Expressions for Solubility Products of $\text{Fe}_3\text{Nb}_3\text{C}$ carbide and Fe_2Nb Laves Phase in Niobium Alloyed Ferritic Stainless Steels

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Precipitation behaviors in niobium alloyed ferritic stainless steels, which are widely used as heat resistant materials in automotive exhausts, were investigated. The solubility products of $\text{Fe}_3\text{Nb}_3\text{C}$ and Fe_2Nb , both of which are prominent precipitates in such steels, were experimentally obtained. The expressions of the solubility products with mass% are given by:

$$\text{Fe}_3\text{Nb}_3\text{C}; \log_{10}\{[\text{Nb}]^3[\text{C}]\} = -11\,613/T + 5.2178$$

$$\text{Fe}_2\text{Nb}; \log_{10}[\text{Nb}] = -3\,780.3/T + 2.4646$$

These were verified with some published experimental data. An attempt was also made to get thermodynamic parameters using the solubility products. The free energy changes for the precipitation reactions from niobium-supersaturated ferrite have been obtained. The expressions with mole fractions in ferrite matrix, e.g. $x_{\text{Nb}}^{\alpha\beta}$, are given by:

$$\text{Fe}_3\text{Nb}_3\text{C} (\beta); \Delta G^\beta = -222\,509 - RT\{6.423 + \ln(x_{\text{Nb}}^{\alpha\beta})^3(x_{\text{C}}^{\alpha\beta})\}$$

$$\text{Fe}_2\text{Nb} (\omega); \Delta G^\omega = -72\,334 - RT\{0.5469 + \ln x_{\text{Nb}}^{\alpha\omega}\}$$

KEY WORDS: precipitation; ferritic steel; stainless steel; niobium alloyed steel; solubility product.

1. Introduction

Recently, it is getting strongly important to consider global warming and air pollution. To protect the environment, automobile manufactures are making great efforts both to improve fuel economy and to clean exhaust gas. To achieve both of them, it is vital to increase the exhaust gas temperature over 900°C in which the conventional material, cast iron, does not have enough high temperature strength. Niobium alloyed ferritic stainless steels are therefore applied to the materials for automotive exhaust manifold.¹⁾ Niobium addition can improve high temperature strength of ferritic stainless steels when in solid solution,²⁾ which allows the operations at such high exhaust gas temperatures. It is therefore important to know how much of the niobium precipitates and the fraction, which remains in solid solution during high temperature service. However, thermodynamic data, which form an essential foundation for kinetics theory, are not available for these steels. In this study, the solubility products of $\text{Fe}_3\text{Nb}_3\text{C}$: M_6C type carbide and Fe_2Nb : Fe_2M type Laves phase (hereafter M stands for metallic atoms), both of which are prominent precipitates in niobium alloyed ferritic stainless steels, were experimentally obtained. An attempt has also been made here to get the thermodynamic parameters of the niobium precipitates using the solubility products.

2. Experimental Procedure

Table 1 shows the chemical compositions of the specimens. These steels were melted by induction heating in vacuum and cast as 25 kg ingots. They are heated at 1250°C for 30 min and hot-rolled to 6 mm thick, cold-rolled to 2 mm thick sheets, annealed at temperatures between 900 and 1000°C for 1 min and then quenched in water.

To obtain solubility products of niobium precipitates, the specimens were aged at temperatures between 700 and 1000°C for the maximum 500 h in argon atmosphere. Electrolytically extracted residues were examined by X-ray diffraction to identify precipitates and chemically analyzed to evaluate the amounts of each alloying element in precipitates. To obtain residues, the specimens were dissolved at the anode at a constant electric potential relative to the platinum in the solution of 10 vol.% acetylacetone and 1 vol.% tetramethylammonium chloride in methanol. The constant electric potential was chosen to be between 100 mV and

Table 1. Chemical compositions of the steels (mass%).

Steels	C	N	Cr	Nb	Ti	Mo
Nb1	0.016	0.009	12.9	0.48	-	-
Nb2	0.014	0.017	19.2	0.40	-	-
Nb3	0.014	0.016	19.6	0.78	-	-
Nb-Ti-Mo	0.011	0.010	14.0	0.31	0.15	0.50
Nb-Ti	0.011	0.011	13.0	0.30	0.08	-

Table 2. A list of the precipitates detected in the extracted residues of the annealed and aged samples by X-ray diffraction for each steel. The abbreviations, VS, S, M, W and VW mean very strong, strong, medium, weak and very weak intensities of X-ray respectively. Concentrations are normalized by the whole amounts of all elements in the alloys including Fe.

