Computer Model for Prediction of Carbonitride Precipitation during Hot Working in Nb–Ti Bearing HSLA Steels

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A computer model which predicts complex precipitation behavior quantitatively in Nb–Ti bearing steel has been developed on a theoretical basis. The solubility and composition of the complex precipitates, and the chemical driving force of the precipitates from supersaturated austenite are estimated by means of thermodynamic analysis of regular solution composed of four-binary compounds. The change in dislocation density which acts as a nucleation site during hot working is calculated by using dislocation theory. And the time dependence of volume fraction and the particle radius of strain induced precipitation are also predicted on the basis of classical nucleation theory. In order to estimate the effect of deformation on nucleation, the change in elastic energy of dislocation with nucleation is calculated.

Experimental results showed that combination of Nb and Ti addition, decreased the solubility of carbonitrides and accelerated the precipitation rate from supersaturated austenite because of the formation of complex precipitates. Such experimental results are in good agreement with the prediction by the present model. And both the acceleration of precipitation rate and the refinement of precipitates particles due to hot deformation are also quantitatively explained.

KEY WORDS: microalloying; complex precipitation; solubility; precipitation kinetics; thermodynamics; hot deformation; dislocation density; computer modelling.

1. Introduction

Microalloying elements, such as Nb, V and Ti which form carbide/nitride precipitates during hot working process, achieve the control of austenite grain and precipitation strengthening of ferrite by controlled formation of precipitates. Some precipitation models of carbonitride in microalloyed austenite have been developed for Nb^{1–3)} and Ti^{4,5)} bearing steels, in order to control the precipitates during and after hot working. These models, however, are applicable only to the steels containing one microalloying element. Therefore, it is necessary to develop the model for the prediction of precipitation in multi-microalloyed HSLA steels.

It is well known that combined addition of microalloying elements leads to formation of complex precipitates (which contains at least two metallic elements in precipitates), since the binary carbide and nitride of Nb, V and Ti are mutually soluble because of their B_1 type structure.^{6,7)} The formation of the complex precipitates changes the grain growth and the recrystallization behavior of austenite and sometimes decreases the tensile strength of controlled rolled plates of Nb–Ti bearing steels.⁸⁾ Therefore it is necessary to take account of the complex precipitation for the precipitation model of multi-microalloyed steels.

The purpose of the present work are to develop a computer model which predicts the precipitation be-

havior in austenite during solution treatment and hot working process in Nb–Ti bearing steel and to examine the experimental data of precipitation behavior compared with the calculated results in the steel.

2. Theoretical Treatment of Precipitation Model

2.1. Outline of the Model

Figure 1 shows the structure of the developed model. The model consists of thermodynamic model, nucleation-

Fig. 1. Block diagram of the present model.

growth model and recovery-recrystallization model. The thermodynamic model calculates the equilibrium fraction of complex precipitates during solution treatment, and it estimates the chemical driving force of strain induced precipitates from hot worked-supersaturated austenite. The nucleation and growth model predicts the time dependence of volume fraction and particle radius of strain induced precipitates. The recovery and recrystallization model estimates the change in dislocation density which act as nucleation site of strain induced precipitates.

2.2. Thermodynamic Model

2.2.1. Solubility of Complex Precipitates

In this model, the solubility of complex precipitate which has B_1 type (NaCl) structure can be estimated. Nb and Ti site on one sub-lattice (which is fcc structure), and C and N site on the other sub-lattice (fcc) in the complex carbonitride precipitates of the form $(\text{Nb}_x\text{Ti}_{1-x})(\text{C}_y\text{N}_{1-y})$. x and y show mole fraction of Nb and C in each sub-lattice, where $0 \leq x \leq 1$ and $0 \leq y \leq 1$. When the precipitates are considered to be aggregates of four kinds of binary compound, namely, NbC, TiC, NbN and TiN, the mole fraction of the binary compound in the precipitates (x_{NbC} , x_{TiC} , x_{NbN} and x_{TiN}) are related to x and y as following equation.

