ORIGINAL RESEARCH ARTICLE

Nitrogen Solubility in Molten Ni, Ni-Cr, Ni-Mo, and Ni-Cr-Mo Alloys Under Pressurized Atmosphere

XU-ZE LI, HUA-BING LI, HAO FENG, SHOU-XING YANG, SHU-CAI ZHANG, HONG-CHUN ZHU, and ZHOU-HUA JIANG

Hastelloy with Ni-Cr-Mo as the main component is a kind of highly corrosion-resistant alloy, and is widely used in aerospace, nuclear industry, and petrochemical. Reasonable addition of nitrogen can improve the mechanical and anti-corrosion properties of Ni-based alloys, thus accurate prediction of nitrogen solubility has important guiding significance for controlling nitrogen content. The solubility of nitrogen in molten Ni, Ni-Cr, Ni-Mo, and Ni-Cr-Mo systems was investigated by sampling method and thermodynamic analysis. The experiments were carried out at temperatures from 1823 K to 1923 K and nitrogen pressures from 0.1 to 1.6 MPa. The nitrogen solubility of molten Ni-35Cr system under high nitrogen pressure deviated significantly from Sieverts' law, and $e_N^N = 0.8234 - 1309.64/T$ was obtained to describe the deviation of nitrogen solubility from Sieverts' law. According to the studies of nitrogen solubility in molten Ni-Cr and Ni-Mo systems with chromium and molybdenum contents up to 35 wt pct, the interaction parameters were obtained as $e_N^{Cr} = 0.0055 - 171.85/T$, $r_N^{Cr} = -0.00050 + 2.102/T$, $e_N^{Mo} = -0.0491 + 29.09/T$, $r_N^{Mo} = 0.00130 - 2.302/T$, respectively. For molten Ni-Cr-Mo system, the second-order cross-interaction parameter was determined as $r_N^{Cr,Mo} = 0.00129 - 1.609/T$. The nitrogen solubility model that could accurately predict the nitrogen solubility of molten Ni-Cr-Mo system under normal pressure and high nitrogen pressure was established.

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I. INTRODUCTION

As one of the most important types of highly corrosion-resistant materials, Ni-based alloys are widely used in aero-engines, nuclear industry, power plants, *etc*.[1–3] In order to obtain higher performance, nitrogen alloying as a new method has been extensively studied in various alloys.[4–9] Some studies have shown that reasonable addition of nitrogen is beneficial to the mechanical and anti-corrosion properties of Ni-based alloys.[10–13] Ni-Cr-Mo system is the main alloy component of Hastelloy, and thus the importance of accurately predicting the nitrogen solubility of this system is not only in the enrichment of basic research, but also in the improvement of product performance.

The thermodynamics of nitrogen dissolution in Fe-based alloys have been extensively studied,[14–25] while the nitrogen dissolution behavior in Ni-based alloys is rarely focused,[26–40] especially in multicomponent systems under high nitrogen pressure.[31–33] Herrera-Trejo and Ablitzer[26] used the Sieverts' method to measure the solubility of nitrogen in molten Ni-Cr system, and obtained the first- and second-order interaction parameters at 0.1 MPa nitrogen pressure. Kowanda and Speidel[27] systematically studied the effects of alloy elements such as Cr, Mo, and W in binary Ni-based systems on nitrogen solubility under high nitrogen pressure. And e_N^N was determined to modify the nitrogen solubility model at high nitrogen pressure. On this basis, the interaction parameters of each alloy element on nitrogen were obtained by regression analysis. Qian *et al*.[31] investigated the nitrogen solubility in Ni-Cr-V and Ni-Cr-Ta ternary systems under low nitrogen pressure, and determined the

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important role of second-order cross-interaction parameter in accurately predicting nitrogen solubility. For complex alloy systems with high alloy content, the second-order cross-interaction parameters play an important role in accurate prediction of nitrogen solubility.[19,20,31,32] However, there is still a lack of research on nitrogen solubility in molten Ni-Cr-Mo ternary system. Therefore, the research and model establishment of nitrogen solubility in molten Ni-Cr-Mo system is of great significance.

In the present study, the equilibrium nitrogen contents in molten Ni, Ni-Cr, Ni-Mo, and Ni-Cr-Mo alloy systems were measured by sampling method. The effects of N, Cr, Mo, and Cr-Mo on the solubility of nitrogen in various molten alloy systems were systematically investigated. An accurate prediction model of nitrogen solubility in molten Ni-Cr-Mo system that is effective at normal pressure and high nitrogen pressure was established.

