamic calculations of the phase equilibria between austenite (γ) and complex carbonitrides containing Nb, Ti and V, (Nb, Ti, V)(C, N), were performed. The solubility product and formation energy of each carbide and nitride as well as the interaction parameters between components were evaluated. Experimental investigation on phase separation in the complex carbonitrides was also carried out using STEM-EDX and X-ray diffraction. The immiscibility of carbonitride was found to strongly affect the phase equilibria even when the content of microalloying elements in IF steels was very low.

KEY WORDS: microalloyed steels; thermodynamic analysis; phase separation; carbide; nitride; solubility product; IF steel.

1. Introduction

It is well known that Nb, Ti and V have a strong affinity for C and N and that a small addition of these elements to steels yields a significant improvement of mechanical properties due to the formation of fine precipitates. Microstructural control of these precipitates plays an extremely important role in improving the overall property of steels. There have been reports on the thermodynamic analysis of complex carbonitrides in microalloyed steels.1-4) These analyses are in reasonable agreement with the experimental values in the area where complex carbonitrides form homogeneous solutions. However, it is known that phase separation occurs in the precipitates depending on the difference of thermodynamic stabilities of terminal components in the (M1,M2)(X1,X2) double pseudobinary system.5) Two-phase separation of some NaCl-type complex carbonitrides was confirmed to appear experimentally by Kieffer et al.6) Taking this finding into consideration, it is expected that two-phase separation of such carbonitrides also occurs in practical steels.

The aim of the present study was to clarify the factors which rule the phase equilibria between complex carbonitride and Fe matrix by thermodynamic analysis. Furthermore, development of a relatively simple procedure for calculating phase equilibria was attempted, taking the phase separation of complex carbonitrides into account.

2. Thermodynamic Model

2.1. Description of Gibbs Energy

The Gibbs energy of the fcc (γ) phase, $G_{\gamma}^\circ$, is described by the two-sublattice compound energy model9) as follows:

$$G_{\gamma}^\circ = \sum_{m} y_m^\gamma \sum_{i} y_i^\gamma \epsilon_{i,m}^{\gamma} + aRT \sum_{i} y_i^\gamma \ln y_i^\gamma + cRT \sum_{m} y_m^\gamma \ln y_m^\gamma$$

$$+ \sum_{m} y_m^\gamma \sum_{i} y_i^\gamma \left\{ \sum_{j>i} y_j^\gamma L_{i,j}^{\gamma} + \sum_{o>m} y_o^\gamma L_{m,o}^{\gamma} \right\}$$

$$\cdots(1)$$

The subscripts $i$ and $j$ denote the metallic atoms (Fe, Nb, Ti and V), and $m$ and $o$ indicate the interstitial atoms (C, N and vacancy symbolized by Va). $a$ and $c$ in the formula show the number of sites of each sublattice, which are given as $a=1$ and $c=1$ for the fcc structure. The site fraction $y_i^\gamma$ is related to the mole fraction $x_i^\gamma$ as follows:

$$y_i^\gamma = x_i^\gamma / (1-x_c^\gamma-x_v^\gamma) \ldots(2)$$

$$y_m^\gamma = (a/c) x_c^\gamma / (1-x_c^\gamma-x_v^\gamma) \ldots(3)$$

$$y_{Fe}^\gamma + y_{Nb}^\gamma + y_{Ti}^\gamma + y_{V}^\gamma = 1 \ldots(4)$$

$G_{i,m}^{\gamma}$ is the Gibbs energy where the first sublattice is filled with $i$ atoms and the second one with $m$ atoms. In the subscripts of interaction parameters $L_{i,j}^{\gamma}$, the components in different sublattices are separated by a colon and in the same sublattice by a comma.