Steels	Aging conditions		Precipitates detected				Each element in precipitates / at %				
	Temperature / °C	Time / h	Nb(C, N)	M ₆ C: Fe ₃ Nb ₃ C	Fe ₂ M: Fe ₂ Nb	Ti(C, N)	Nb	Fe	Cr	Ti	Mo
Nb-1 ; 13Cr-0.5Nb mass% steel	As annealed at 900°C		VS	W	W	-	9.89E-02	3.57E-02	9.58E-03		
	800	100	S	S	S	-	2.32E-01	2.06E-01	2.13E-02		
	850	100	S	S	S	-	2.17E-01	2.11E-01	2.02E-02		
	900	100	S	VS	W	-	2.21E-01	8.73E-02	3.09E-02		
		500	S	VS	W	-	2.55E-01	6.94E-02	7.45E-02		
Nb-2 ; 19Cr-0.4Nb mass% steel	As annealed at 900°C		VS	W	-	-	1.38E-01	1.58E-02	5.30E-03		
	700	20	VS	S	-	-	2.11E-01	8.88E-02	2.12E-02		
		100	VS	VS	-	-	2.15E-01	8.68E-02	2.33E-02		
		200	VS	VS	-	-	2.16E-01	9.87E-02	2.01E-02		
		500	VS	VS	-	-	2.11E-01	9.37E-02	2.12E-02		
	800	20	VS	VS	-	-	1.89E-01	6.31E-02	6.99E-02		
		100	VS	VS	-	-	2.08E-01	7.60E-02	2.23E-02		
		200	VS	VS	-	-	2.22E-01	8.68E-02	3.07E-02		
		500	VS	VS	-	-	2.15E-01	7.89E-02	3.92E-02		
	850	100	VS	VS	-	-	1.90E-01	8.78E-02	2.01E-02		
		20	VS	VS	-	-	1.89E-01	4.34E-02	4.45E-02		
		100	VS	VS	-	-	1.83E-01	3.95E-02	3.71E-02		
		200	VS	VS	-	-	1.89E-01	5.52E-02	3.18E-02		
	900	500	VS	VS	-	-	1.84E-01	4.93E-02	3.39E-02		
		100	VS	VS	-	-	1.49E-01	3.35E-02	1.06E-02		
	As annealed at 1000°C		S	VS	W	-	1.21E-01	2.11E-01	4.46E-02		
	950	1	VS	VS	VS	-	2.42E-01	3.22E-01	5.41E-02		
		50	VW	VS	VW	-	2.57E-01	2.44E-01	4.67E-02		
		100	VW	VS	-	-	2.63E-01	2.31E-01	4.35E-02		
	1000	20	W	VS	-	-	2.15E-01	1.69E-01	3.93E-02		
Nb-Ti-Mo ; 14Cr-0.3Nb- 0.1Ti-0.5Mo mass% steel	As annealed at 900°C		VS	-	VS	VS	4.56E-02	4.93E-03	3.18E-03	5.62E-02	4.02E-03
	700	20	VS	-	S	VS	1.54E-01	3.32E-01	4.34E-02	9.75E-02	3.73E-02
		100	VS	-	VS	VS	1.58E-01	3.49E-01	4.24E-02	1.03E-01	4.54E-02
		200	VS	-	VS	VS	1.57E-01	3.54E-01	4.24E-02	1.03E-01	4.82E-02
		500	VS	-	VS	VS	1.57E-01	3.67E-01	4.45E-02	1.07E-01	5.45E-02
	800	20	VS	-	S	VS	1.35E-01	2.51E-01	2.75E-02	8.72E-02	1.95E-02
		100	VS	-	VS	VS	1.32E-01	2.50E-01	2.65E-02	8.72E-02	2.07E-02
		200	VS	-	VS	VS	1.32E-01	2.50E-01	2.65E-02	8.61E-02	2.07E-02
		500	VS	-	VS	VS	1.13E-01	2.21E-01	2.12E-02	7.46E-02	1.89E-02
	850	100	VS	-	VS	VS	1.14E-01	1.87E-01	2.44E-02	6.43E-02	1.72E-03
		20	VS	-	VS	VS	8.71E-02	1.36E-01	1.59E-02	7.46E-02	7.46E-03
	900	100	VS	-	VS	VS	7.29E-02	1.17E-01	1.59E-02	5.51E-02	6.31E-03
		200	VS	-	VS	VS	7.59E-02	1.34E-01	1.59E-02	6.88E-02	7.46E-03
		500	VS	-	VS	VS	8.77E-02	1.50E-01	2.33E-02	6.20E-02	1.03E-02
Nb-Ti ; 13Cr-0.3Nb- 0.1Ti mass% steel	As annealed at 900°C		S	-	W	S	4.17E-02	2.28E-02	1.06E-02	6.11E-02	
	850	100	VS	-	VS	VS	9.88E-02	1.58E-02	1.59E-02	9.79E-02	
	900	100	VS	M	M	VS	6.31E-02	1.98E-02	5.32E-03	8.52E-02	

