Nitrogen Solubility in Liquid Fe–Nb, Fe–Cr–Nb, Fe–Ni–Nb and Fe–Cr–Ni–Nb Alloys

Shouxing YANG,¹⁾ Huabing LI,^{1,2)*} Hao FENG,¹⁾ Xuze LI,¹⁾ Zhouhua JIANG^{1,2)} and Tong HE³⁾

1) School of Metallurgy, Northeastern University, Shenyang, China.

2) State Key Laboratory of Rolling and Automation, Northeastern University, Shenyang, China.

3) Analysis and Testing Centre, Northeastern University, Shenyang, China.

(Received on October 14, 2020; accepted on January 18, 2021; J-STAGE Advance published date: February 24, 2021)

The N-containing Fe–Cr–Ni–Nb austenitic heat-resistant steels have become the research focus of high-temperature material. Nitrogen plays an important role on the strength and structural stability of the steels, and thus the accurate control of nitrogen content is of great significance to the smelting process. In this paper, the nitrogen solubility in liquid Fe, Fe–Nb, Fe–Cr–Nb, Fe–Ni–Nb and Fe–Cr–Ni–Nb systems from 1 823 to 1 873 K were investigated by gas-liquid metal equilibrium experiments. In liquid Fe–Nb system with a niobium content of 5 to 20%, the solubility of nitrogen increased with niobium content. The first-order interaction parameter of niobium on nitrogen at 1 873 K and its relationship with temperature were determined as follows: $e_{N(1\ 873\ K)}^{Nb} = -0.0672$, $e_N^{Nb} = -375.6/T + 0.133$. In the liquid Fe–Cr–Nb and Fe–Ni–Nb systems, the second-order cross-interaction parameters of chromium or nickel with niobium on nitrogen were determined as follows: $\gamma_N^{Cr,Nb} = 36.2/T - 0.01728$, $\gamma_N^{Ni,Nb} = 4.59/T - 0.00187$. Furthermore, a more accurate nitrogen solubility prediction model for the liquid Fe–Cr–Ni–Nb system was established based on the existing thermodynamic parameters and the interaction parameters obtained in this study.

KEY WORDS: nitrogen solubility; niobium; Fe–Cr–Ni–Nb system; interaction parameter.

1. Introduction

The N-containing austenitic stainless steels have attracted considerable attention due to their excellent corrosion resistance and mechanical properties.^{1,2)} Among them, the Fe–Cr–Ni–Nb–N alloy system is a new variety widely used in harsh and elevated temperature environments.^{3–6)} The addition of nitrogen contributes to sufficient structural stability and outstanding processability of the austenitic heat-resistant steel, and the nitride precipitation has a critical influence on its high-temperature creep strength.^{2,5–9)} A better understanding and accurate control of the nitrogen content in Fe–Cr–Ni–Nb–N melt is particularly essential. Therefore, the establishment of a model that can accurately predict nitrogen solubility is of great significance to the smelting process of N-containing heat-resistant steel.

At present, many scholars have conducted extensive researches on the thermodynamics of nitrogen dissolution in simple Fe-based alloy systems.^{10–16)} Morita *et al.*¹⁴⁾ measured the equilibrium nitrogen content in liquid Fe–Nb system and investigated the effect of niobium on the nitrogen activity coefficient in the range of niobium content less than 30%.

Wada and Pehlke¹⁵⁾ investigated the nitriding thermodynamics of Fe–Cr–Ni alloy, and determined the second-order cross-interaction parameter of chromium with nickel on nitrogen, and further established a nitrogen solubility model for Fe–Cr–Ni system. Lee *et al.*¹⁶⁾ conducted nitrogen dissolution equilibrium experiments on Fe–Cr–Nb system with a chromium content of 10 to 18% and a niobium content of 0.2 to 2.0% at 1 823 to 1 923 K. And the influence of chromium with niobium on the dissolution behavior of nitrogen was determined. However, few studies reported the nitrogen solubility in the Fe–Cr–Nb or Fe–Ni–Nb systems, and there is still lack of accurate prediction model for nitrogen solubility in liquid Fe–Cr–Ni–Nb quaternary system. Therefore, it is quite necessary to further investigate the influence of chromium, nickel and niobium on the thermodynamics of nitrogen dissolution for predicting the nitrogen solubility.

In this study, the nitrogen solubility in liquid Fe–Nb, Fe–Cr–Nb, Fe–Ni–Nb and Fe–Cr–Ni–Nb alloy systems were measured through the gas-liquid metal equilibrium experiments. By thermodynamic analysis of the results, the influence of Nb, Cr–Nb and Ni–Nb on nitrogen dissolution in liquid alloys and the relationship with temperature were investigated. Then, the nitrogen solubility model for the liquid Fe–Cr–Ni–Nb alloy system within the temperature

* Corresponding author: E-mail: lihb@smm.neu.edu.cn

range of 1 823 to 1 873 K was established and verified accordingly.