$$\begin{aligned} x &= x_{\text{NbC}} + x_{\text{NbN}}, & y &= x_{\text{TiC}} + x_{\text{NbN}} \\ 1 &= x_{\text{NbC}} + x_{\text{TiC}} + x_{\text{NbN}} + x_{\text{TiN}} \end{aligned} \quad (1)$$

Based on the assumption that the complex precipitate is regular solution of the binary compounds, the free energy of the precipitates G^P is given by

$$\begin{aligned} G^P &= x_{\text{NbC}} G_{\text{NbC}} + x_{\text{TiC}} G_{\text{TiC}} + x_{\text{NbN}} G_{\text{NbN}} + x_{\text{TiN}} G_{\text{TiN}} \\ &+ RT \{ x_{\text{NbC}} \ln x_{\text{NbC}} + x_{\text{TiC}} \ln x_{\text{TiC}} + x_{\text{NbN}} \ln x_{\text{NbN}} \\ &+ x_{\text{TiN}} \ln x_{\text{TiN}} \} + E_{G_m} \end{aligned} \quad (2)$$

where G_{NbC} , G_{TiC} , G_{NbN} and G_{TiN} are the free energy of binary compounds, NbC, TiC, NbN and TiN, respectively. And E_{G_m} shows the excess molar free energy of mixing. R is the gas constant, and T is the absolute temperature. G^P in Eq. (2) is different from the free energy derived by the sub-lattice model,⁹⁾ with respect to the expression of combination of binary compounds in the precipitates (Eq. (1)). The degree of freedom is larger in the present model than that in the sub-lattice model.

In order to estimate the partial free energy of binary compounds in the precipitates, Roozeboom's equation which calculates chemical potential for binary solution was extrapolated to the solution of n components.

$$\mu_i = G + (1 - x_i) \cdot (\partial G / \partial x_i) - \sum_{j \neq i} x_j \cdot (\partial G / \partial x_j) \quad (3)$$

where x_i and μ_i are the mole fraction and the partial free energy of i -component. When the excess free energy is assumed to be negligible with regard to Nb-Ti complex precipitates, the partial free energy of binary carbide/nitride μ^P , is given as following equation.

$$\begin{aligned} \mu_{\text{NbC}}^P &= G_{\text{NbC}} + RT \ln x_{\text{NbC}}, & \mu_{\text{TiC}}^P &= G_{\text{TiC}} + RT \ln x_{\text{TiC}} \\ \mu_{\text{NbN}}^P &= G_{\text{NbN}} + RT \ln x_{\text{NbN}}, & \mu_{\text{TiN}}^P &= G_{\text{TiN}} + RT \ln x_{\text{TiN}} \end{aligned} \quad (4)$$

Equation (4) means that the activities of binary

compounds are equal to the mole fraction of binary compounds in complex precipitates.

When austenite precipitates are in equilibrium, the chemical potential of each element in both phases are equal. With respect to the binary carbide/nitride in the precipitates, following equations of equilibrium condition are obtained.

$$\begin{aligned} \mu_{\text{NbC}}^P &= \mu_{\text{Nb}} + \mu_{\text{C}}, & \mu_{\text{TiC}}^P &= \mu_{\text{Ti}} + \mu_{\text{C}} \\ \mu_{\text{NbN}}^P &= \mu_{\text{Nb}} + \mu_{\text{N}}, & \mu_{\text{TiN}}^P &= \mu_{\text{Ti}} + \mu_{\text{N}} \end{aligned} \quad (5)$$

where μ_i is the partial free energy of each element in austenite.