200 mV against the standard of the saturated calomel electrode, where only the iron matrix dissolves.³⁾ The residue was filtered using a sub-micron mesh to trap fine particles. To get as much amount of residue as possible in a short time, the filtration has been done with sucking by vacuum pump. The residue was dissolved in the acid solution and quantitatively analyzed using Inductively Coupled Plasma (termed ICP) measurement. The microstructures were characterized mainly with carbon extraction replicas using Transmission Electron Microscopy (termed TEM), particularly to identify the precipitates by electron diffraction and Energy Dispersive Spectrometry (termed EDS). TEM observations were carried out between 160 and 200 kV. To make the replica specimens, a carbon film was applied on the sample surface using vacuum evaporation. Then, the carbon replicas could be collected on 3 mm diameter copper grids. The samples were etched in a solution of 10 g/L

tetramethylammonium chloride, 10 vol% acetylacetone in methanol at the potential between 0 and 200 mV.

3. Results and Discussion

3.1. Analysis of Extracted Residues and Microstructure Observation

Table 2 summarizes the results of X-ray analysis of the extracted residues from the annealed and aged samples. Concentrations are expressed to be normalized by the whole amounts of all elements in the alloys including Fe. In Nb-1 steel, Nb(C, N), Fe₂Nb: Fe₂M type Laves phase and Fe₃Nb₃C: M₆C type carbide were detected in the specimens as annealed and aged for short time. As the aging time was longer, Fe₃Nb₃C was clearly found and the X-ray intensities of other precipitates, such as Nb(C, N) and Fe₂Nb, were getting weak. In Nb-2 steel, the trend of the precipitation

Fig. 1. Micrographs and the analysis results of the aged samples for (a) Nb-1, (b) Nb-2, (c) Nb-3 (d) Nb-Ti-Mo steels. The arrows indicate the particles analyzed.

sequence to $\text{Fe}_3\text{Nb}_3\text{C}$ is similar to that in Nb-1. Because the details of chemical compositions are different between Nb-1 and Nb-2 steels, *i.e.* amounts of chromium and nitrogen in Nb-2 are greater than those in Nb-1, Laves phase does not precipitate dominantly but $\text{Nb}(\text{C}, \text{N})$ mainly precipitates in the early stage of aging in Nb-2. In Nb-3 steel, in the early stage of aging, $\text{Nb}(\text{C}, \text{N})$, Fe_2Nb and $\text{Fe}_3\text{Nb}_3\text{C}$ were clearly detected. When the aging time was greater, the intensity of Fe_2Nb was getting weaker and $\text{Fe}_3\text{Nb}_3\text{C}$ became a prominent phase.

In Nb-Ti and Nb-Ti-Mo steels, $\text{Nb}(\text{C}, \text{N})$ and $\text{Ti}(\text{C}, \text{N})$ were always detected. As the aging time was longer, Fe_2Nb was clearly detected in Nb-Ti-Mo steel, while both of Fe_2Nb and $\text{Fe}_3\text{Nb}_3\text{C}$ were still found in Nb-Ti steel. Chromium contents in both steels are almost same. Niobium and titanium additions are in excess for the stoichiometry of MC carbide and MN nitrides so that the amounts of carbon and nitrogen in solid solution in both steels must be very small. The effective factor on precipitation behavior difference between Nb-Ti and Nb-Ti-Mo steels could therefore be molybdenum addition. As shown in Table 2, Laves phase: Fe_2M includes small amount of molybdenum. So, it implies that Mo addition enhances precipitation of Laves phase even if the addition is as small as

0.5 mass%.