2. Experimental

The gas-liquid metal equilibrium experiments of liquid Fe–Nb, Fe–Cr–Nb, Fe–Ni–Nb and Fe–Cr–Ni–Nb alloy systems were carried out in the tubular resistance furnace, and the equilibrium nitrogen content was determined by sampling method,^{17,18)} as shown in Fig. 1. The temperature range of the experiment was from 1 823 to 1 873 K, and the nitrogen pressure was an atmospheric pressure (1.0 atm).

The total weight of about 500 g of electrolytic iron (99.95% purity), chromium (99.32% purity), nickel (99.99% purity) and niobium (99.8% purity) were melted in a magnesia crucible (outer diameter (OD): 56 mm, inner diameter (ID): 50 mm, height (H): 96 mm), which was placed in a graphite crucible (OD: 62 mm, ID: 58 mm, H: 120 mm). Ar was used as protective atmosphere, and the bottom blowing

Fig. 1. Experimental device. (Online version in color.)

Table 1. The measured chemical compositions of the alloys.

System	[mass% Nb]	[mass% Cr]	[mass% Ni]	[mass% Fe]
Fe	/	/	/	bal.
Fe–Nb	0.51	/	/	bal.
	1.98	/	/	bal.
	4.01	/	/	bal.
	5.99	/	/	bal.
Fe–Cr–Nb	0.50	9.99	/	bal.
	2.02	10.01	/	bal.
	0.51	25.01	/	bal.
	1.8	25.02	/	bal.
Fe–Ni–Nb	3.98	/	10.08	bal.
	6.01	/	10.02	bal.
	3.97	/	25.04	bal.
	5.98	/	25.05	bal.
Fe–Cr–Ni–Nb	0.49	22.53	25.06	bal.

flow rate was kept at 5 L/min until the alloy was completely melted. The Pt/Pt-13 mass% Rh thermocouple placed in an alumina tube (OD: 6 mm) was immersed into liquid steel to measure the melt temperature. The temperature during the experiments was maintained within ± 2 K of the setting value. After the temperature of the liquid steel reached the setting level, the alumina tube (OD: 5 mm) was inserted into the liquid steel and kept about 10 mm above the bottom of the crucible. N₂ was blown into the liquid steel at 0.1 L/min flow rate through the alumina tube, while maintaining the bottom nitrogen blowing flow rate at 5 L/min.

To ensure the accuracy of the experimental results, the holding time of each experiment in this study was set as 150 min. The time at which the nitrogen gas started to be blown was defined as the starting time ($t=0$ min), and samples were taken at eight nitriding times: 0, 10, 20, 40, 60, 90, 120 and 150 min, respectively. Each time, about 10 g of the molten alloy sample was extracted by a quartz tube (ID: 4 mm), and quickly quenched in water. The nitrogen and oxygen contents in the metal sample were detected by the nitrogen/oxygen analyzer (LECO TC-500). The chemical compositions of the alloy ingots were determined by the inductively coupled plasma atomic emission spectroscopy (ICP-AES, SPECTRO ARCOS) as listed in Table 1, in which Fe–0.51Nb means that the mass of niobium content in alloy is 0.51%.

3. Results and Discussion

The dissolution reaction of nitrogen in the alloy melt can be generally expressed as:

$$\frac{1}{2} N_2 (g) = [N] \dots\dots\dots (1)$$

The equilibrium constant K_N of the dissolution reaction of nitrogen can be described as:

$$K_N = \frac{a_N}{\sqrt{P_{N_2}}} = \frac{f_N [\%N]}{\sqrt{P_{N_2}}} \dots\dots\dots (2)$$

where K_N is the equilibrium constant for Eq. (1); a_N and f_N are the nitrogen activity and Henrian activity coefficient of nitrogen for which the reference state is the hypothetical 1 wt.% N solution, i.e., $f_N \rightarrow 1$ when $[\%N] \rightarrow 0$; $[\%N]$ is the weight percentage of nitrogen dissolved; and P_{N_2} is the nitrogen partial pressure in the gas phase.

3.1. Equilibrium Time

In this experiment, in addition to the occurrence of gas phase nitriding on the surface of the liquid alloy, an alumina tube was also used to blow nitrogen gas into the melt. By increasing the gas-phase nitriding surface area to accelerate nitriding, the reaction equilibrium time can be substantially shortened. The variation of nitrogen content with nitriding time in different liquid alloy systems is shown in Fig. 2. The nitrogen content in each alloy rose rapidly in the first 40 min, and then reached saturation after 90 min.

3.2. Equilibrium Constant of Nitrogen Dissolution

The reliability of the experimental device and method of the present work were firstly examined by measuring the equilibrium nitrogen content in liquid pure iron, which is the

Fig. 2. The change of nitrogen content with time in experiment. (Online version in color.)

basis for further research. **Table 2** summarizes the nitrogen solubility data in liquid pure iron at 1 873 K and 1.0 atm nitrogen pressure measured by different researchers.^{19–29} According to the experimental results in literatures, the nitrogen solubility in liquid pure iron is mainly concentrated in the range of 0.043% to 0.046%.^{22,24–29} The nitrogen solubility in liquid pure iron is determined to be 0.0448% in the present work, which is close to those reported in literature. This proves that the data obtained through the current experiments are credible.