The content of alloying elements in the $\gamma$ phase in equilibrium with carbonitride is so dilute that the chemical potential of these elements can be written by the following simplified manner:

$$\mu_{Nb}^\gamma = \gamma_{Nb}^{\gamma} + RT \ln y_{Nb}^\gamma + L_{Nb,Fe,Nb,Va}^{\gamma} \ldots(5)$$

$$\mu_{Ti}^\gamma = \gamma_{Ti}^{\gamma} + RT \ln y_{Ti}^\gamma + L_{Fe,Ti,Va}^{\gamma} \ldots(6)$$

$$\mu_{V}^\gamma = \gamma_{V}^{\gamma} + RT \ln y_{V}^\gamma + L_{Fe,V,Va}^{\gamma} \ldots(7)$$

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represents the precipitate in the matrix. The chemical potential of each carbide and nitride can be approximated as follows, considering the small solubility of Fe and V.

\[ \mu_{NbC}^C = \mu_{NbC}^{\text{fcc}} - y_{NbC}^{\text{f}} y_{NbC}^{\text{v}} K_{NbC} + RT \ln y_{NbC}^{\text{f}} + L_1 \]

\[ \mu_{TiC}^C = \mu_{TiC}^{\text{fcc}} + y_{NbC}^{\text{f}} y_{NbC}^{\text{v}} K_{TiC} + RT \ln y_{NbC}^{\text{f}} + L_2 \]

\[ \mu_{VC}^C = \mu_{VC}^{\text{fcc}} + y_{NbC}^{\text{f}} y_{NbC}^{\text{v}} K_{VC} + RT \ln y_{NbC}^{\text{f}} + L_3 \]

\[ \mu_{NbN}^N = \mu_{NbN}^{\text{fccc}} + y_{NbN}^{\text{f}} y_{NbN}^{\text{v}} K_{NbN} + RT \ln y_{NbN}^{\text{f}} + L_4 \]

\[ \mu_{TiN}^N = \mu_{TiN}^{\text{fccc}} + y_{NbN}^{\text{f}} y_{NbN}^{\text{v}} K_{TiN} + RT \ln y_{NbN}^{\text{f}} + L_5 \]

\[ \mu_{VN}^N = \mu_{VN}^{\text{fccc}} + y_{NbN}^{\text{f}} y_{NbN}^{\text{v}} K_{VN} + RT \ln y_{NbN}^{\text{f}} + L_6 \]

\[ K \text{ and } L \text{ values are the aggregates of several parameters which will be explained in Appendices 1 and 2.} \]

2.2. Equilibrium Conditions

The equilibrium between \( \gamma \) and the complex carbonitride in the Fe–Nb–Ti–V–C–N system is represented by the following conditions:

\[ \mu_{NbC}^{\text{fccc}} = \mu_{NbC}^{\text{f}} + \mu_{NbC}^{\text{c}} \]

\[ \mu_{TiC}^{\text{fccc}} = \mu_{TiC}^{\text{f}} + \mu_{TiC}^{\text{c}} \]

\[ \mu_{VC}^{\text{fccc}} = \mu_{VC}^{\text{f}} + \mu_{VC}^{\text{c}} \]

\[ \mu_{NbN}^{\text{fccc}} = \mu_{NbN}^{\text{f}} + \mu_{NbN}^{\text{c}} \]

\[ \mu_{TiN}^{\text{fccc}} = \mu_{TiN}^{\text{f}} + \mu_{TiN}^{\text{c}} \]

\[ \mu_{VN}^{\text{fccc}} = \mu_{VN}^{\text{f}} + \mu_{VN}^{\text{c}} \]

Inserting Eqs. (5) through (15) into the above equilibrium conditions yields the following equations:

\[ [\text{NbC}] = [\text{NbC}]^{\text{f}} y_{NbC}^{\text{f}} y_{NbC}^{\text{c}} \]

\[ \exp \{(-y_{NbC}^{\text{f}} y_{NbC}^{\text{v}} K_{NbN} + L_1)/RT \} \]

\[ [\text{TiC}] = [\text{TiC}]^{\text{f}} y_{NbC}^{\text{f}} y_{NbC}^{\text{c}} \]

\[ \exp \{(y_{NbC}^{\text{f}} y_{NbC}^{\text{v}} K_{TiN} + L_2)/RT \} \]

\[ [\text{VC}] = [\text{VC}]^{\text{f}} y_{NbC}^{\text{f}} y_{NbC}^{\text{c}} \]

\[ \exp \{(-y_{NbC}^{\text{f}} y_{NbC}^{\text{v}} K_{VC} + L_3)/RT \} \]