II. EXPERIMENTAL PROCEDURE

The nitrogen dissolution equilibrium experiments of molten Ni, Ni-Cr, Ni-Mo, and Ni-Cr-Mo alloy systems were conducted in a pressurized induction furnace (Yuanteng Electric Furnace Technology Co., Ltd.) with a capacity of 2 kg. Figure 1 shows the pressurized induction furnace with automatic sampling function. The experimental temperature range was 1823 K to 1923 K, and the nitrogen pressure range was 0.1 to 1.6 MPa.

The alloy material with total weight about 1800 g that consisted of nickel (99.96 wt pct), chromium (99.32 wt pct), and molybdenum (99.98 wt pct) were placed in a magnesium aluminum spinel crucible. The pressure in the furnace chamber was evacuated to below 4.0 Pa, and then filled with 0.02 MPa high-purity argon (99.999 wt pct). The power of the induction coil was gradually increased and then kept until the alloy material melted. The thermocouple was inserted into the alloy melt to measure the temperature in real time and controlled the experimental temperatures within ± 5 K of the target value. Then, high-purity nitrogen (99.999 wt pct) was charged into the furnace chamber, and the nitrogen pressure was controlled to the target value until the end of the experiment (control accuracy: ± 0.002 MPa).

When the nitrogen dissolution reached equilibrium, a quartz tube sampler was used for sampling, and the sample obtained each time was about 10 g. Based on the design of a sufficiently small sampler, it provided rapid cooling conditions for the sample, which could effectively inhibit the escape of nitrogen in the sample.[21] The Cr and Mo contents were analyzed by the inductively coupled plasma atomic emission spectrometry instrument (ARCOS, Spectro Analytical Instruments). Meanwhile, the N content was determined by LECO TC-500 analyzer.

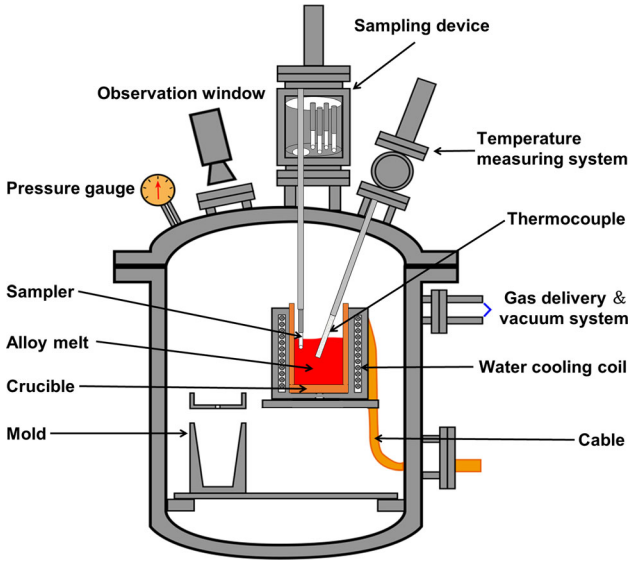

Fig. 1—Schematic diagram of the pressurized induction furnace in the present experiments.

III. RESULTS AND DISCUSSION

The present work firstly measured the solubility of nitrogen in molten nickel under 0.1 MPa to verify the reliability of the experimental setup and sampling method. Figure 2 shows the nitrogen solubility of molten nickel in the present study and various literatures. It can be seen that the nitrogen solubility in molten nickel was linear with temperature and increased with temperature. As shown in Figure 2, the equilibrium nitrogen contents in molten nickel at 1873 K in various literatures ranged from 0.0009 to 0.0020 wt pct.[28,32–35] In the present work, the nitrogen solubility of molten nickel at 1873 K was measured to be 0.0016 wt pct, which is within the range of results reported in the literatures. This proves that the current experimental method and results are credible.