According to Eq. (2), the equilibrium constant of nitrogen dissolution reaction can be further expressed as:

$$\log K_N = \log f_N + \log [\%N] - \frac{1}{2} \log P_{N_2} \dots\dots\dots (3)$$

Therefore, when the nitrogen pressure in the smelting gas phase is 1.0 atm, the relationship between the equilibrium constant of nitrogen and the nitrogen solubility in liquid pure iron can be expressed as:

$$\log K_N = \log [\%N] \dots\dots\dots (4)$$

Figure 3 shows the effect of temperature on the nitrogen solubility in liquid pure iron, which also contains results obtained by other researchers. The nitrogen solubility in liquid pure iron has a positive relationship with temperature, which increases with the increasing of temperature.^{15,26,28,30–33} The equilibrium nitrogen contents in liquid pure iron at different temperatures obtained in the present work are remarkably consistent with the nitrogen solubility values calculated by Turkdogan.³³ Therefore, the Gibbs free energy change of nitrogen dissolution in liquid pure iron can be taken as:³³

$$\Delta G_N^\circ = 3\,598 + 23.89T \dots\dots\dots (5)$$

According to the Gibbs free energy change obtained by Turkdogan,³³ the equilibrium constant of nitrogen dissolution in liquid pure iron can be written as:

$$\log K_N = \log [\%N] = -\frac{187.9}{T} - 1.248 \dots\dots\dots (6)$$

Table 2. Nitrogen solubility in liquid pure iron at 1 873 K and 1.0 atm nitrogen pressure.

Author	Year	Nitrogen content (%)	Method	Ref.
Chipman and Murphy	1935	0.040	Sieverts' method	(19)
Sieverts and Zap	1935	0.032	Sieverts' method	(20)
Vaughan and Chipman	1939	0.041	Sieverts' method	(21)
Kootz	1941	0.046	Sampling method	(22)
Taylor and Chipman	1942	0.040	Sampling method	(23)
Saito	1949	0.044	Sampling method	(24)
Kasamatsu and Matoba	1957	0.044	Sampling method	(25)
Pehlke and Elliott	1960	0.0451	Sieverts' method	(26)
Turnock and Pehlke	1966	0.045	Sieverts' method	(27)
Ishii <i>et al.</i>	1982	0.0458	Sampling method	(28)
Kim <i>et al.</i>	2012	0.0448	Sampling method	(29)
Yang <i>et al.</i>	2020	0.0448	Sampling method	Present study

Fig. 3. The effect of temperature on the nitrogen solubility in liquid pure iron. (Online version in color.)

3.3. e_N^{Nb} in Fe–Nb System

Figure 4 shows the effect of temperature on nitrogen solubility in liquid Fe–Nb system, in which the dotted lines are parallel to the x-axis. For liquid pure iron without niobium, the relationship between nitrogen solubility and temperature is positive, and higher nitrogen solubility can be obtained at higher temperature. For liquid Fe–Nb alloy system, the addition of over 2.0% niobium reverses the temperature dependence of nitrogen dissolution reaction. That is, the logarithm of nitrogen solubility decreases with the increasing of temperature.

The Gibbs free energy change in liquid alloy system can be expressed as:

$$\Delta G_N^{alloy} = \Delta H_N^{alloy} - T\Delta S_N^{alloy} \dots\dots\dots (7)$$

where ΔH_N^{alloy} and ΔS_N^{alloy} are the enthalpy change and entropy change of solution, respectively.

According to Wagner formalism,³⁴ the nitrogen activity coefficient in the alloy melt can be expressed as:

Fig. 4. The effect of temperature on nitrogen solubility in liquid Fe–Nb system. (Online version in color.)

$$\begin{aligned} \log f_N &= \frac{1}{19.155T} (\Delta G_N^{\text{alloy}} - \Delta G_N^\circ) \\ &= \frac{1}{19.155T} [(\Delta H_N^{\text{alloy}} - \Delta H_N^\circ) - T(\Delta S_N^{\text{alloy}} - \Delta S_N^\circ)] \\ &= \sum e_N^i [\%i] + \sum \gamma_N^i [\%i]^2 + \sum \gamma_N^{i,j} [\%i][\%j] \dots\dots (8) \end{aligned}$$

where ΔH_N° and ΔS_N° are the enthalpy change and entropy change in liquid pure iron; e_N^i and γ_N^i represent the first- and second-order interaction parameters of element i on nitrogen, respectively; $\gamma_N^{i,j}$ represents the second-order cross-interaction parameter of element i with j on nitrogen; $[\%i]$ and $[\%j]$ represent the weight percentage of element i and j , respectively.