\[ [\text{NbN}] = [\text{NbN}]^{\text{f}} y_{NbC}^{\text{f}} y_{NbC}^{\text{c}} \]

\[ \exp \{(y_{NbC}^{\text{f}} y_{NbC}^{\text{v}} K_{NbN} + L_4)/RT \} \]

\[ [\text{TiN}] = [\text{TiN}]^{\text{f}} y_{NbC}^{\text{f}} y_{NbC}^{\text{c}} \]

\[ \exp \{(-y_{NbC}^{\text{f}} y_{NbC}^{\text{v}} K_{TiN} + L_5)/RT \} \]

\[ [\text{VN}] = [\text{VN}]^{\text{f}} y_{NbC}^{\text{f}} y_{NbC}^{\text{c}} \]

\[ \exp \{(y_{NbC}^{\text{f}} y_{NbC}^{\text{v}} K_{VN} + L_6)/RT \} \]

where [MX] is the solubility product of MX in the multi-component system, where M = Nb, Ti or V and X = C or N, while [MX]* denotes that in the Fe–M–X ternary system. The values of [MX]*, selected from references 10–15 are listed in Table 1.

2.3. Estimate of Thermodynamic Parameters

The K value represents the difference in the free energy of each component carbide and nitride, as described in Appendix 1. According to the literature values for the formation energy of each carbide and nitride as listed in Table 1, K_{NbTi}, K_{NbN} and K_{TiN} are estimated to be -107.800 + 10.74 T, -25.170 – 13.11 T and -82.630 + 23.85 T (J/mol), respectively. These are shown in Fig. 1.

The L value is composed of several interaction parameters between complex carbonitrides as shown in Appendix 2. It is rather difficult to accurately evaluate the parameters because of a lack of experimental data. However, it has been shown that a linear relationship between the lattice constant and the mole fraction holds in the case of the NaCl-type carbonitrides. Therefore, interaction energies of complex carbonitrides were arranged with respect to the lattice mismatch factors (\( \Delta a/a \)), where \( \Delta a \) is the compositional average of the lattice constant of two terminal components and \( a \) is the difference from the average. This attempt has been applied to the analysis of the thermodynamic properties of alloy semiconductors. The theoretical basis of this treatment is that the mixing enthalpy is ascribed to the bond distortions related to macroscopic elastic properties of crystal. The experimental interaction energies of (Ti, Zr)(C, N) (Hf, Ti)(C, N) (Nb, V)(C, N) and (Hf, V)(C, N) are plotted in Fig. 2. The empirical relation between the interaction energy and the lattice mismatch factors as shown by this figure can be represented by the following equation:

\[ L^{\text{fccc}} = 6.03 \times 10^7 (\Delta a/a)^2 \] (J/mol) ............(28)

Lattice constants of each carbide and nitride composed of Nb, Ti and V are quoted from a reference and are listed in Table 1. The interaction parameters of the pseudobinary
2.4. Experimental Investigation of Phase Separation in Carbonitrides

Rudy, Hillert and Staffansson pointed out that a miscibility gap forms in the double-pseudobinary system due to the difference in the Gibbs energy of formation of terminal compounds. This means that a phase separation occurs depending on the $K$ values defined in the present study. Although there have been reports on the experimental determination of phase equilibria between NaCl-type carbonitrides, the data are still quite limited because of the difficulty of attaining equilibrium due to low diffusivity in the carbonitrides. Therefore, experimental identification of the immiscibility in carbonitride system was attempted in the present study. The miscibility gaps in the carbonitrides were measured using the Fe-base specimens listed in Table 3, since the solubility of Fe in the NaCl-type carbonitrides is negligibly small in most cases. This method is useful for obtaining equilibrium through the rapid diffusion of C and N in the austenite.