Figure 1 shows the microstructures and the analysis results of the aged samples for a) Nb-1, b) Nb-2, c) Nb-3 and d) Nb-Ti-Mo steels. The intensity ratio of niobium to iron Nb/Fe in EDS analysis for M_6C type carbide is larger than that for Laves phase. Both M_6C type carbide and Laves phase include a small amount of chromium. However, the amounts of chromium in both precipitates are much less than those of niobium and iron. Laves phase in Nb-Ti-Mo steel does not include much of molybdenum, although its addition is supposed to enhance Laves phase precipitation. Figure 2 shows the amounts of each element in the precipitates in the residues extracted from the samples aged for 100 h for Nb-1, Nb-2, Nb-3 and Nb-Ti-Mo steels. Amounts of chromium and molybdenum in the precipitates are smaller than those of niobium or iron in many cases. This trend corresponds to the results of EDS analysis shown in Fig 1. In Nb-1 and Nb-2 steels, the ratio of niobium to iron often becomes more than unity even though $\text{Fe}_3\text{Nb}_3\text{C}$ is a prominent phase, with which the ratio is expected to be unity. Because $\text{Nb}(\text{C}, \text{N})$ is clearly detected in these cases as indicated in Table 2, the ratio of niobium to iron is larger than expected from a prominent phase of $\text{Fe}_3\text{Nb}_3\text{C}$. On the contrary, in the Nb-1 samples aged at 800

and 850°C and the Nb-3 samples aged at 950°C, the ratio of niobium to iron is almost unity. For the Nb-1 samples aged at 800 and 850°C, not only $\text{Fe}_3\text{Nb}_3\text{C}$ but also Laves

phase are detected so that there are more iron contents in the precipitates than expected with $\text{Fe}_3\text{Nb}_3\text{C}$ and $\text{Nb}(\text{C}, \text{N})$. For the Nb-3 samples aged at 950°C, the intensity for

Fig. 2. Amounts of each element in the precipitates in the residues extracted from the samples aged for 100 h. (a) Nb-1, (b) Nb-2, (c) Nb-3, (d) Nb-Ti-Mo.

Fig. 3. Changes of amounts of niobium concentrations in the precipitates with aging time for each steel.

Nb(C, N) became weak and $\text{Fe}_3\text{Nb}_3\text{C}$ is dominantly detected so that the ratio is almost same as expected from $\text{Fe}_3\text{Nb}_3\text{C}$.

Figure 3 shows the changes of niobium amounts in the precipitates with aging time for each steel. The amounts of niobium in the precipitates seem to be constant after aging time is long enough. Figure 4 shows the relationship between the amounts in atomic % of iron and niobium in the precipitates in the specimens aged for enough time when the amounts in the precipitates became constant for each steel. The slope for the Nb alloyed steels (Nb-1, Nb-2 and Nb-3) is approximately unity and that for the Nb-Ti-Mo steel (Nb-Ti-Mo) is nearly 0.5. It implies that $\text{Fe}_3\text{Nb}_3\text{C}$ dominantly remains in the Nb alloyed ferritic stainless steels and Fe_2Nb mainly remains in the Nb-Ti-Mo alloyed ferritic stainless steel. As a result, Nb(C, N) and $\text{Fe}_3\text{Nb}_3\text{C}$ can be equilibrium phases in the Nb alloyed ferritic stainless steels and (Nb, Ti)(C, N) and Fe_2Nb are equilibrium phases in the Nb-Ti-Mo alloyed ferritic stainless steel. The experimental data of niobium concentrations, with which solubility products can be obtained, are listed in Table 3.

3.2. Method to Obtain Solubility Products

When precipitate of M_mX_n (X , m and n stand for the third alloying element and the precipitate composition respectively) forms from supersaturated matrix of Fe-M-X ternary system, the reaction is as follows:

where $[\text{M}]$ and $[\text{X}]$ are the elements in solution in matrix. The activities of pure solid M_mX_n and the concentration of Fe as matrix can be taken to be unity. Assuming that the activities of other elements are equivalent to the concentrations, the solubility products for $\text{M}_m\text{X}_n(\gamma)$ in matrix of Fe-M-X (α) can be expressed as;⁴⁾

$$(x_M^{\alpha\gamma})^m (x_X^{\alpha\gamma})^n = K_0^\gamma \exp(-\Delta G_0^\gamma / RT) \dots \dots \dots (2)$$

where $x_M^{\alpha\gamma}$ and $x_X^{\alpha\gamma}$ are the concentrations in solution in matrix (α), K_0^γ is constant and ΔG_0^γ is standard free energy change for the precipitation reaction. The Eq. (1) can be changed.

$$\ln(x_M^{\alpha\gamma})^m (x_X^{\alpha\gamma})^n = A_i / T + B_i$$

$$\text{with } A_i = \Delta G_0^\gamma / R \text{ and } B_i = -\ln K_0^\gamma \dots \dots \dots (3)$$

where R is gas constant and T is temperature in K. If the constants of A_i and B_i are obtained, the driving force for the precipitate ΔG^γ can be estimated and is given by;

$$\Delta G^\gamma = \Delta G_0^\gamma + RT \ln \{1 / (x_M^{\alpha\gamma})^m (x_X^{\alpha\gamma})^n\} \dots \dots \dots (4)$$