In the Fe–Nb binary system, Eq. (8) can be expressed as:

$$\log f_N = e_N^{\text{Nb}} [\%Nb] + \gamma_N^{\text{Nb}} [\%Nb]^2 \dots\dots\dots (9)$$

In this study, the experiments were all carried out at 1.0 atm nitrogen pressure, that is, $\log P_{N_2} = 0$. Therefore, according to Eq. (3), the activity coefficient of nitrogen can be expressed as:

$$\log f_N = \log K_N - \log [\%N] = -\frac{187.9}{T} - 1.248 - \log [\%N] \dots\dots\dots (10)$$

The value of $\log f_N$ can be determined by using the equilibrium constant K_N (Eq. (6)) and the measured solubility $[\%N]$. **Figure 5** shows the change of $\log f_N$ with niobium content at different temperatures. It can be seen that the logarithmic scale of the nitrogen activity coefficient has an evident linear relationship with the niobium content. Thus, the effect of niobium on the activity coefficient of nitrogen can be characterized by the first-order term from the slope of line for each temperature.

Through the regression analysis of the nitrogen activity coefficient in liquid Fe–Nb system, the first-order interaction parameters of niobium on nitrogen at different temperatures are:

Fig. 5. The variation of $\log f_N$ with niobium content at different temperatures. (Online version in color.)

Fig. 6. The variation of e_N^{Nb} with temperature.

$$e_N^{\text{Nb}}(1873 \text{ K}) = -0.0672 \dots\dots\dots (11)$$

$$e_N^{\text{Nb}}(1848 \text{ K}) = -0.0698 \dots\dots\dots (12)$$

$$e_N^{\text{Nb}}(1823 \text{ K}) = -0.0727 \dots\dots\dots (13)$$

Figure 6 shows the variation of e_N^{Nb} with temperature under 1.0 atm N_2 . The value of e_N^{Nb} is negative, indicating that the addition of niobium would reduce the nitrogen activity coefficient in the melt and thereby have a positive effect on increasing nitrogen solubility. Moreover, the value of e_N^{Nb} increases with the increasing of temperature, thus niobium has a more significant effect on improving nitrogen solubility at low temperatures. Therefore, the addition of niobium can reverse the change trend of nitrogen solubility in liquid pure iron with temperature.

The first-order interaction parameters e_N^{Nb} is defined as the coefficient of first-order term of Nb content ($[\%Nb]$) in the nitrogen activity coefficient (Eq. (8)), and it is not affected by other elements. In Fe–Nb binary system, it can be considered as a function of temperature.¹⁷⁾ According to the above experimental results, the functional relationship between e_N^{Nb} and temperature is determined as:

$$e_N^{Nb} = -\frac{375.6}{T} + 0.133 \quad \dots\dots\dots (14)$$

Table 3 summarizes the influence of niobium on nitrogen solubility studied by different scholars.^{14,16,26,27,35–39} The values of e_N^{Nb} at 1 873 K in literatures are mainly concentrated between -0.063 and -0.072 .^{26,27,35–39} In the present work, the value of e_N^{Nb} was measured in the range of 0.5 to 6.0% niobium content in liquid state, which is in good agreement with the results of Pehlke *et al.*,²⁶ Chipman,³⁵ Tumock *et al.*²⁷ and others.^{37,38} The interaction parameter of niobium on nitrogen obtained by Morita *et al.*¹⁴ in 1971 is determined as -0.086 . However, Morita *et al.*³⁷ gained new experimental results in 1982. Not only e_N^{Nb} at 1 873 K, but also the temperature dependence equation of e_N^{Nb} is very consistent with this research.

Given the value of e_N^{Nb} , the first-order interaction parameter e_{Nb}^N at 1 873 K can be determined as:

$$e_{Nb(1873\text{ K})}^N = e_{N(1873\text{ K})}^{Nb} \frac{M_{Nb}}{M_N} + 0.434 \times 10^{-2} \times \frac{M_N - M_{Nb}}{M_N} = -0.4704 \quad \dots (15)$$

where M_{Nb} and M_N are the relative atomic masses of Nb and N, respectively.

3.4. $\gamma_N^{Cr,Nb}$ and $\gamma_N^{Ni,Nb}$ in Fe–Cr–Nb and Fe–Ni–Nb Systems

Figures 7 and 8 show the effect of temperature on nitrogen solubility in liquid Fe–Cr–Nb and Fe–Ni–Nb systems under 1.0 atm N_2 . The solubility of nitrogen in liquid Fe–Cr–Nb alloy decreases with increasing of temperature, and increases with the increasing of niobium and chromium contents. The solubility of nitrogen in liquid Fe–Ni–Nb alloy also decreases with the increasing of temperature and increases with the increasing of niobium content, but it decreases with the increasing of nickel content.

In Fe–Cr–Nb ternary system, it is considered that the value of e_N^{Nb} still depends on temperature and is independence of other alloying elements based on literature.^{17,18,40} Meanwhile, given the strong affinity of Cr and N as reported by Lee *et al.*,¹⁶ the second-order cross interaction parameters of Cr with Nb on N can be applied to describe the cross effect of Cr with Nb on nitrogen activity coefficient, which is the same for Fe–Ni–Nb ternary system.

According to Eq. (8), considering the effect of chromium or nickel with niobium on nitrogen, the activity coefficient of nitrogen in liquid ternary alloys should be written as the

Fig. 7. The effect of temperature on nitrogen solubility in liquid Fe–Cr–Nb system. (Online version in color.)