All specimens were prepared by induction melting under an Ar atmosphere and nitrogen was added to the alloys by introducing N$_2$ gas in the furnace. The specimens were sealed in quartz capsules in an Ar atmosphere and annealed at 1 473 K for 120 h, 1 373 K for 240 h and 1 273 K for 480 h. In case of the (Nb, V)C system, following heat treatments were also carried out: 1 303 K for 480 h, 1 403 K for 240 h, 1 503 K for 120 h and 1 573 K and 1 603 K for 24 h. After annealing, the Fe, Nb, Ti and V contents in the precipitations extracted by means of carbon replica were determined by STEM-EDX. The C and N contents were determined according to Vegard’s law in the complex carbonitride. Precipitates were extracted electrochemically with 0.5 N-HCl solution, and back-reflection X-ray photographs of the residue were taken to determine the lattice constant. According to Vegard’s law, the lattice constant of the (M$_1$,M$_2$)(C, N) complex compound is expressed by Eq. (29) based on the assumption shown by Eq. (30) which represents the stoichiometry of the compound and which shows that the solubility of Fe in the carbonitride is negligibly small.

$$a_{M_1C} = a_{M_1}^{p} + y_{M_1}^{p} a_{M_2C}$$

$$a_{M_2C} = a_{M_2}^{p} + y_{M_2}^{p} a_{M_1C}$$

$$y_{M_1} = 1, \quad y_{M_2} = 1$$

In the above equations, $a_{MX}$ represents the lattice constant of MX; the values are listed in Table 1. $y_p$ is the fraction of the component in the sublattice. The values of $y_p$ and $a$ were determined experimentally in this work, and $y_p$ was calculated from Eqs. (29) and (30).

The experimental data of each system are listed in Tables 4 and 5. Figure 3 shows the experimental results, where the solid and dotted lines represent the calculated binodal and

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**Table 1.** Lattice constants and thermodynamic data of binary carbides and nitrides.

| phase | lattice constant /nm | formation free energy /J mol$^{-1}$ | solubility product in γ |
|-------|----------------------|---------------------------------|-------------------------|
| NbC   | 0.4470               | -139000 + 2.30 T$^{10}$         | 1.74 - 5600 / T + (mass% C) (1380 / T - 0.027) $^{10}$ |
| TiC   | 0.4338               | -184640 + 11.00 T$^{10}$       | 3.23 - 7430 / T + (mass% C) (1300 / T - 0.03) $^{11}$ |
| VC    | 0.4165               | -101630 + 7.90 T$^{10}$        | 1.32 - 2980 / T + (mass% C) (1160 / T - 0.2) $^{12}$ |
| NbN   | 0.4392               | -229240 + 94.85 T$^{13}$       | 5.09 - 11880 / T $^{13}$ |
| TiN   | 0.4244               | -382680 + 114.29 T$^{14}$      | 4.35 - 14890 / T $^{14}$ |
| VN    | 0.4139               | -217040 + 87.34 T$^{15}$       | 2.21 - 6680 / T $^{15}$ |

**Table 2.** Interaction energies estimated by Eq. (28).

| Interaction parameter / J mol$^{-1}$ |
|-------------------------------------|
| $L_{NaC}$                           |
| 6280                                |
| $L_{NbC}$                           |
| 30090                               |
| $L_{SiC}$                           |
| 8880                                |
| $L_{NaCN}$                          |
| 7080                                |
| $L_{NbVN}$                          |
| 21210                               |
| $L_{TiC}$                           |
| 3780                                |
| $L_{TiN}$                           |
| 1870                                |
| $L_{FeC}$                           |
| 2320                                |
| $L_{FeN}$                           |
| 240                                 |

**Table 3.** Chemical compositions of the experimental steels (mass%).

| System | Nb | Ti | V | C | N |
|--------|----|----|---|---|---|
| Fe(Nb, V)C | 8.8 | -  | 8.1 | 3.1 | - |
| Fe(Nb, Ti)C | 13.3 | -  | 12.1 | 4.6 | - |
| Fe(Nb, Ti)C | 17.4 | -  | 15.9 | 6.0 | - |
| Fe(Nb, Ti)C | 0.44 | 5.07 | 1.31 | 1.51 | - |
| Fe(Nb, Ti)C | 0.45 | 3.49 | 3.49 | 1.21 | - |
| Fe(Nb, Ti)C | 0.58 | 0.17 | -  | 0.18 | 0.068 |
| Fe(Nb, Ti)C | 0.67 | 0.13 | -  | 0.13 | 0.068 |
| Fe(Nb, Ti)C | 0.17 | 0.25 | -  | 0.13 | 0.070 |
| Fe(Nb, Ti)C | 0.61 | 0.45 | 0.20 | 0.057 |
| Fe(Nb, Ti)C | 0.43 | 0.62 | 0.18 | 0.064 |
| Fe(Nb, Ti)C | 2.08 | 2.29 | 0.42 | 0.119 |
| Fe(Nb, Ti)C | -  | 0.20 | 0.63 | 0.42 | 0.062 |
| Fe(Nb, Ti)C | -  | 0.23 | 0.73 | 0.40 | 0.068 |
Table 4. Precipitate compositions of Fe–Nb–V–C system.

