

Equilibrium Precipitation of Niobium Carbonitride in Austenite

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Abstract: The equilibrium between niobium carbonitride and austenite has been studied. Experimentally, X-ray diffraction technique was adopted to verify that the precipitates have the same composition and structure. Theoretically, Hillert and Staffansson's regular model about stoichiometric phase was used to describe the thermodynamic properties of multi-component precipitate. Calculated results agree well with experimental values from literatures.

Key words: equilibrium; niobium precipitate; austenite

Since niobium has a strong affinity to carbon and nitrogen, niobium carbide and nitride form easily in HSLA steels. They play an important role in grain refining and precipitate strengthening. The equilibrium solution-precipitation law of niobium carbide and nitride in γ -Fe is described by use of the following formula

$$\lg ([\text{Nb}] \cdot [\bar{X}]_v) = A + B/T$$

where X is carbon or nitrogen mole fraction in γ -Fe, T is thermodynamic temperature, A and B are constants.

Many researchers have done systematical work on the solubility products for niobium carbide and nitride. Although reliable data have been obtained, those data are not suitable for practical microalloyed steels, since there are simultaneous carbon and nitrogen in steels. It has been shown that there exist multi-component carbonitrides in microalloyed steels, the composition of which varies with both the original composition of steel and temperature at which it precipitates. Therefore, a problem arises as to how to describe precisely the equilibrium precipitation behaviour of microalloying element carbonitride in austenite.

In this paper, based on the consideration of the structure and composition of equilibrium carbonitride

precipitate in niobium microalloyed steels, theoretically, the thermodynamic model has been adopted to predict the thermodynamic properties of the equilibrium between niobium carbonitride and austenite.

1 Experimental Materials and Methods

Experimental materials were melted in 5 kg vacuum induction furnace. Casts were held at 1300 °C for 8 h in order that alloying elements were homogenized and then forged to $\phi 8$ mm in diameter at temperatures between 1150 and 900 °C. Compositions of the specimens were shown in **table 1**. Steel rods were machined to samples with $\phi 6$ mm \times 60 mm for electrolysis.

Under protection of argon, the samples were heat treated in Mo wire furnace. They were first solution treated at 1350 °C and quenched into brine. Isothermal heat treatments were then carried out at 900 °C for more than 50 h and interrupted by quenching in brine. The specimens always had clean surfaces after the heat treatments. Electrochemical means [1] was adopted and precipitates were collected for X-ray diffraction analysis, which was carried out in DMAX-RC diffractometer.

Table 1 The composition of tested steels (mass fraction in %)

No.	C	Mn	Si	S	P	Nb	N	O
1	0.089	1.31	0.478	0.007	0.009	0.074	0.004 0	0.003 3
2	0.062	1.37	0.489	0.005	0.008	0.125	0.003 9	0.003 2
3	0.099	1.86	0.480	0.005	0.009	0.079	0.017 8	0.004 6

2 Experimental Results and Analysis

Figure 1 illustrates the diffraction results for the precipitates electrochemically isolated from samples 1~3 which were equilibrium heat treated at 900 °C.

The results from figure 1 show that besides α -MnS, the residues mainly contain one type of precipitate and the structure is FCC.

Since lattice parameter $a = \sqrt{h^2 + k^2 + l^2}$ and $d(111) = 0.254 \sim 0.256$ nm from figure 1, $a = 0.4399 \sim 0.4434$ nm. The values of the lattice parameters of NbC and NbN from ASTM cards are 0.447 and 0.437

nm, respectively. Therefore, the experimental values are between those values of NbC and NbN from GCPDS cards. Pol Duwez *et al.* [2] reported the complete miscibility of niobium carbide and nitride, and measured the lattice parameters of solid solutions with a mixture of NbN and NbC at various mole ratios. Such an inference that the precipitates are niobium carbonitride can be derived.