Fig. 8. The effect of temperature on nitrogen solubility in liquid Fe–Ni–Nb system. (Online version in color.)

Table 3. Effect of niobium on nitrogen solubility.

Author	Year	Temp. (K)	e_N^{Nb}	Temp. Dependency	γ_N^{Nb}	Ref.
Pehlke and Elliott	1960	1 873	-0.067			(26)
Chipman	1965	1 873	-0.067			(35)
Evans and Pehlke	1965	1 873	-0.063			(36)
Tumock and Pehlke	1966	1 873	-0.067			(27)
Morita <i>et al.</i>	1971	1 873	-0.086	$-830/T + 0.36$	0.0019	(14)
Morita <i>et al.</i>	1982	1 873	-0.068	$-280/T + 0.0816$		(37)
Ishii <i>et al.</i>	1983	1 873	-0.068			(38)
Grigorenko and Pomarin	1990	1 873	-0.072	$-237/T + 0.055$		(39)
Yang <i>et al.</i>	2020	1 873	-0.0671	$-375.6/T + 0.133$		Present study

following equations:

For liquid Fe–Cr–Nb system,

$$\begin{aligned} \log f_{N(Fe-Cr-Nb)} = \\ \log f_{N(Fe-Cr)} + e_N^{Nb} [\%Nb] + \gamma_N^{Cr,Nb} [\%Cr][\%Nb] \dots (16) \end{aligned}$$

For liquid Fe–Ni–Nb system,

$$\begin{aligned} \log f_{N(Fe-Ni-Nb)} = \\ \log f_{N(Fe-Ni)} + e_N^{Nb} [\%Nb] + \gamma_N^{Ni,Nb} [\%Ni][\%Nb] \dots (17) \end{aligned}$$

The activity coefficient of nitrogen in liquid Fe–Cr system can be expressed by e_N^{Cr} and γ_N^{Cr} , thus $\log f_{N(Fe-Cr)}$ can be written as:

$$\log f_{N(Fe-Cr)} = e_N^{Cr} [\%Cr] + \gamma_N^{Cr} [\%Cr]^2 \dots (18)$$

The activity coefficient of nitrogen in liquid Fe–Ni system can be expressed by e_N^{Ni} and γ_N^{Ni} , thus $\log f_{N(Fe-Ni)}$ can be given by the following equation:

$$\log f_{N(Fe-Ni)} = e_N^{Ni} [\%Ni] + \gamma_N^{Ni} [\%Ni]^2 \dots (19)$$

According to relative data,¹⁵⁾ in liquid Fe–Cr–Nb and Fe–Ni–Nb systems, the activity coefficient of nitrogen can be specifically expressed as:

$$\begin{aligned} \log f_{N(Fe-Cr-Nb)} = & (-164/T + 0.0415) \times [\%Cr] \\ & + (1.685/T - 0.0006) \times [\%Cr]^2 \\ & + (-375.6/T + 0.133) \times [\%Nb] \\ & + \gamma_N^{Cr,Nb} [\%Cr][\%Nb] \dots (20) \end{aligned}$$

$$\begin{aligned} \log f_{N(Fe-Ni-Nb)} = & (8.33/T + 0.0019) \times [\%Ni] \\ & + (-1.835/T + 0.00105) \times [\%Ni]^2 \\ & + (-375.6/T + 0.133) [\%Nb] \\ & + \gamma_N^{Ni,Nb} [\%Ni][\%Nb] \dots (21) \end{aligned}$$

Figures 9 and 10 show the combined effect of chromium (or nickel) and niobium contents on the nitrogen activity coefficient, in which the ordinate represents the second-order cross-interaction term. For alloys containing low chromium, nickel or niobium content, the corresponding second-order cross-interaction term has little influence; while the influence on nitrogen solubility becomes significant with the increasing of chromium, nickel or niobium content. The second-order cross-interaction parameters of chromium (or nickel) with niobium on nitrogen can be determined, through regression analysis of the nitrogen activity coefficient:

$$\gamma_N^{Cr,Nb} = 36.2/T - 0.01728 \dots (22)$$

$$\gamma_N^{Ni,Nb} = 4.59/T - 0.00187 \dots (23)$$

If the second-order cross-interaction parameter is positive, it would have a negative impact on nitrogen solubility; otherwise, it is opposite. In this study, $\gamma_N^{Cr,Nb}(1873\text{ K}) = 0.00204$ and $\gamma_N^{Ni,Nb}(1873\text{ K}) = 0.00058$ at 1873 K. Therefore, $\gamma_N^{Cr,Nb}$ has a negative impact on the solubility of nitrogen, which is close to 0.0018 that obtained in the literature.¹⁶⁾ $\gamma_N^{Ni,Nb}$ has a negative impact on the solubility of nitrogen as well, but

Fig. 9. The combined effect of chromium and niobium on the nitrogen activity coefficient in liquid Fe–Cr–Nb system at different temperatures. (Online version in color.)