The reaction of nitrogen dissolution in molten Ni-based alloys is represented by the following equation:

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

The K_N of nitrogen dissolution reaction in molten Ni-based alloys is expressed as

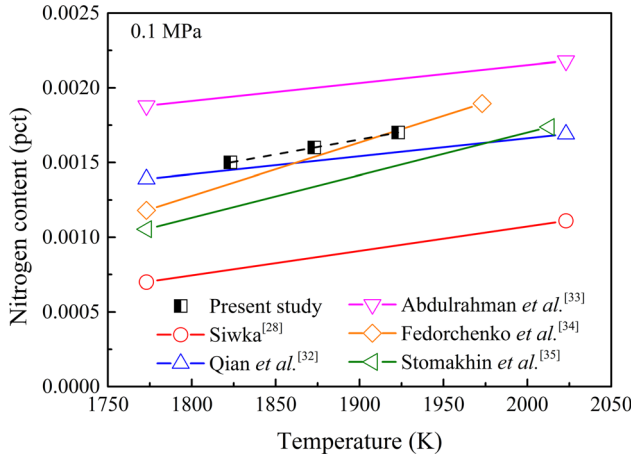

Fig. 2—Nitrogen solubility of molten nickel in the present study and various literatures.

$$K_N = \frac{a_N}{\sqrt{P_{N_2}/P^0}} = \frac{f_N[\text{pct N}]}{\sqrt{P_{N_2}/P^0}}, \quad [2]$$

where K_N is the equilibrium constant; a_N is the nitrogen activity; P_{N_2} and P^0 are gas-phase nitrogen pressure and standard atmospheric pressure ($P^0 = 1.01325$ atm), MPa; [pct N] is the weight percentage of nitrogen in the melt when the dissolution reaction reaches equilibrium; f_N is the Henrian activity coefficient of nitrogen for which the reference state is the hypothetical 1 wt pct N solution, *i.e.*, $f_N \to 1$ when [pct N] $\to 0$.

By taking logarithm on Eq. [2], K_N is also expressed by the following equation:

$$\log K_N = \log f_N + \log[\text{pct N}] - \frac{1}{2}\log(P_{N_2}/P^0). \quad [3]$$

For molten nickel, its nitrogen solubility is very low, and it can be considered that f_N approaches 1. Therefore, when the nitrogen pressure in the experiment is standard atmospheric pressure, the relationship between the nitrogen dissolution reaction equilibrium constant and the solubility of nitrogen in molten nickel is

$$\log K_N = \log[\text{pct N}] = -\frac{1905.66}{T} - 1.779 \quad [4]$$

Therefore, ΔG_N^0 for nitrogen dissolution is expressed as

$$\Delta G_N^0 = 36481.37 + 34.06T, \quad [5]$$

where ΔG_N^0 is the standard Gibbs free energy change, J/mol.

A. *Correction for Nitrogen Solubility Under High Nitrogen Pressure*

Figure 3 shows the variation of the nitrogen solubility in molten Ni-Cr and Ni-Mo systems with the square root of nitrogen pressure at 1823 K. The nitrogen solubility increased with the increase of nitrogen pressure. For the above binary systems of Ni-Cr (Cr content: 5 to 25 pct wt) and Ni-Mo (Mo content: 5 to 35 pct wt), the relationship between nitrogen solubility and nitrogen pressure followed Sieverts' law. However, with the increase of nitrogen pressure, the nitrogen solubility of molten Ni-35Cr system had a significant negative deviation from the nitrogen solubility determined by Sieverts' law. At present, the researches on nitrogen solubility of Ni-based binary alloy system were mostly conducted at low nitrogen pressure, and the nitrogen solubility could be accurately predicted just by the first-order or first- and second-order interaction parameters.[26,31,33] The interaction of nitrogen on itself in Fe-based alloys was also difficult to verify at low nitrogen pressures.[18–20] However, with the study of nitrogen solubility in molten Ni-based and Fe-based alloy systems under high nitrogen pressures, it can be found that the nitrogen solubility in systems with high alloy content, such as molten Ni-Cr and Fe-Cr, deviated from Sieverts' law.[15,29] Since then, the interaction between nitrogen and nitrogen has been considered, and the interaction term of nitrogen on itself has become an integral part of the nitrogen solubility model at high nitrogen pressure.