3 Theoretical Calculation

3.1 Two assumptions in theoretical calculation

(1) There is the same composition for the precipi-

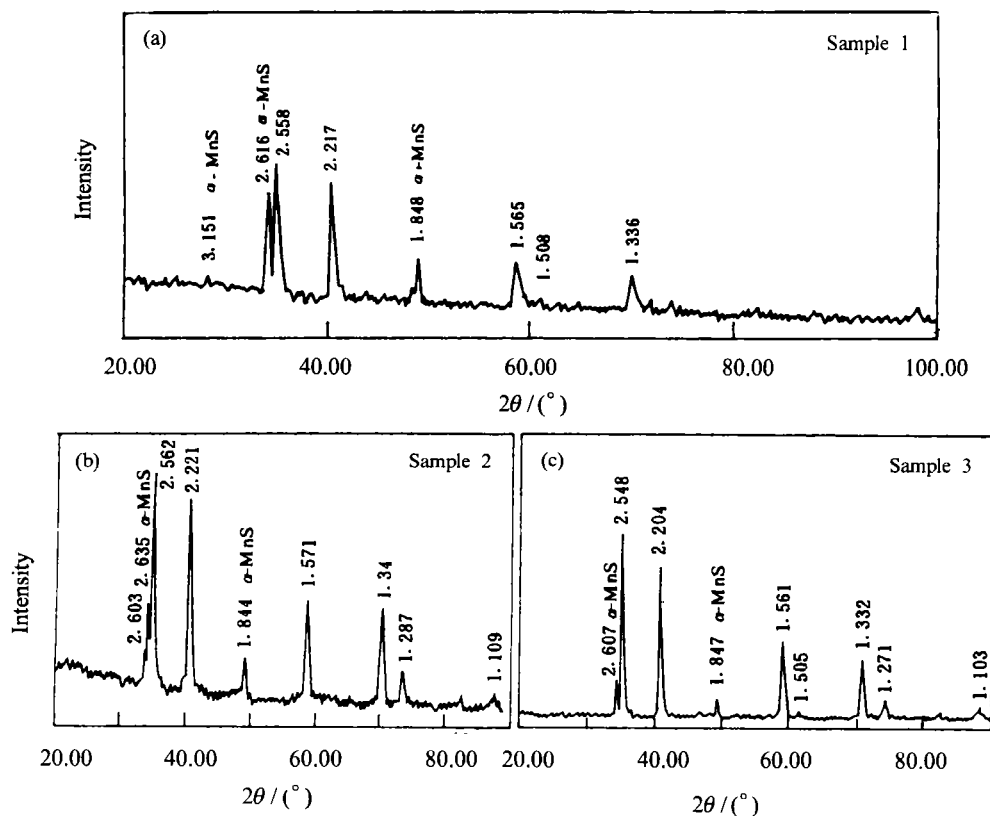


Figure 1 X-ray diffraction results for the precipitate isolated from samples

tates forming during equilibrium heat treatment. This assumption has been verified by X-ray diffraction analysis.

(2) The precipitate is stoichiometric. Therefore, the formula of the precipitate is $\text{NbC}_x\text{N}_{1-x}$, where x represents the mole fraction of lattice sites occupied by carbon in the interstitial sublattice occupied by carbon and nitrogen; the mole fraction of lattice sites for niobium is the same as that of interstitial site.

3.2 Thermodynamic model

The sublattice model, which was suggested by Hillert and Staffansson [3], was applied to describe

the interstitial solid solution.

Consider 1 mol of $\text{NbC}_x\text{N}_{1-x}$, the molar Gibbs free energy $G_{\text{NbC}_x\text{N}_{1-x}}$ has the following expressions

$$G_{\text{NbC}_x\text{N}_{1-x}} = G_m^{\text{ref}} - T \cdot S^m + {}^E G^m \quad (1)$$

$$G_m^{\text{ref}} = xG_{\text{NbC}}^0 + (1-x)G_{\text{NbN}}^0 \quad (2)$$

where G_{NbC}^0 and G_{NbN}^0 are the Gibbs free energies of the compounds NbC and NbN, respectively. T is thermodynamic temperature, and ${}^I S^m$ is ideal mixing entropy.

$${}^I S^m = -R[x \ln x + (1-x) \ln (1-x)] \quad (3)$$

${}^E G^m$ is excess Gibbs free energy according to regu-

lar solution model

$${}^E G^m = x(1-x)L_{CN}^{Nb} \quad (4)$$

where L_{CN}^{Nb} represents the interaction parameter of carbon and nitrogen in the same sublattice with the other sublattice taken by niobium.