Fig. 10. The combined effect of nickel and niobium on the nitrogen activity coefficient in liquid Fe–Ni–Nb system at different temperatures. (Online version in color.)

there is no related literature value for comparison at present. It can be found that since the value of $\gamma_N^{Cr,Nb}$ is higher than $\gamma_N^{Ni,Nb}$, $\gamma_N^{Cr,Nb}$ has a greater influence on the nitrogen activity coefficient than $\gamma_N^{Ni,Nb}$.

3.5. Nitrogen Solubility Model of Fe–Cr–Ni–Nb System

The nitrogen solubility model of the Fe–Cr–Ni–Nb quaternary system with 10–25% Cr, 10–25% Ni and 0.5–6% Nb was established, based on the above-mentioned thermodynamic analysis and the thermodynamic parameters of the predecessors. The nitrogen activity coefficient in liquid Fe–Cr–Ni–Nb system can be written as:

$$\begin{aligned} \log f_{N(Fe-Cr-Ni-Nb)} = & e_N^{Cr} [\%Cr] + \gamma_N^{Cr} [\%Cr]^2 + e_N^{Ni} [\%Ni] \\ & + \gamma_N^{Ni} [\%Ni]^2 + e_N^{Nb} [\%Nb] + \gamma_N^{Cr,Nb} [\%Cr][\%Nb] \\ & + \gamma_N^{Ni,Nb} [\%Ni][\%Nb] + \gamma_N^{Cr,Ni} [\%Cr][\%Ni] \dots (24) \end{aligned}$$

Combining Eqs. (3) and (24), the logarithm of the nitrogen solubility can be expressed as

Fig. 11. The influence of $\gamma_N^{Cr,Nb}$ and $\gamma_N^{Ni,Nb}$ on the nitrogen solubility in liquid Fe–Cr–Nb, Fe–Ni–Nb, and Fe–Cr–Ni–Nb systems. (Online version in color.)

$$\begin{aligned} \log[\%N] &= \log K_N - \log f_N + \frac{1}{2} \log P_{N_2} \\ &= -187.9/T - 1.248 - ((-164/T + 0.0415) \times [\%Cr] \\ &\quad + (1.685/T - 0.0006) \times [\%Cr]^2 + (8.33/T + 0.0019) \\ &\quad \times [\%Ni] + (-1.835/T + 0.00105) \times [\%Ni]^2 \quad \dots (25) \\ &\quad + (-375.6/T + 0.133) [\%Nb] + (36.2/T - 0.01728) \\ &\quad \times [\%Cr][\%Nb] + (1.6/T - 0.0009) \times [\%Cr][\%Ni] \\ &\quad + (4.59/T - 0.00187) \times [\%Ni][\%Nb]) + \frac{1}{2} \log P_{N_2} \end{aligned}$$

Figure 11 shows the effect of the second-order cross-interaction terms on the calculation accuracy of nitrogen solubility in liquid Fe–Cr–Nb, Fe–Ni–Nb and Fe–Cr–Ni–Nb systems. The solid lines in Fig. 11 are calculated by the nitrogen solubility model including $\gamma_N^{Cr,Nb}$, $\gamma_N^{Ni,Nb}$ and $\gamma_N^{Cr,Ni}$, where $\gamma_N^{Cr,Ni}$ is measured by Wada *et al.*¹⁵⁾ The dashed lines are calculated by omitting the influence of second-order cross-interaction parameters $\gamma_N^{Cr,Nb}$ and $\gamma_N^{Ni,Nb}$ on nitrogen solubility. Each solid point is the equilibrium nitrogen content measured in the experiment. It can be observed that the estimated values of the model that established in this study show better agreement with the experimental results. In addition, the improvement is more obvious for the alloys with high nitrogen solubility. Besides, the influence of the cross-interaction term is not significant for Fe–10Ni–Nb and Fe–25Ni–Nb alloy systems. For Fe–10Cr–Nb, Fe–25Cr–Nb, and Fe–22.5Cr–25Ni–Nb alloy systems, however, the second-order cross-interaction terms plays a more beneficial role in model accuracy with the increasing of niobium content. In order to predict the solubility of nitrogen more accurately, it is essential to consider the second-order cross-interaction terms for Nb-containing systems with high nitrogen content or high chromium and nickel contents.

Moreover, the Eq. (25) can also be applied to estimate the nitrogen solubility in liquid Fe–Nb and Fe–Cr–Nb systems. Correlations between calculated and measured nitrogen solubility in liquid Fe–Nb, Fe–Cr–Nb and Fe–Cr–Ni–Nb systems are shown in **Fig. 12**. The equilibrium nitrogen contents in liquid Fe–Cr–Ni–Nb system measured

Fig. 12. Correlation between the measured value and the value calculated by this nitrogen solubility model. (Online version in color.)

in the present work are very consistent with the calculated values of the nitrogen solubility model. The predicted values of nitrogen solubility in liquid Fe–Nb system are consistent with the equilibrium nitrogen content obtained by Morita *et al.*,¹⁴⁾ in the range of 0.5 to 5.0% niobium content at 1 873 K. The predicted values of nitrogen solubility in liquid Fe–Cr–Nb system are in good agreement with the equilibrium nitrogen content obtained by Lee *et al.*¹⁶⁾ as well, in the range of 10 to 18% chromium content and 0.5 to 2.0% niobium content at 1 873 K. It is proved that the nitrogen solubility model for the liquid Fe–Cr–Ni–Nb alloy system established in this paper is widely effective in predicting nitrogen solubility of the alloys including liquid Fe–Nb and Fe–Cr–Nb systems.