| Temperature / K | Precipitate Composition | Site Fraction |
|-----------------|-------------------------|--------------|
| 1273            | NbC 0.832 V 0.168       |              |
|                 | VC 0.078 V 0.922        |              |
|                 | NbC 0.881 V 0.119       |              |
|                 | VC 0.058 V 0.942        |              |
|                 | NbC 0.915 V 0.085       |              |
|                 | VC 0.101 V 0.899        |              |

Table 5. Precipitate compositions of Fe–Nb–Ti–V–C and Fe–M1–M2–C–N systems.

| System          | Temperature / K | Precipitate Composition | Site Fraction |
|-----------------|-----------------|-------------------------|--------------|
| (Nb, Ti)V/C     | 1273            | NbC 0.674 Ti 0.0847 Nb 0.2411 |              |
|                 |                 | VC 0.0851 Ti 0.0240 Nb 0.8909 |              |
|                 |                 | NbC 0.8190 Ti 0.0346 Nb 0.1464 |              |
|                 |                 | VC 0.0449 Ti 0.0087 Nb 0.9464 |              |
|                 |                 | NbC 0.6223 Ti 0.1144 Nb 0.2656 |              |
|                 |                 | VC 0.0650 Ti 0.0151 Nb 0.9199 |              |
|                 |                 | NbC 0.7419 Ti 0.0745 Nb 0.1836 |              |
|                 |                 | VC 0.0327 Ti 0.0105 Nb 0.9568 |              |
|                 |                 | NbC 0.6807 Ti 0.0967 Nb 0.2266 |              |
|                 |                 | VC 0.0059 Ti 0.0282 Nb 0.8859 |              |
|                 |                 | NbC 0.6515 Ti 0.0346 Nb 0.3139 |              |
|                 |                 | VC 0.1534 Ti 0.0373 Nb 0.8093 |              |
|                 |                 | NbC 0.6457 Ti 0.0934 Nb 0.2609 |              |
|                 |                 | VC 0.1653 Ti 0.0502 Nb 0.7845 |              |
| (Nb, Ti)(C,N)   | 1273            | NbC 0.915 Ti 0.0793 Nb 0.915 |              |
|                 |                 | VC 0.107 Ti 0.083 Nb 0.028 |              |
|                 |                 | NbC 0.984 Ti 0.016 Nb 0.844 |              |
|                 |                 | VC 0.097 Ti 0.093 Nb 0.022 |              |
|                 |                 | NbC 0.916 Ti 0.084 Nb 0.872 |              |
|                 |                 | VC 0.106 Ti 0.094 Nb 0.023 |              |
|                 |                 | NbC 0.967 Ti 0.033 Nb 0.749 |              |
|                 |                 | VC 0.140 Ti 0.086 Nb 0.043 |              |
|                 |                 | NbC 0.894 Ti 0.086 Nb 0.812 |              |
|                 |                 | VC 0.078 Ti 0.092 Nb 0.013 |              |
|                 |                 | NbC 0.909 Ti 0.091 Nb 0.758 |              |
|                 |                 | VC 0.117 Ti 0.083 Nb 0.158 |              |
|                 |                 | NbC 0.885 Ti 0.115 Nb 0.778 |              |
|                 |                 | VC 0.087 Ti 0.093 Nb 0.048 |              |
| (Nb, V)C(N)     | 1273            | NbC 0.858 V 0.142 V 0.967 |              |
|                 |                 | VC 0.120 V 0.880 V 0.752 |              |
|                 |                 | NbC 0.884 V 0.116 V 0.941 |              |
|                 |                 | VC 0.090 V 0.091 V 0.648 |              |
|                 |                 | NbC 0.848 V 0.152 V 0.840 |              |
|                 |                 | VC 0.218 V 0.782 V 0.656 |              |
|                 |                 | NbC 0.842 V 0.158 V 0.908 |              |
|                 |                 | VC 0.116 V 0.082 V 0.433 |              |
|                 |                 | NbC 0.806 V 0.019 V 0.862 |              |
|                 |                 | VC 0.155 V 0.005 V 0.500 |              |
| (Ti, V)C(N)     | 1273            | TiN - 0.923 V 0.007 V 0.124 |              |
|                 |                 | VC - 0.053 V 0.094 V 0.105 |              |
|                 |                 | TiN - 0.097 V 0.010 V 0.124 |              |
|                 |                 | VC - 0.078 V 0.022 V 0.049 |              |
spinodal curves, respectively. Tie lines are shown in Figs. 3 (b)–3(d), which shows good agreement with the experimental results. This fact suggests that the thermodynamic parameters determined in this work are reasonable for phase equilibrium calculations of NaCl-type complex carbonitride systems. In the (Nb, V)C system, the miscibility gap between NbC and VC is consistent with the result of Kieffer et al.\textsuperscript{8}) It is found that this region is almost symmetrical with respect to the composition and that the critical temperature is about 1 800 K. Although the miscibility gap is extended to the (Nb, Ti, V)C system, the difference of composition between NbC and VC decreases with increasing Ti contents. On the other hand, separation between TiN and NbC or VC occurred in the (Nb, Ti)(C, N) and the (Ti, V)(C, N) systems, respectively, depending on the K values. The effect of this parameter is clarified quantitatively by the estimation of critical temperature, $T_C$, of the ideal solution. $T_C$ of the miscibility gap in $(M_1, M_2)(X_1, X_2)$ without taking the interaction energy into account is given by $T_C=|K/4R|$,\textsuperscript{7}) and therefore, these values are obtained as 2 450 K for the (Nb, Ti)(C, N), 1 249 K for the (Nb, V)(C, N) and 1 447 K for (Ti, V)(C, N) systems. It is noted that the miscibility gap in the (Nb, Ti)(C, N) system is extremely stable and that the separation between TiN and NbC occurs even at high temperature.