From Eqs. (4) and (5), the equations of equilibrium condition are rewritten by using the activities of soluble atoms in austenite a_i and the standard free energy of formation of the precipitates ΔG .

$$\begin{aligned} \Delta G_{\text{NbC}} &= RT \ln \{ a_{\text{Nb}} \cdot a_{\text{C}} / x_{\text{NbC}} \}, \\ \Delta G_{\text{TiC}} &= RT \ln \{ a_{\text{Ti}} \cdot a_{\text{C}} / x_{\text{TiC}} \}, \\ \Delta G_{\text{NbN}} &= RT \ln \{ a_{\text{Nb}} \cdot a_{\text{N}} / x_{\text{NbN}} \}, \\ \Delta G_{\text{TiN}} &= RT \ln \{ a_{\text{Ti}} \cdot a_{\text{N}} / x_{\text{TiN}} \} \end{aligned} \quad (6)$$

The solute in the austenite are assumed to obey Henry's law since the solution is very dilute. Hence Eq. (6) is rewritten by using the solubility products of binary precipitates K_{MX} .

$$\begin{aligned} {}^eC_{\text{Nb}} \cdot {}^eC_{\text{C}} &= x_{\text{NbC}} \cdot K_{\text{NbC}}, & {}^eC_{\text{Ti}} \cdot {}^eC_{\text{C}} &= x_{\text{TiC}} \cdot K_{\text{TiC}} \\ {}^eC_{\text{Nb}} \cdot {}^eC_{\text{N}} &= x_{\text{NbN}} \cdot K_{\text{NbN}}, & {}^eC_{\text{Ti}} \cdot {}^eC_{\text{N}} &= x_{\text{TiN}} \cdot K_{\text{TiN}} \end{aligned} \quad (7)$$

where eC_i shows equilibrium concentration of i in austenite.

The equilibrium amounts of soluble elements can be estimated from the combination of the equilibrium conditions (Eq. (6) or (7)) and the mass balance for each elements in the precipitates and the austenite. The mass balance equation can be written as

$$\begin{aligned} {}^0C_{\text{Nb}} &= {}^eC_{\text{Nb}} + x \cdot Z1, & {}^0C_{\text{Ti}} &= {}^eC_{\text{Ti}} + (1 - x) \cdot Z1 \\ {}^0C_{\text{C}} &= {}^eC_{\text{C}} + y \cdot Z2, & {}^0C_{\text{N}} &= {}^eC_{\text{N}} + (1 - y) \cdot Z2 \\ Z1 &= ({}^0C_{\text{Nb}} - {}^eC_{\text{Nb}}) + ({}^0C_{\text{Ti}} - {}^eC_{\text{Ti}}), \\ Z2 &= ({}^0C_{\text{C}} - {}^eC_{\text{C}}) + ({}^0C_{\text{N}} - {}^eC_{\text{N}}) \end{aligned} \quad (8)$$

where, 0C_i shows the total (initial) amount of i element in the steel.

The solubility data of the binary compounds used in the present study are summarized in Table 1.

2.2.2. Driving Force of Precipitation

The amount of soluble microalloying elements in

Table 1. Solubility products of NbC, TiC, NbN and TiN in austenite used for calculation. [] shows amount of element dissolved in austenite (mass%).
 $\log_{10} K_{MX} = A - B/T(K)$, $K_{MX} = [M] \cdot [X]$

	A	B	Reference
NbC	2.96	7510	21)
TiC	2.75	7000	22)
NbN	4.04	10230	21)
TiN	0.322	8000	23)

austenite during solution treatment can be estimated by the calculation of the equilibrium condition discussed in Sec. 2.2.1, because equilibrium is easily reached at high temperature ($\geq 1200^\circ\text{C}$). At the first stage of hot working, however, microalloys are in supersaturated austenite. The chemical driving force of precipitation from the supersaturated austenite can be estimated as the difference of free energy between precipitates and embryo which is composed of elemental atoms that have the identical chemical potential with those in austenite. Therefore, the chemical driving force of complex precipitates ($\text{Nb}_x\text{Ti}_{1-x}$) (C_yN_{1-y}) per unit volume ΔG_v is given as

$$\Delta G_v = RT \left\{ \ln(C_{\text{Nb}}^x \cdot C_{\text{Ti}}^{1-x} \cdot C_{\text{C}}^y \cdot C_{\text{N}}^{1-y}) - \ln(C_{\text{Nb}}^x \cdot C_{\text{Ti}}^{1-x} \cdot C_{\text{C}}^y \cdot C_{\text{N}}^{1-y}) \right\} / V_p \quad (9)$$

where C_i is concentration of element i in supersaturated austenite and V_p shows the molar volume of the complex precipitates. In the present study, V_p is estimated as the molar volume of mixture of binary precipitates.