4. Conclusion

In this study, the nitrogen solubility in liquid Fe, Fe–Nb, Fe–Cr–Nb, Fe–Ni–Nb and Fe–Cr–Ni–Nb alloy systems were investigated by sampling method at a temperature ranging from 1 823 to 1 873 K under an atmospheric pressure of nitrogen. The effects of chromium, nickel and niobium on thermodynamic of nitrogen dissolution were further studied for precise estimation of nitrogen solubility. The main findings can be summarized as follows:

(1) For the liquid Fe–Nb alloy system, in the range of 0.5 to 6.0% niobium content, the interaction parameter of niobium on nitrogen at 1 873 K was determined as $e_N^{Nb} = -0.0672$; the relationship between e_N^{Nb} and temperature was determined as $e_N^{Nb} = -375.6/T + 0.133$.

(2) For the liquid Fe–Cr–Nb and Fe–Ni–Nb alloy systems, the combined effects of chromium or nickel with niobium on nitrogen activity coefficient from 1 823 to 1 873 K were respectively determined as: $\gamma_N^{Cr,Nb} = 36.2/T - 0.01728$, $\gamma_N^{Ni,Nb} = 4.59/T - 0.00187$.

(3) For alloy systems with 10–25% Cr, 10–25% Ni and 0.5–6% Nb, taking the second-order cross-interaction parameters into account is essential to the improvement of calculation accuracy of nitrogen solubility. Accordingly, an accurate nitrogen solubility model for Fe–Cr–Ni–Nb system was elaborated, and well verified with experimental results.

Acknowledgements

This research was sponsored by the Shanxi Municipal Major Science & Technology Project [Grant No. 20181101014], National Natural Science Foundation of China [Grant Nos. U1960203/51774074/52004060], China National Postdoctoral Program for Innovative Talents [Grant No. BX20200076], China Postdoctoral Science Foundation [Grant No. 2020M670775], Fundamental Research Funds for the Central Universities [Grant Nos. N172512033 and N2024005-4], and Talent Project of Revitalizing Liaoning [Grant No. XLYC1902046].