**Fig. 4.** Phase equilibria between γ and (Nb, Ti, V)C at 1 273 K, keeping (mass% C)$_\gamma$=0.01. (mass% Ti)$_\gamma$ are (a) 0.003, (b) 0.006 and (c) 0.01, respectively.

**Fig. 5.** Phase equilibria between γ and (Nb, Ti)(C, N) at 1 473 K, keeping (mass% Nb)$_\gamma$+(mass% Ti)$_\gamma$=0.02. Contents of alloying elements in γ are (a) 0.00001 mass% Ti, 0.01999 mass% Nb, (b) 0.0005 mass% Ti, 0.0195 mass% Nb, (c) 0.01 mass% Ti, 0.01 mass% Nb and (d) 0.015 mass% Ti, 0.005 mass% Nb.
3. Calculation of Phase Equilibria

3.1. \( \gamma'\) (Nb, Ti, V)C Equilibrium

The equilibrium between \( \gamma \) and precipitates in the steel containing Nb, Ti, V and C was calculated by applying the method described in the foregoing section. The equilibrium conditions in this case are shown by Eqs. (22) to (24). These three equations contain six independent variables, i.e., \((\%\text{Nb}), (\%\text{Ti}), (\%\text{V})\) and \((\%\text{C})\) for \( \gamma \) and \( \gamma^p_{\text{M1}} \) and \( \gamma^p_{\text{M2}} \) for carbide. Therefore, if any three variables among them are fixed, the remainders are uniquely determined by solving these simultaneous equations. In the present study, the equilibrium calculation was performed by keeping \((\%\text{Ti})\) and \((\%\text{C})\) constant. The other constant parameter is \((\%\text{Nb})\) or \((\%\text{V})\), but the value was changed for each calculation.