Figure 2 compares the driving forces of the precipitates ($\Delta G_v \cdot V_p$) in 0.03% Nb, 0.04% Ti and 0.03%Nb–0.04%Ti bearing steels with a base composition of 0.1%C–1.5%Mn–0.002%N. It was postulated that the steels were reheated at 1250 or 1100°C and then cooled to a temperature between 1100 and 800°C. In the case of 1250°C reheating, ΔG_v in Nb–Ti bearing steel is higher than ΔG_v in Nb bearing steel. Whereas in the case of 1100°C reheating, ΔG_v in Nb–Ti bearing steel is less than

Fig. 2. Comparison of chemical driving forces of precipitation among 0.03% Nb, 0.04% Ti and 0.03%Nb–0.04%Ti bearing steels with a base composition of 0.1%C–1.5%Mn–0.002%N. (a) 1250°C reheating, (b) 1100°C reheating

in Nb bearing steel, because the amount of dissolved atoms in Nb–Ti bearing steel decreases by the formation of complex precipitates.

2.3. Nucleation and Growth Model

2.3.1. Nucleation on Dislocation

In order to estimate the acceleration effect of hot deformation on precipitation kinetics quantitatively, the model calculates the precipitation kinetics on dislocations based on the classical nucleation theory. Akamatsu *et al.*³⁾ assumed that the strain energy of nucleation (which enhances precipitation) changes with dislocation density. However, dislocation density itself is not considered to change the thermal activated process of nucleation. Therefore this model calculates the elastic energy change of the system with nucleation on dislocations derived by Cahn¹⁰⁾ and Umemoto *et al.*,¹¹⁾ for the estimation of the acceleration effect by hot deformation.

When spheroidal precipitates nucleate on a dislocation, free energy change (ΔG) associated with the nucleation is given by using the driving force of precipitation, ΔG_v and interface face energy between precipitates and austenite per unit area, γ_p .

$$\Delta G = 4/3 \cdot \pi r^3 (\Delta G_v / V_p) - \Delta E_d(r) + 4\pi r^2 \gamma_p \quad (10)$$

where r is the radius of the precipitates and $\Delta E_d(r)$ is the elastic energy change of dislocation within the spherical region with radius r . $\Delta E_d(r)$ of screw dislocation is given as¹¹⁾:

$$\Delta E_d(r) = Gb^2 r / 2\pi \cdot \ln(2r/r_0) + Gb^2 r / 5 \quad (11)$$

where G and b are shear modulus ($7.5 \times 10^{10} \text{ N} \cdot \text{m}^{-2}$) and Burger's vector ($2.5 \times 10^{-10} \text{ m}$) of austenite. r_0 means the radius of dislocation core ($2.0 \times 10^{-10} \text{ m}$). **Figure 3** compares the change of ΔG with the radius of precipitates among homogeneous nucleation, grain boundary nucleation and dislocation nucleation in 0.1%C–0.03%Nb–0.02%Ti–0.002%N steel. In the calculation, γ_p and V_p

Fig. 3. Relationship between free energy and particle radius of precipitates, in the case of homogeneous, boundary and dislocation nucleation in 0.03%Nb–0.02%Ti steel.

of precipitate were estimated at $0.8 \text{ (J/m}^{-2}\text{)}$ and $1.3 \times 10^{-5} \text{ (m}^3 \cdot \text{mol}^{-1}\text{)}$, respectively. It was assumed that the steel was cooled to a precipitation temperature of 950°C , after solution treatment at 1200°C . Figure 3 shows that both the maximum energy (ΔG^*) and the critical radius for dislocation nucleation (r^*) are much smaller than those of homogeneous and boundary nucleation. This means that dislocations act as the effective nucleation site of precipitates.

In the present model, ΔG^* does not change with a magnitude of dislocation density. Since nuclei is sufficiently small, the stress field of dislocation does not change with nucleation. The dislocation density affects the number of nucleation sites.