In this case, it is necessary to consider several effects on precipitation reactions of M_6C and Fe_2M , which are Cr and Mo additions and other precipitates of Nb(C, N) or (Ti, Nb)(C, N) in multi-component systems. Cr and Mo additions must affect precipitation reactions of M_6C and Fe_2M . In case of the ferrite in Fe-Nb-C, M_6C does not seem to be found. As shown in Table 2, small amount of Cr is included in M_6C but not so much is in $\text{M}(\text{C}, \text{N})$, which could make driving force for M_6C formation increase. Fe_2M is a prominent precipitate in the Nb-Ti-Mo steel but M_6C also still remained in the Nb-Ti steel as shown in Table 2. Small amount of Mo is included in Fe_2M in Nb-Ti-Mo

Fig. 4. Relationships between niobium and iron concentrations in the precipitates in the aged specimens for each steel.

Table 3. A list of niobium concentrations (atomic %) experimentally obtained. Concentrations are normalized by the whole amounts of all elements in the alloys including Fe.

Steels	Aging temperature / °C	Nb addition / at%	Nb in precipitates / at%	Nb in solid solution / at%
Nb-1	900	2.86E-01	2.55E-01	3.16E-02
Nb-2	700	2.37E-01	2.15E-01	2.25E-02
	800		2.13E-01	2.37E-02
	850		1.90E-01	4.68E-02
	900		1.84E-01	5.34E-02
	950		1.48E-01	8.90E-02
Nb-3	950	4.63E-01	2.55E-01	2.08E-01
	1000		2.02E-01	2.61E-01
Nb-Ti-Mo	700	1.84E-01	1.62E-01	2.13E-02
	800		1.24E-01	5.93E-02
	850		1.14E-01	6.94E-02
	900		8.30E-02	1.01E-01

steel, which may make the Fe_2M formation easy. If each effect is dealt rigorously, it must be very complicated. To avoid complexity, several assumptions are set. It is assumed that M_6C and Fe_2M are dealt as Fe_2Nb and $\text{Fe}_3\text{Nb}_3\text{C}$ respectively because Cr and Mo amounts in the precipitates are not very much compared with Nb and Fe. The details to deal with other precipitates, such as Nb(C, N) and (Ti, Nb)(C, N), will be described in the following sections.

3.3. Solubility Product of $\text{Fe}_3\text{Nb}_3\text{C}$; M_6C Type Carbide

In case of $\text{Fe}_3\text{Nb}_3\text{C}$ (β), assuming that the activity of pure solid $\text{Fe}_3\text{Nb}_3\text{C}$ and the concentration of Fe in ferrite (α) are taken to be unity, the solubility product is given by;

$$\ln(x_{\text{Nb}}^{\alpha\beta})^3 (x_{\text{C}}^{\alpha\beta}) = A_1 / T + B_1$$

$$\text{with } A_1 = \Delta G_0^\beta / R \text{ and } B_1 = -\ln K_0^\beta \dots \dots \dots (5)$$

where $x_{\text{Nb}}^{\alpha\beta}$ and $x_{\text{C}}^{\alpha\beta}$ are equilibrium mole fractions in solution in ferrite. The free energy change of precipitation ΔG^β

can be given by:

$$\Delta G^\beta = \Delta G_0^\beta - RT \ln(x_{\text{Nb}}^{\alpha\beta})^3 (x_{\text{C}}^{\alpha\beta}) \dots \dots \dots (6)$$

ΔG^β can be estimated, if values of A_1 and B_1 are available. To obtain both constants, the equilibrium concentrations are necessary. In Nb steels, there are also Nb(C, N). Assuming that all the nitrogen is precipitated as NbN and that Nb(C, N) becomes NbN at equilibrium, it is possible to calculate the equilibrium concentrations of niobium and carbon in the ferrite with $\text{Fe}_3\text{Nb}_3\text{C}$. For mass balances of carbon and nitrogen,

$$x_{\text{C}}^\alpha = (1 - f^\beta) x_{\text{C}}^{\alpha\beta} + f^\beta x_{\text{C}}^{\beta\alpha} \dots \dots \dots (7-1)$$