The calculated \( \gamma' \)/carbide equilibria in the Fe–Nb–Ti–V–C system are shown in Figs. 4(a)–4(c). Three levels of Ti content in \( \gamma \) were employed in the calculation, namely, (a) 0.003, (b) 0.006 and (c) 0.01 (mass%). Phase separation in the carbide phase results in the three-phase triangle between \( \gamma \), Nb-rich carbide and V-rich carbide as shown in Figs. 4(a) and 4(b). These results show that a small amount of Ti promotes the uniformity of the carbide phase. This is because the lattice constant of TiC is between those of NbC and VC, and the dissolution of Ti to the complex carbide causes a relaxation of distortion in the (Nb, V)C lattice.

3.2. \( \gamma'\) (M1, M2)(C, N) Equilibrium

The equilibrium condition between \( \gamma \) and \((\%\text{Nb}, \%\text{Ti})(\%\text{C}, \%\text{N})\), for instance, is described by Eqs. (22), (23), (25) and (26). In this calculation, \((\%\text{M1})\) and \((\%\text{M2})\) were kept constant and the value of \((\%\text{X})\) was also fixed but changed for each calculation. The calculated phase equilibria of the \( \gamma'(\%\text{Nb}, \%\text{Ti})(\%\text{C}, \%\text{N}) \) at 1 473 K are shown in Figs. 5(a)–5(d), where the ratio of \((\%\text{Ti})\) to \((\%\text{Nb})\) was changed in four steps keeping 0.02% of their total amount. When the amount of \((\%\text{Ti})\) is extremely small, carbonitride in equilibrium with \( \gamma \) is homogeneous as shown in Fig. 5(a). However, a further increase in \((\%\text{Ti})\) results in the phase separation of precipitates as shown in Figs. 5(b) and 5(c).

3.3. \( \gamma'\) (Nb, Ti, V)(C, N) Equilibrium

The equilibrium condition between \( \gamma \) and \((\%\text{Nb}, \%\text{Ti}, \%\text{V})(\%\text{C}, \%\text{N})\) is defined by Eqs. (22) to (27). However, only four of these equations are independent, while this system contains eight unknown variables. Therefore, these equations can be solved by keeping four unknown variables constant. In this study, \((\%\text{Nb}), (\%\text{Ti})\) and \((\%\text{V})\) were kept constant and the value of \((\%\text{X})\) was fixed but changed for each calculation.

An example of the calculated phase diagrams at 1 273 K is shown in Fig. 6. The contents of Nb and Ti in \( \gamma \) phase are 0.01992 and 0.00008 mass%, respectively. As seen in Fig. 1, \( K_{\text{NbTi}} \) has a larger negative value than other \( K \) values, which causes the separation of Nb-rich carbide and Ti-rich nitride in the \( \gamma \) phase. Additional V may possibly be consumed for the formation of carbide or nitride. However, precipitation of these particles in the \( \gamma \) phase may hardly occur because a stable three-phase equi-
librium has already been achieved. Thus, V will be dissolved in the Nb-rich carbide or Ti-rich nitride. Considering the large difference in the lattice constants, V is unlikely to form a complex carbide with Nb. Therefore, V forms a complex nitride with Ti whose lattice constant is comparatively close to that of the vanadium nitride.

3.4. Mass Fraction of Precipitates

There is relatively little experimental data on phase equilibria of carbonitrides in practical steels, which make it difficult to examine the validity of the present calculation by comparison with experimental findings. However, the data of Okaguchi and Hashimoto,4) who measured the fraction of precipitates in some steels, are available for such comparison. Figure 8 shows a comparison of the fraction of precipitates calculated by using Eq. (31) with their experimental values for Ti, Ti–V and Nb–Ti steels. The calculation was made using the following relation:

\[ x_j^{\text{alloy}} = \frac{1}{2} y_j^p \sum f_j^p + x_j^\gamma \left(1 - \sum f_j^p\right), \] (31)

where \( x_j^{\text{alloy}} \), \( y_j^p \) and \( x_j^\gamma \) are the alloy composition, equilibrium compositions in the precipitate and \( \gamma \) phase, respectively. \( f_j^p \) is the molar fraction of a precipitate in an alloy. The experimental values and the results of calculation correspond within the limit of error.