2.3.2. Nucleation Rate

The nucleation rate of precipitation is given on the basis of classical nucleation theory, as following equation.

$$I(t) = A \cdot \rho(t) \cdot D_X \cdot C_X(t) \cdot \gamma_p^{0.5} \cdot V_p \cdot (kT)^{-0.5} \cdot L_r^{-4} \cdot \exp(-\Delta G^*/kT) \quad \dots\dots(12)$$

where A is constant and k is Boltzmann's constant, D_X and C_X are the diffusivity (m^2/s) and the concentration of X in austenite, respectively. And L_r is the lattice constant of austenite ($4 \times 10^{-10} \text{ m}$) and ρ is the dislocation density (m^{-2}). For simplicity, D_X and C_X for the complex precipitates are estimated as average diffusivity and average concentration as follows

$$D_X = x \cdot D_{\text{Nb}} + (1-x) \cdot D_{\text{Ti}}, \quad C_X = x \cdot C_{\text{Nb}} + (1-x) \cdot C_{\text{Ti}} \quad \dots\dots\dots(13)$$

2.3.3. Growth Rate

The precipitate particle is considered to grow to be controlled by the matrix diffusion of microalloying elements. The growth rate is estimated from the profile of concentration of microalloys in austenite in the vicinity of interface of particle. In the present model, the concentration profiles of microalloys are approximated by the straight line. From the mass balance between the necessary amount for growth of spheroidal particle and the influx of atoms into particle by diffusion, the growth rate of precipitate particle is given as follows.

$$r(t) = \alpha \cdot (t - t_0)^{1/2} \quad \dots\dots\dots(14)$$

$$\alpha = [2 \cdot (C_E - C_r) / (C_P - C_r) \cdot D_X]^{1/2}$$

where C_P and C_r are the equilibrium concentration of microalloys of precipitates and austenite at the interface, C_E is the concentration of microalloys at the end of diffusion area, which is equal to the initial concentration of soluble elements in austenite (C_0) at the first stage of growth. t_0 is the time when a precipitate particle nucleates.

When the particles are small, diffusion area of precipitates does not influence each other. As precipitates grow, however, the overlapping of diffusion area occurs (soft impingement of precipitation), and then the growth rate will decrease. Since the value of C_P is much larger than those of C_r and C_0 in HSLA steel, the volume fraction of precipitates which the soft impingement takes place is approximated by a half of final volume fraction

X_F in the case of one dimensional diffusion. In three dimension, the volume fraction at which soft impingement will occur is estimated to be about $0.11X_F$. In the present model, it is assumed that the change of C_E with time is equal to the change of average soluble concentration C_X after the soft impingement.

2.3.4. Precipitation Kinetics

Volume fraction of precipitates at time t can be described by the following equation:

$$X(t) = 1 - \exp \left\{ -4\pi/3 \cdot \int_0^t I(\tau) \cdot \alpha(\tau)^3 \cdot (t - \tau)^{2/3} d\tau \right\} \quad \dots\dots(15)$$

Precipitation ratio f to the equilibrium volume fraction (X_F) at time t is defined as:

$$f = X(t)/X_F, \quad \text{where } X_F = (C_0 - C_r)/(C_P - C_r) \quad \dots\dots(16)$$

From the relationship among the volume fraction, radius and the number of precipitates, the average radius of precipitate particle r can be calculated as:

$$r = (3 \cdot X_F \cdot V_p / 4\pi \cdot N_F)^{1/3} \quad \dots\dots\dots(17)$$

where N_F is the total number of nuclei nucleated throughout precipitation. In the present model, N_F is approximated by the total number of nuclei nucleated until $0.95X_F$:

$$N_F = \int_0^{t_{0.95}} I(t) \cdot (1 - X(t)) dt \quad \dots\dots\dots(18)$$

where $t_{0.95}$ means the time when volume fraction reaches to $0.95X_F$.