REFERENCES

- 1) M. O. Speidel: *Materialwiss. Werkstofftech.*, **37** (2006), 875 (in German). <https://doi.org/10.1002/mawe.200600068>
- 2) H. Hänninen, J. Romu, R. Ilola, J. Tervo and A. Laitinen: *J. Mater. Process. Technol.*, **117** (2001), 424. [https://doi.org/10.1016/S0924-0136\(01\)00804-4](https://doi.org/10.1016/S0924-0136(01)00804-4)
- 3) J. Polák, R. Petráš, M. Heczko, I. Kuběna, T. Kruml and G. Chai: *Mater. Sci. Eng. A*, **615** (2014), 175. <https://doi.org/10.1016/j.msea.2014.07.075>
- 4) G. Chai, J. O. Nilsson, M. Boström, J. Högberg and U. Forsberg: *Advanced Steels*, Springer, Berlin, Heidelberg, (2011), 385. https://doi.org/10.1007/978-3-642-17665-4_40
- 5) G. Chai and U. Forsberg: *Materials for Ultra-Supercritical and Advanced Ultra-Supercritical Power Plants*, Woodhead Publishing, Cambridge, UK, (2017), 391. <https://doi.org/10.1016/B978-0-08-100552-1.00012-9>
- 6) G. Chai, M. Boström, M. Olaison and U. Forsberg: *Procedia Eng.*, **55** (2013), 232. <https://doi.org/10.1016/j.proeng.2013.03.248>
- 7) Y. U. Kim, W. S. Jung, Y. H. Chung and S. I. Kwun: *Key Eng. Mater.*, **385–387** (2008), 425. <https://doi.org/10.4028/www.scientific.net/KEM.385-387.425>
- 8) R. Sandström, M. Farooq and J. Zurek: *Mater. Res. Innov.*, **17** (2013), 355. <https://doi.org/10.1179/1433075X13Y.0000000120>
- 9) M. Heczko, B. D. Esser, T. M. Smith, P. Beran, V. Mazánová, T. Kruml, J. Polák and M. J. Mills: *J. Mater. Res.*, **32** (2017), 4342. <https://doi.org/10.1557/jmr.2017.311>
- 10) J. M. Jang, D. H. Kim, M. K. Paek and J. J. Pak: *ISIJ Int.*, **58** (2018), 1185. <https://doi.org/10.2355/isijinternational.ISIJINT-2017-689>
- 11) J. M. Jang, S. H. Seo, M. Jiang, M. K. Paek, X. Wang and J. J. Pak: *ISIJ Int.*, **54** (2014), 32. <https://doi.org/10.2355/isijinternational.54.32>
- 12) W. Y. Kim, C. O. Lee, C. W. Yun and J. J. Pak: *ISIJ Int.*, **49** (2009), 1668. <https://doi.org/10.2355/isijinternational.49.1668>
- 13) S. Maekawa and Y. Nakagawa: *Tetsu-to-Hagane*, **46** (1960), 972 (in Japanese). https://doi.org/10.2355/tetsutohagane1955.46.9_972
- 14) Z. Morita, K. Hachisuka, Y. Iwanaga and A. Adachi: *J. Jpn. Inst. Met.*, **35** (1971), 831 (in Japanese). https://doi.org/10.2320/jinstmet1952.35.9_831
- 15) H. Wada and R. D. Pehlke: *Metall. Trans. B*, **8** (1977), 443. <https://doi.org/10.1007/BF02696931>
- 16) S. B. Lee, M. C. Jung, H. Song and C. H. Rhee: *ISIJ Int.*, **42** (2002), 603. <https://doi.org/10.2355/isijinternational.42.603>
- 17) K. Qian, B. Chen, P. X. Zhao, M. S. Zhang and K. Liu: *ISIJ Int.*, **59** (2019), 2220. <https://doi.org/10.2355/isijinternational.ISIJINT-2019-187>
- 18) M. K. Paek, H. S. Son, J. M. Jang and J. J. Pak: *ISIJ Int.*, **60** (2020), 640. <https://doi.org/10.2355/isijinternational.ISIJINT-2019-490>
- 19) J. Chipman and D. W. Murphy: *Tech. Publ. Am. Inst. Min. Metall. Eng.*, **591** (1935), 12.
- 20) A. Sieverts and G. Zapf: *Z. Phys. Chem.*, **172A** (1935), 314 (in German).
- 21) J. C. Vaughan and J. Chipman: *Trans. Met. Soc. AIME*, **140** (1940), 224.
- 22) T. Kootz: *Arch. Eisenhüttenwes.*, **15** (1941), 77.
- 23) C. R. Taylor and J. Chipman: *Trans. Am. Inst. Min. Metall. Pet. Eng.*, **154** (1943), 228.
- 24) T. Saito: *Sci. Rep. Res. Inst., Tohoku Univ., Ser. A*, **1** (1949), 411.
- 25) Y. Kasamatsu and S. Matoba: *Tetsu-to-Hagane*, **45** (1959), 100 (in Japanese). https://doi.org/10.2355/tetsutohagane1955.45.2_100
- 26) R. D. Pehlke and J. F. Elliott: *Trans. Metall. Soc. AIME*, **218** (1960), 1088.
- 27) P. H. Turnock and R. D. Pehlke: *Trans. Metall. Soc. AIME*, **236** (1966), 1540.
- 28) F. Ishii, S. Ban-Ya and T. Fuwa: *Tetsu-to-Hagane*, **68** (1982), 946 (in Japanese). https://doi.org/10.2355/tetsutohagane1955.68.8_946
- 29) D. H. Kim, M. S. Jung, H. Nam, M. K. Paek and J. J. Pak: *Metall. Mater. Trans. B*, **43** (2012), 1106. <https://doi.org/10.1007/s11663-012-9677-8>
- 30) Z. Morita and K. Kunisada: *Tetsu-to-Hagane*, **63** (1977), 1663 (in Japanese). https://doi.org/10.2355/tetsutohagane1955.63.10_1663
- 31) H. Wada and R. D. Pehlke: *Metall. Trans. B*, **12** (1981), 333. <https://doi.org/10.1007/BF02654467>
- 32) H. Wada, S. W. Lee and R. D. Pehlke: *Metall. Trans. B*, **17** (1986), 238. <https://doi.org/10.1007/BF02670840>
- 33) E. T. Turkdogan: *Physical Chemistry of High Temperature Technology*, Academic Press, New York, (1980), 5. <https://doi.org/10.1002/anie.198009461>
- 34) C. Wagner: *Thermodynamics of Alloys*, Addison-Wesley Press, Cambridge, MA, (1952), 47. https://doi.org/10.1007/978-3-662-04884-9_2
- 35) J. Chipman: *Tetsu-to-Hagane*, **51** (1965), 1477 (in Japanese).
- 36) D. B. Evans and R. D. Pehlke: *Trans. Met. Soc. AIME*, **233** (1965), 1620.
- 37) T. I. Chung, J. B. Lee, J. G. Kang, J. O. Jo, B. H. Kim and J. J. Pak: *Mater. Trans.*, **49** (2008), 854. <https://doi.org/10.2320/matertrans.MER2007286>
- 38) F. Ishii, Y. Iguchi and S. Ban-ya: *Tetsu-to-Hagane*, **69** (1983), 913 (in Japanese). https://doi.org/10.2355/tetsutohagane1955.69.8_913
- 39) G. M. Grigorenko and Y. M. Pomarin: *Nitrogen and Hydrogen in Molten Metals and Alloys*, Vol. 1, CRC Press, Boca Raton, (1990), 1.
- 40) H. Wada and R. D. Pehlke: *Metall. Trans. B*, **8** (1977), 675. <https://doi.org/10.1007/BF02669347>