Molar Gibbs free energy $G_{NbC,N_{1-x}}$ can be obtained from formula (1) by inserting the expressions of G_m^{ref} , ${}^I S^m$ and ${}^E G^m$. $G_{NbC,N_{1-x}}$ is taken as G_m . Therefore

$$G_m = xG_{NbC}^0 + (1-x)G_{NbN}^0 + RT[x \ln x + (1-x) \ln(1-x)] + x(1-x)L_{CN}^{Nb} \quad (5)$$

$$\begin{cases} \mu_{NbC} = G_m + \frac{\partial G_m}{\partial y_C} - y_C \frac{\partial G_m}{\partial y_C} - y_N \frac{\partial G_m}{\partial y_N} \\ \mu_{NbN} = G_m + \frac{\partial G_m}{\partial y_N} - y_C \frac{\partial G_m}{\partial y_C} - y_N \frac{\partial G_m}{\partial y_N} \end{cases} \quad (6)$$

According to equation (6), the following equation can be got

$$\begin{cases} \mu_{NbC} = G_{NbC}^0 + RT \ln x + (1-x)^2 L_{CN}^{Nb} \\ \mu_{NbN} = G_{NbC}^0 + RT \ln x + x^2 L_{CN}^{Nb} \end{cases} \quad (7)$$

3.3 Chemical potential of elements in austenite

The following formula was applied

$$U_i = U_i^0 + RT \ln a_i$$

where the infinite dilute in austenite of solutes is taken as the reference state, and the concentrations of niobium, carbon and nitrogen in austenite are in terms of atomic fraction.

Therefore, the chemical potential of Nb, C and N in austenite are, respectively, shown as

$$\mu_{Nb}^{\gamma} = \mu_{Nb}^0 + RT \ln a_{Nb} \quad (8)$$

$$\mu_C^{\gamma} = \mu_C^0 + RT \ln a_C \quad (9)$$

$$\mu_N^{\gamma} = \mu_N^0 + RT \ln a_N \quad (10)$$

where

$$\ln a_{Nb} = \ln x_{Nb} + \varepsilon_{Nb}^{Nb} x_{Nb} + \varepsilon_{Nb}^C x_C + \varepsilon_{Nb}^N x_N +$$

$$\varepsilon_{Nb}^{Mn} x_{Mn} + \varepsilon_{Nb}^{Si} x_{Si}$$

$$\ln a_C = \ln x_C + \varepsilon_C^C x_C + \varepsilon_C^N x_N + \varepsilon_C^{Nb} x_{Nb} +$$

$$\varepsilon_C^{Mn} x_{Mn} + \varepsilon_C^{Si} x_{Si}$$

$$\ln a_N = \ln x_N + \varepsilon_N^N x_N + \varepsilon_N^{Nb} x_{Nb} + \varepsilon_N^C x_C +$$

$$\varepsilon_N^{Mn} x_{Mn} + \varepsilon_N^{Si} x_{Si}$$

x_i represents mole fraction of element i in austenite at equilibrium; a_i , activity of element i in austenite and ε_i^j , activity coefficient in austenite.

3.4 Conditions of equilibrium between precipitate and austenite

(1) Thermodynamic equilibrium condition

$$\mu_{NbC} = \mu_{Nb}^{\gamma} + \mu_C^{\gamma} \quad (11)$$

$$\mu_{NbN} = \mu_{Nb}^{\gamma} + \mu_N^{\gamma} \quad (12)$$

According to equations (7) ~ (12), the following equations are obtained

$$\ln(x k_{NbC}) = \ln(a_{Nb} a_C) - \frac{(1-x)^2}{RT} L_{CN}^{Nb} \quad (13)$$

$$\ln[(1-x) k_{NbN}] = \ln(a_{Nb} a_N) - \frac{x^2}{RT} L_{CN}^{Nb} \quad (14)$$

(2) Mass conservation conditions

$$x_{Nb}^0 = \frac{1}{2} Z + (1-Z) x_{Nb} \quad (15)$$

$$x_C^0 = \frac{x}{2} Z + (1-Z) x_C \quad (16)$$

$$x_N^0 = \frac{1-x}{2} Z + (1-Z) x_N \quad (17)$$

where x_i^0 represents mole fraction of element i ($i = Nb, C, N, \dots$) before precipitation, and Z , mole fraction of precipitates at equilibrium.