2.4. Recovery and Recrystallization Model

It is very important to estimate the change of dislocation density during hot working, since dislocation plays the significant part in nucleation of precipitation in the present model. For simplicity, the model deals with average dislocation density in spite of the heterogeneity of dislocation distribution in deformed austenite. The average dislocation ρ is defined as follows:

$$\rho = X_R \cdot \rho_R + (1 - X_R) \cdot \rho_d \quad \dots\dots\dots(19)$$

Fig. 4. Calculation of dislocation density in deformed austenite during holding after deformation. The marks of t_{rx} indicate the time which static recrystallization starts, and the dot lines show dislocation density in deformed austenite in the case without recrystallization. (0.01 % Ti steel, $\dot{\epsilon} = 5 \text{ s}^{-1}$, $\epsilon = 0.25$)

where X_R is the volume fraction of recrystallized austenite, ρ_R and ρ_d are the dislocation densities of recrystallized austenite ($\approx 10^{12} \text{ m}^{-2}$) and unrecrystallized austenite, respectively. The effect of hot working on ρ_d has been quantitatively estimated¹²⁾ on the basis of dislocation theory.¹³⁾ And the recrystallization kinetics after hot deformation also can be calculated,¹²⁾ based on the empirical expression by Sellars.¹⁴⁾

The calculated change in dislocation densities with time after hot deformation in 0.1%C–1.5%Mn–0.01%Ti–0.002%N steel is shown in Fig. 4. The hot deformation is postulated that strain rate is 5 s^{-1} and strain is 0.25 at each deformation temperature (1 050, 950 and 850°C). It is shown that higher dislocation density is formed by deformation and maintains during holding in the case of lower temperature deformation and holding, since both the degree of dynamic and static recovery is smaller at lower temperature than those at higher temperature.

3. Experimental Procedure

The chemical compositions of the steels used in the present study are listed in Table 2. The steels were melted as vacuum-induction melts in 150 kg ingots with a base composition of 0.09%C–1.6%Mn–0.02%Al–0.002%N. After hot forging the steels were hot rolled to 20 mm thick plates.

Steels A1 to A3 were used for the experiment on the solubility of complex precipitates. Small test pieces ($20 \text{ mm} \times 30 \text{ mm} \times 120 \text{ mm}$) machined from the steels were solution treated at a temperature between 900 and 1 250°C for 5 h followed by water quenching. Precipitates were extracted with carbon replicas from the specimens

for observation. Compositions of the individual particles on the replicas were measured by the STEM-EDX quantitative microanalysis. Total amount of microalloys in precipitates in solution treated specimens were determined by the chemical analysis of electro-chemically extracted residue.

For the experiment on the kinetics of strain-induced precipitation after hot deformation, steel B was used. Cylindrical specimens of 8 mm in diameter and 12 mm in height were machined from the steels. After solution treatment at 1 250°C for 10 min, the specimens were cooled to a precipitation temperature between 1 000 and 900°C, and then compressed at a strain rate of 1 s^{-1} . After the deformation, they were held at the precipitation temperature for various period (0 to 3 000 sec) followed by water quenching. In order to investigate the effect of hot deformation on precipitation kinetics, the precipitation tests without deformation were carried out. Volume fraction of precipitates were determined by means of chemical analysis of microalloys in the electro-chemically extracted residue from the specimens.

4. Correlation between Experimental Results and Theory

4.1. Volume Fraction of Complex Compounds Precipitated during Solution Treatment

Reports are available on the presence of the complex precipitates in several HSLA steels, like Nb–V,¹⁵⁾ V–Ti^{7,16)} and Nb–Ti⁶⁾ bearing steels and on the thermodynamic analysis of the complex compounds.^{6,17)} However there are few research on the complex precipitates from the viewpoint of comparison between experimental results and theoretical analysis on both chemistry and volume fraction of precipitates.