$$x_{\text{N}}^\alpha = (1 - f^{\text{NbN}}) x_{\text{N}}^{\alpha\text{NbN}} + f^{\text{NbN}} x_{\text{N}}^{\text{NbN}\alpha} \dots \dots \dots (7-2)$$

where x_{C}^α and x_{N}^α are alloying compositions of carbon and nitrogen respectively, $x_{\text{C}}^{\alpha\beta}$ and $x_{\text{N}}^{\alpha\text{NbN}}$ are equilibrium concentrations of carbon in ferrite with $\text{Fe}_3\text{Nb}_3\text{C}$ and of nitrogen in ferrite with NbN respectively, $x_{\text{C}}^{\beta\alpha}$ and $x_{\text{N}}^{\text{NbN}\alpha}$ are concentrations of carbon in $\text{Fe}_3\text{Nb}_3\text{C}$ and of nitrogen in NbN respectively and f^β and f^{NbN} are equilibrium fractions of $\text{Fe}_3\text{Nb}_3\text{C}$ and NbN respectively. All of concentrations are given or can be estimated with the assumptions mentioned above so that equilibrium fractions f^β and f^{NbN} can be calculated. By subtracting Nb as NbN from alloying composition, mass balance of niobium is given by;

$$x_{\text{Nb}}^\alpha - f^{\text{NbN}} x_{\text{Nb}}^{\text{NbN}\alpha} = \{(1 - f^{\text{NbN}}) - f^\beta\} x_{\text{Nb}}^{\alpha\beta} + f^\beta x_{\text{Nb}}^{\beta\alpha} \dots \dots \dots (8)$$

where x_{Nb}^α is alloying composition of niobium, $x_{\text{Nb}}^{\beta\alpha}$ and $x_{\text{Nb}}^{\text{NbN}\alpha}$ are niobium concentrations in $\text{Fe}_3\text{Nb}_3\text{C}$ and NbN respectively, $x_{\text{Nb}}^{\alpha\beta}$ are equilibrium concentration of niobium in ferrite with $\text{Fe}_3\text{Nb}_3\text{C}$. All of concentrations and fractions except $x_{\text{Nb}}^{\alpha\beta}$ are given or can be estimated so that equilibrium concentration of niobium $x_{\text{Nb}}^{\alpha\beta}$ can be calculated. The amounts of niobium in precipitates and in solid solution, which are experimentally obtained, are listed in Table 3. The values can be assumed to represent the equilibrium concentrations. The calculated equilibrium mole fractions are listed in Table 4.

By plotting the relationship between $\ln(x_{\text{Nb}}^{\alpha\beta})^3 (x_{\text{C}}^{\alpha\beta})$ and $1/T$, the constants A_1 and B_1 in the Eq. (5) can be obtained. Figure 5 shows the relationship between $\ln(x_{\text{Nb}}^{\alpha\beta})^3 (x_{\text{C}}^{\alpha\beta})$ and $1/T$ in Nb alloyed ferritic stainless steels with the values indicated in Table 4. Table 5 shows the calculated values of A_1 , B_1 and ΔG_0^β . Expressions of A_1 and B_1 with mass% and common logarithm are also presented because of their pop-

ularity.

3.4. Solubility Product of Fe_2Nb ; Fe_2M Type Laves Phase

By the same way as for $\text{Fe}_3\text{Nb}_3\text{C}$, the several parameters for Laves phase: $\text{Fe}_2\text{Nb}(\omega)$ can be calculated. The solubility product is expressed as the solubility of Nb with the following equation.

$$\ln x_{\text{Nb}}^{\alpha\omega} = A_2/T + B_2$$

$$\text{with } A_2 = \Delta G_0^\omega/R \text{ and } B_2 = -\ln K_0^\omega \dots \dots \dots (7)$$

For the driving force ΔG^ω

$$\Delta G^\omega = \Delta G_0^\omega - RT \ln x_{\text{Nb}}^{\alpha\omega} \dots \dots \dots (8)$$