The Equations (13) ~ (16) are combined and the method of Newton iteration is used to get the values of x , x_{Nb} , x_C , x_N and Z .

(3) Data of solubility products

Early in 1960s, many researchers did studies on the equilibrium between the binary precipitate (NbN, NbC) and γ -Fe. Because of the difficulties in experimental techniques, the results obtained were in disagreement with each other. Facing this case, this paper adopted Narita's data as **table 2**.

(4) Selection of ε_i^j in γ -Fe

The selection ε_i^j in γ -Fe is shown in **table 3**.

(5) L_{CN}^{Nb}

According to reference [14], $L_{CN}^{Nb} = 2.4$ kJ/mol.

3.5 Comparison of calculated and experimental results

Nordberg and Aronsson [15] suggested that nitrogen content can be considered in terms of an equivalent carbon content, *i.e.*, the effective carbon content is $C + 12/14 N$.

Irvine *et al.* [16] held the same view. They used chemical analysis techniques for soluble and insoluble

Table 2 Solubility products of the precipitate in γ -Fe
($\log K = A - B/T$)

Precipitate	A	B	Reference
NbC	3.42	7 900	[8]
NbN	2.80	8 500	[4]

Table 3 ϵ_i in γ -Fe

ϵ_i	Value	Reference
ϵ_C^C	$8878.5/T + 2.02$	[9]
ϵ_N^N	$6294/T$	[10]
ϵ_C^{Nb}	$-66.257/T$	[11]
ϵ_N^{Nb}	$-106.956/T$	[12]
ϵ_{Nb}^{Nb}	-2	[13]
ϵ_{Nb}^{Mn}	2.1	[13]
ϵ_{Nb}^{Si}	-0.7	[13]

niobium, carbon and nitrogen. The solubility product K_s was determined at temperatures from 900 to 1 200 °C, namely

$$K_s = [\text{Nb}] \left[\text{C} + \frac{12}{14} \text{N} \right]$$

where the concentrations were expressed in mass fraction. The variation of the solubility product K_s with temperature is as follows:

$$\lg [\text{Nb}] \cdot \left[\text{C} + \frac{12}{14} \text{N} \right] = \frac{-6670}{T} + 2.26$$

The above expression was widely adopted in the composition design and heat treatment of niobium alloyed steels. Using above-mentioned solubility product formula and theoretical method, the complete equilibrium solution temperature for 1, 2, 3 and WX60 are calculated, respectively. The composition of WX60 (mass fraction in %) is: C, 0.082; Mn, 1.09; Si, 0.20; P, 0.004; S, 0.004; Cu, 0.085; N, 0.007; Nb, 0.028. The results are shown in **table 4**.

Table 4 Comparison of complete equilibrium solution temperature °C

	C method	Theoretical method
1	1 256	1 240
2	1 284	1 280
3	1 299	1 305
WX60	1 115	1 130

Note: C method — According to $\lg \left\{ [\text{Nb}] \left[\text{C} + \frac{12}{14} \text{N} \right] \right\} = \frac{-6670}{T} + 2.26$

The results of the experimental and theoretical methods are in good agreement. It is successful to use Hillert-Staffansson's regular model about stoichiometric phase to describe the thermodynamic properties of multi-component precipitate. Since titanium, niobium and vanadium have the similarity in thermodynamics, the above-mentioned theoretical method is applicable to predict the equilibrium between titanium or vanadium carbonitride and the austenite.

4 Conclusions

(1) After equilibrium heat treatment of Nb-alloyed steel within austenitizing temperature, the precipitates are mainly with one type of composition and structure. The formula is $\text{NbC}_x\text{N}_{1-x}$, structure FCC.

(2) It is successful to use Hillert-Staffanon's regular model about stoichiometric phase to describe the thermodynamic properties of multi-component microalloying element carbonitrides.

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