An example of complex precipitates formed in 0.028%Nb–0.048%Ti steel (A1) which was reheated to 1 250°C for 5 h is shown in Fig. 5. The energy dispersive X-ray (EDX) from the particle (indicated by an arrow) shown in Fig. 5(b) indicates the sharp peaks of both Nb and Ti, while the electron diffraction pattern of the particle shown in Fig. 5(c) indicates the single crystal of B_1 rock salt structure. This suggests that Nb and Ti were

Table 2. Chemical compositions of the steels investigated. (mass%)

Steel	C	Si	Mn	S	Nb	Ti	sol.Al	N
A1	0.09	0.44	1.60	0.005	0.028	0.048	0.014	0.0020
A2	0.08	0.44	1.57	0.005	0.027	0.063	0.013	0.0022
A3	0.09	0.43	1.57	0.005	0.028	0.132	0.018	0.0021
B	0.09	0.20	1.62	0.003	0.020	0.042	0.039	0.0020

Fig. 5.

Complex precipitate particle observed in 0.028%Nb–0.048%Ti steel (A1) solution treated at 1 250°C for 5 h followed by water quenching. (b) and (c) show result of energy dispersive X-ray (EDX) analysis and diffraction pattern (shows single crystal of B_1 rock salt structure) from the particle shown by an arrow in (a), respectively.

mutually significantly soluble in the precipitates, as previously reported.⁶⁾ Figure 6 shows the calculated and microanalyzed composition for the precipitate particles in 0.028%Nb–0.048%Ti (A1) and 0.027%Nb–0.063%Ti steel (A2) reheated at a temperature between 900 and 1250°C. The experimental data of composition (Nb/(Nb+Ti) ratio) in precipitates were measured from 8 to 10 particles for each specimen by EDX microanalysis and denoted by error bars in the figure. The calculated results of microalloys (Nb/(Nb+Ti)) and interstitial elements (C/(C+N)) by the present model are denoted

Fig. 6. Relationship between calculated composition by the present model and microanalyzed composition for precipitates particles in Nb–Ti steels (A1, A2).

by solid line and broken line, respectively. It is shown that the measured value of Nb/(Nb+Ti) ratio varied from 0.1 to 0.3 with the peak at about 1100°C in both steels. The calculation predicts the complete mixing of Nb and Ti in precipitates and the tendency to form a TiN-rich compound at higher temperature. The calculated Nb/(Nb+Ti) ratio by the present model is good agreement with the measured one, especially on the presence of the peak at about 1100°C in both steels.

Figure 7 shows the relationship between measured and calculated results with respect to the amount of microalloys as precipitates in Nb, Ti and Nb–Ti bearing steels. The amounts of Nb and Ti as precipitates in steels were measured by means of chemical analysis of the electro-chemically extracted residue from the specimens. For the prediction of precipitation, two types of calculations were carried out. One is the complex precipitates $(\text{Nb}_x\text{Ti}_{1-x})(\text{C}_y\text{N}_{1-y})$ by the present model (denoted by solid line) and the other is independent precipitation $(\text{NbC} + \text{TiC} + \text{TiN})$ model by Keown and Wilson¹⁸⁾ (denoted by broken line). For the estimation of Ti in precipitates, it was presumed that all titanium sulfides had already precipitated in all Ti bearing steels. When comparing the calculated weights with the measured weights of Nb+Ti as precipitates, the calculated values by the independent precipitation model were much lower than the measured values in the steels. In particular, there is a considerable difference between the calculated and measured amount of Nb; the calculation predicted that all Nb was soluble in austenite above 1100°C in three Nb–Ti steels, while the measurements showed that only 4 to 27% of Nb was dissolved in austenite at 1100°C. On the other hand, the calculated results by the complex precipitation model were in good agreement with the measured values for both Nb and Nb+Ti. This suggests that the mixing of Nb and Ti increased the stability of the precipitates, so that the solubility of precipitates decreases in Nb–Ti

Fig. 7. Comparison between calculated and measured amounts of microalloys as precipitates in three Nb–Ti bearing steels (A1–A3). Solid line and broken line show calculated amounts by the present model and the independent precipitation model,¹⁸⁾ respectively.

Fig. 8. Precipitation-time-temperature (PTT) diagrams in undeformed (a) and deformed austenite (b) of 0.020%Nb-0.048%Ti steel (steel B) calculated by the present model. The numbers indicate measured fraction of precipitates. Broken lines show precipitation start time curves ($f=5\%$) calculated by the independent precipitation model.¹⁹⁾

bearing steels through the formation of complex precipitates. Thus, the formation of complex precipitates should be taken into consideration in the design of chemical composition and thermomechanical condition in Nb-Ti bearing steel.