ΔG^ω can be estimated, if values of A_2 and B_2 are available. In Nb-Ti-Mo steel, there are also Nb(C, N) and Ti(C, N). As shown in Table 2, it can be assumed that the titanium are precipitated as TiC and TiN, that all the nitrogen is precipitated as TiN and that the all the carbon is precipitated as TiC and NbC at equilibrium.⁵⁾ It is then possible to calculate the equilibrium concentrations of niobium in the ferrite with Fe_2Nb . At first, the Ti amount as TiN is subtracted from alloying amount of Ti and all the remained Ti is assumed to from TiC so that the amount of remained carbon can be obtained. For mass balances of nitrogen and titanium,

$$x_{\text{N}}^\alpha = (1 - f^{\text{TiN}}) x_{\text{N}}^{\alpha\text{TiN}} + f^{\text{TiN}} x_{\text{N}}^{\text{TiN}\alpha} \dots \dots \dots (9-1)$$

$$x_{\text{Ti}}^\alpha - f^{\text{TiN}} x_{\text{Ti}}^{\text{TiN}\alpha} = \{(1 - f^{\text{TiN}}) - f^{\text{TiC}}\} x_{\text{Ti}}^{\alpha\text{TiN}} + f^{\text{TiC}} x_{\text{Ti}}^{\text{TiC}\alpha} \dots \dots \dots (9-2)$$

where $x_{\text{N}}^{\alpha\text{TiN}}$ and $x_{\text{N}}^{\text{TiN}\alpha}$ are equilibrium concentrations of ni-

Fig. 5. Relationship between $\ln(x_{\text{Nb}}^{\alpha\beta})^3 (x_{\text{C}}^{\alpha\beta})$ and $1/T$ for Nb alloyed ferritic stainless steels.

Table 4. Calculated equilibrium mole fractions at the interface $\text{Fe}_3\text{Nb}_3\text{C}(\beta)/\text{ferrite}(\alpha)$ for Nb and C between 700°C and 1000°C in Nb alloyed ferritic stainless steels.

Steels	Aging temperature / °C	$x_{\text{Nb}}^{\alpha\beta}$ for $\text{Fe}_3\text{Nb}_3\text{C}$	$x_{\text{C}}^{\alpha\beta}$ for $\text{Fe}_3\text{Nb}_3\text{C}$
Nb-1	900	3.18E-04	6.97E-04
Nb-2	700	2.26E-04	6.13E-04
	800	2.38E-04	6.11E-04
	850	4.70E-04	5.77E-04
	900	5.36E-04	5.68E-04
	950	8.92E-04	5.16E-04
Nb-3	950	2.09E-03	3.47E-04
	1000	2.62E-03	2.70E-04

Table 5. Calculated values of A_1 , B_1 and ΔG_0^β for $\text{Fe}_3\text{Nb}_3\text{C}(\beta)$ in Nb alloyed ferritic stainless steels.

For $\text{Fe}_3\text{Nb}_3\text{C}$	A_1 / K^{-1}	B_1	$\Delta G_0^\beta / \text{J mol}^{-1}$
values for mole fraction and natural logarithm	-26776	-6.423	-222508.56
values for mass% and common logarithm	-11613	5.2178	-

Table 6. Calculated equilibrium mole fractions at the interface $\text{Fe}_2\text{Nb}(\omega)/\text{ferrite}(\alpha)$ for Nb between 700 and 900°C in Nb–Ti–Mo alloyed ferritic stainless steels.

Steels	Aging temperature / °C	X_{Nb}^{ω} for Fe_2Nb
Nb–Ti–Mo	700	2.14E-04
	800	5.95E-04
	850	6.96E-04
	900	1.01E-03

Fig. 6. Relationship between $\ln x_{\text{Nb}}^{\omega}$ and $1/T$ for Nb–Ti–Nb–Ti–Mo alloyed ferritic stainless steels.

trogen in ferrite and TiN respectively, f^{TiN} is equilibrium fraction of TiN, x_{Ti}^{α} , $x_{\text{Ti}}^{\text{TiN}\alpha}$ and $x_{\text{Ti}}^{\alpha\text{TiN}}$ are alloying composition of titanium, equilibrium concentrations of titanium in ferrite and TiN respectively and f^{TiC} is equilibrium fraction of TiC. All of parameters in Eqs. (9-1) and (9-2) can be obtained. Secondly, all the remained carbon is assumed to form NbC at equilibrium. The amount of Nb as NbC can then be obtained. For carbon mass balance,

$$x_{\text{C}}^{\alpha} - f^{\text{TiC}} x_{\text{C}}^{\text{TiC}\alpha} = \{(1 - f^{\text{TiC}}) - f^{\text{NbC}}\} x_{\text{C}}^{\alpha\text{NbC}} + f^{\text{NbC}} x_{\text{C}}^{\text{NbC}\alpha} \dots (10)$$

where $x_{\text{C}}^{\text{TiC}\alpha}$ is carbon concentration in TiC, $x_{\text{C}}^{\alpha\text{NbC}}$ and $x_{\text{C}}^{\text{NbC}\alpha}$ are equilibrium concentrations of carbon in ferrite and NbC respectively and f^{NbC} is equilibrium fraction of NbC. Finally, Nb amount as NbC is subtracted from alloying amount of Nb and the Nb amount for Laves phase formation can then be calculated. All of concentrations are given or can be estimated so that equilibrium fractions f^{NbC} can be obtained. By subtracting Nb as NbC from whole concentration, mass balance of niobium is given by;