4. Conclusions

(1) To calculate the phase equilibria between \( \gamma \) and (Nb, Ti, V)(C, N) in microalloyed steels, the Gibbs free energy of each phase was described using a two-sublattice description. The simultaneous equations derived from the equilibrium condition consist of several thermodynamic properties of terminal carbide and nitride, namely, the solubility product, formation energy and interaction parameters between the components. The solubility product and the formation energy were selected from the reported experimental data. The interaction parameters were obtained from lattice mismatches, assuming that Vegard’s law holds well in complex carbonitride systems. Calculated phase equilibria in the carbonitride systems based on these thermodynamic parameters were in good agreement with experimental data obtained by STEM-EDX and X-ray diffraction.

(2) The method was applied to the phase equilibria calculation between \( \gamma \) and (Nb, Ti, V)(C, N) and (Nb, Ti, V)(C, N)-type precipitates. The phase separation behavior in the precipitates could be understood in accordance with the relationship of \( K \) values. In general, the carbonitride separates into TiN and NbC, and V tends to...
dissolve into the nitride. An attempt was made to estimate the mass fraction of complex carbonitride in some steels and to compare calculated results with corresponding experimental data, which showed good agreement within the limit of experimental error.

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Appendix 1

K parameters symbolize the difference in Gibbs energy of formation for boundary component. In this study, they are defined as follows.

\[ K_{NbTi} = \frac{G_{NbC}}{G_{TiC}} - \frac{G_{NbN}}{G_{TiN}} = \frac{G_{NbTi}}{G_{NbN} + G_{TiN}} \]  

(A-1)

\[ K_{NbV} = \frac{G_{NbC}}{G_{VC}} - \frac{G_{NbN}}{G_{VN}} = \frac{G_{NbV}}{G_{NbN} + G_{VN}} \]  

(A-2)

\[ K_{TiV} = \frac{G_{EC}}{G_{TiC}} - \frac{G_{VN}}{G_{VTi}} = \frac{G_{TiV}}{G_{VN} + G_{VTi}} \]  

(A-3)

Rudy et al. reported that when the value of \( K = \Delta G_{M,N}^{\text{f,cr}} - \Delta G_{M,X}^{\text{f,cr}} \) in the理想 (\( M_1, M_2, X_1, X_2 \)) double-pseudobinary system, the Gibbs energy curves on the \( M_1X_1-M_2X_2 \) cross section are convex upward below the critical temperature and the miscibility gap appears in the direction of \( M_1X_1-M_2X_2 \).

Appendix 2

In Eqs. (10) through (15), L parameters are represented as follows:

\[ L_1 = (\frac{p_{Nb}y_{Nb} + p_{C}y_{C}}{p_{Ti}y_{Ti} + p_{Nb}y_{Nb} + p_{C}y_{C}})^{\frac{f_{NbC}}{f_{TiC}}} \]  

(A-4)

\[ L_2 = (\frac{p_{Nb}y_{Nb} + p_{C}y_{C}}{p_{Ti}y_{Ti} + p_{Nb}y_{Nb} + p_{C}y_{C}})^{\frac{f_{NbC}}{f_{TiC}}} \]  

(A-5)

\[ L_3 = (\frac{p_{Nb}y_{Nb} + p_{C}y_{C}}{p_{Ti}y_{Ti} + p_{Nb}y_{Nb} + p_{C}y_{C}})^{\frac{f_{NbC}}{f_{TiC}}} \]  

(A-6)

\[ L_4 = (\frac{p_{Nb}y_{Nb} + p_{C}y_{C}}{p_{Ti}y_{Ti} + p_{Nb}y_{Nb} + p_{C}y_{C}})^{\frac{f_{NbC}}{f_{TiC}}} \]  

(A-7)

\[ L_5 = (\frac{p_{Nb}y_{Nb} + p_{C}y_{C}}{p_{Ti}y_{Ti} + p_{Nb}y_{Nb} + p_{C}y_{C}})^{\frac{f_{NbC}}{f_{TiC}}} \]  

(A-8)

\[ L_6 = (\frac{p_{Nb}y_{Nb} + p_{C}y_{C}}{p_{Ti}y_{Ti} + p_{Nb}y_{Nb} + p_{C}y_{C}})^{\frac{f_{NbC}}{f_{TiC}}} \]  

(A-9)