4.2. Kinetics of Strain-induced Precipitation during Hot Deformation

Figure 8 shows precipitation-time-temperature (PTT) diagrams for 0.020%Nb-0.042%Ti bearing steel (steel B) in the case of without hot deformation (Fig. 8(a)) and with hot deformation (Fig. 8(b)). The numbers in the figure indicate the measured fraction precipitated, f defined by Eq. (16). The solid line shows the calculated results of precipitation kinetics by the model of complex precipitates $(\text{Nb}_x\text{Ti}_{1-x})(\text{C}_y\text{N}_{1-y})$ and the broken lines in Fig. 8(b) show the calculated result by the model assumed that NbC and TiC precipitate separately. The precipitation start time curve (time for 5% precipitation) shows a C-curve with a nose at a minimum time of about 1000 sec at 1000°C in undeformed austenite. The precipitation start time in deformed austenite ($\epsilon=0.25$) was about 100 sec, which was about an order faster than that in undeformed austenite. The degree of acceleration by deformation was more significant at 900°C than at 1000°C, so that the nose temperature was lower in deformed material.

Fig. 9. Average radius of precipitates in deformed (solid) and undeformed (open mark) austenite denoted by error bars in steel B. Solid and broken lines show the calculated results for precipitation on dislocation and on grain boundary, respectively.

The calculated precipitation curves predict the classical C-shape in both deformed and undeformed austenite. The good agreement can be seen between the calculated curves by the present model and the experimental data, especially on the acceleration of precipitation kinetics and the decrease of nose temperature by deformation. When comparing the curves predicted by the present model with the curves by the independent precipitation model,¹⁹⁾ it is noted that the complex precipitates starts earlier than the binary precipitates, NbC, TiC. The complex precipitates have larger driving force of precipitation than the binary compounds, as shown in Fig. 2. This suggests the retardation effect of strain induced precipitation on recrystallization during hot working in multi-microalloyed (Nb-Ti) steel is larger than that in Nb or Ti bearing steel.²⁰⁾

Figure 9 shows the average radius of precipitates measured on the replicas extracted from both undeformed and deformed 0.020%Nb-0.042%Ti steels (steel B) compared with predicted radius by the model. It is shown that hot deformation considerably decreased the radius of precipitate particles. The decrease in particle size is due to the increase in nucleation rate of precipitation corresponding to the decrease of ΔG^* and the increase of nucleation site. The calculated results of precipitate radius agreed with the experimental data.

5. Conclusion

A theoretical model has been developed which predicts complex precipitation behavior quantitatively in Nb-Ti bearing steel. In the model, the formation of complex precipitates in the steel is taken into account. From the results of the calculation by the model and experiments, the following conclusions are obtained.

- (1) In Nb-Ti bearing steel, the complex precipitates

(Nb–Ti carbonitrides) formed during solution treatment. In the complex precipitates, Nb/(Nb+Ti) mole ratio varied from 0.1 to 0.3 with the peak at about 1100°C.

(2) The changes in both micro-chemistry and fraction of the complex precipitates can be well predicted as a function of temperature in Nb–Ti bearing steel by the present model. The mixing of Nb and Ti in the precipitates increases the stability of the precipitates, so that the combined addition of Nb and Ti decreases the solubility of precipitates through the formation of the complex precipitates.

(3) The precipitation start time in deformed austenite ($\varepsilon=0.25$) was about an order faster than in undeformed austenite. The degree of acceleration by deformation was more significant at 900°C than at 1000°C. The precipitation particles precipitated in deformed austenite were smaller than those in undeformed austenite.

(4) The calculated precipitation curves were good agreement with the experimental precipitation curves in both deformed and undeformed austenite. The combined addition of Nb and Ti accelerates the precipitation start time, because the complex precipitates have larger driving force of precipitates than the binary compounds.

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