$$x_{\text{Nb}}^{\alpha} - f^{\text{NbC}} x_{\text{Nb}}^{\text{NbC}\alpha} = \{(1 - f^{\text{NbC}}) - f^{\omega}\} x_{\text{Nb}}^{\alpha\omega} + f^{\omega} x_{\text{Nb}}^{\omega\alpha} \dots (11)$$

where $x_{\text{Nb}}^{\omega\alpha}$ and $x_{\text{Nb}}^{\text{NbC}\alpha}$ are niobium concentrations in Fe_2Nb and NbC respectively, $x_{\text{Nb}}^{\alpha\omega}$ are equilibrium concentration of niobium in ferrite with Fe_2Nb . All of concentrations and fractions except $x_{\text{Nb}}^{\alpha\omega}$ are given or can be estimated with the assumptions mentioned above so that equilibrium concentration of niobium $x_{\text{Nb}}^{\alpha\omega}$ can be calculated.

Table 6 shows the calculated equilibrium mole fractions. **Figure 6** shows relationship between $\ln x_{\text{Nb}}^{\omega}$ and $1/T$ with the values indicated in **Table 6**. The values of A_2 , B_2 and ΔG_0^{ω} in the Eq. (7) were calculated and listed in **Table 7**.

Table 7. Calculated values of A_2 , B_2 and ΔG_0^{ω} for $\text{Fe}_2\text{Nb}(\omega)$ in Nb–Ti–Mo alloyed ferritic stainless steels.

For Fe_2Nb	A_2 / K^{-1}	B_2	$\Delta G_0^{\omega} / \text{J mol}^{-1}$
values for mole fraction and natural logarithm	-8704.4	0.5469	-72333.564
values for mass% and common logarithm	-3780.3	2.4646	-

Fig. 7. Phase boundaries for Ferrite/ $\text{Fe}_3\text{Nb}_3\text{C}$ and the published experimental data.⁶⁾

Fig. 8. Phase boundary for Ferrite/ Fe_2Nb Laves phase and the published experimental data.^{7,8)}

For A_2 and B_2 , expressions with mass% and common logarithm are also presented.

3.5. Verification with Experimental Data in Literatures

Although there are few experimental data about both precipitates in previous literatures, the verification has been carried out. **Figures 7** and **8** show the calculated phase boundaries for ferrite/ $\text{Fe}_3\text{Nb}_3\text{C}$ and ferrite/ Fe_2Nb respectively. In these figures, the published experimental data

[6–8] were plotted. The data were experimentally obtained by the extracted residues from 0.01C–0.01N–18Cr–0.5Nb–2Mo mass% steel aged at 950°C for Fe₃Nb₃C⁽⁶⁾ and 0.008C–0.007N–15Cr–0.46Nb–0.08Mo mass% steel aged at 700°C for Fe₂Nb^(7,8) respectively. The solubility products obtained here are good agreement with the experimental data in the previous literatures.

4. Summary

New experimental data giving the solubility products have been generated for Fe₃Nb₃C; M₆C type carbide and Fe₂Nb; Fe₂M type Laves phase in Nb alloyed ferritic stainless steels. The expressions of the solubility products with mass% are given by:

$$\text{Fe}_3\text{Nb}_3\text{C}; \log_{10}\{[\text{Nb}]^3[\text{C}]\} = -11613/T + 5.2178$$

$$\text{Fe}_2\text{Nb}; \log_{10}[\text{Nb}] = -3780.3/T + 2.4646$$

These have been verified with some published experimental data. The free energy changes for the precipitation

reactions from niobium-supersaturated ferrite have been also obtained using the solubility products. The expressions with mole fractions in ferrite matrix, *e.g.* $x_{\text{Nb}}^{\alpha\beta}$, are given by:

$$\text{Fe}_3\text{Nb}_3\text{C}(\beta); \Delta G^\beta = -222\,509 - RT\{6.423 + \ln(x_{\text{Nb}}^{\alpha\beta})^3(x_{\text{C}}^{\alpha\beta})\}$$

$$\text{Fe}_2\text{Nb}(\omega); \Delta G^\omega = -72\,334 - RT\{-0.5469 + \ln x_{\text{Nb}}^{\alpha\omega}\}$$

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