For high nitrogen pressure conditions, the interaction term of nitrogen on itself is necessary to accurately predict nitrogen solubility.[15,29] For complex alloy systems with high alloy content, in order to achieve accurate prediction of nitrogen solubility, the second-order cross-interaction parameters of alloy elements on nitrogen are also indispensable.[19,20,31,32]

As mentioned above, the logarithm of nitrogen activity coefficient for a multicomponent molten alloy system under high nitrogen pressure is as follows:

$$\log f_N = e_N^N[\text{pct N}] + \sum e_N^i[\text{pct } i] + \sum r_N^i[\text{pct } i]^2 + \sum_{i \neq j} r_N^{i,j}[\text{pct } i][\text{pct } j], \quad [6]$$

where e_N^N is the first-order interaction parameter of nitrogen on itself; e_N^i and r_N^i are the first- and second-order interaction parameters of i on nitrogen, respectively; $r_N^{i,j}$ is the second-order cross-interaction

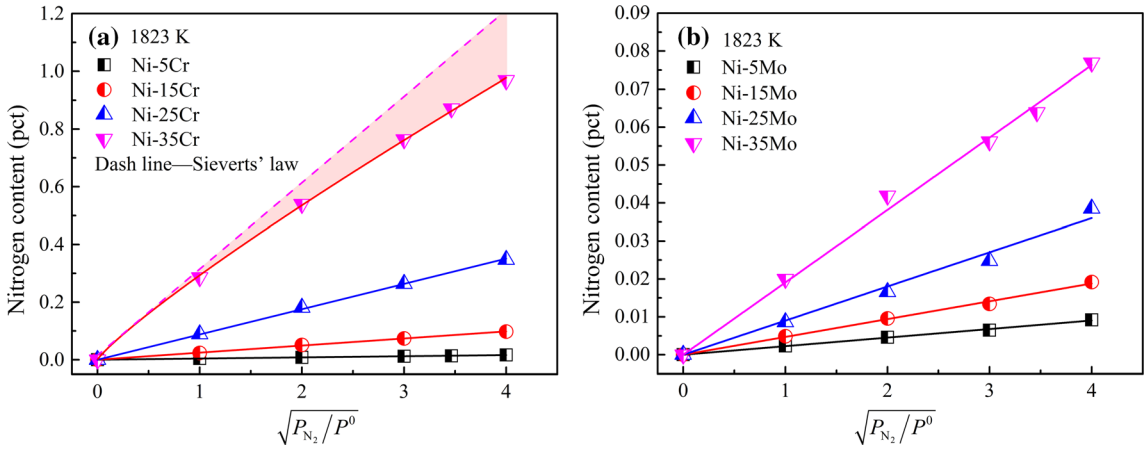

Fig. 3—Variation of the nitrogen solubility in molten (*a*) Ni-Cr system and (*b*) Ni-Mo system with the square root of nitrogen pressure at 1823 K.

parameter of i with j on nitrogen; [pct i] and [pct j] are the weight percentage of i and j, respectively. Therefore, for the molten Ni-Cr system, the logarithmic value of the nitrogen activity coefficient is represented as follows:

$$\log f_N = e_N^N[\text{pct N}] + e_N^{Cr}[\text{pct Cr}] + r_N^{Cr}[\text{pct Cr}]^2. \quad [7]$$

The logarithmic value of the nitrogen activity coefficient is calculated as follows:

$$\log f_N = \log K_N - \log[\text{pct N}] + \frac{1}{2}\log(P_{N_2}/P^0). \quad [8]$$

Based on Eqs. [7] and [8], the difference between $\log f_N$ of molten Ni-35Cr system at high nitrogen pressure and 0.1 MPa nitrogen pressure is expressed and calculated as follows:

$$\log f_{N,High} - \log f_{N,0.1MPa} = e_N^N([\text{pct N}]_{High} - [\text{pct N}]_{0.1MPa}) \quad [9]$$

$$\log f_{N,High} - \log f_{N,0.1MPa} = -\log[\text{pct N}]_{High} + \log[\text{pct N}]_{0.1MPa} + \frac{1}{2}\log(P_{N_2,High}/P^0), \quad [10]$$

where $f_{N,High}$ and $f_{N,0.1MPa}$ are the activity coefficient of nitrogen at high nitrogen pressure and 0.1 MPa nitrogen pressure, respectively; $[\text{pct N}]_{High}$ and $[\text{pct N}]_{0.1MPa}$ are the nitrogen solubility at high nitrogen pressure and 0.1 MPa nitrogen pressure, respectively; $P_{N_2,High}$ is the above-mentioned high nitrogen pressure, MPa.

As shown in Figure 4, according to the variation of the nitrogen solubility in molten Ni-35Cr alloy with the square root of nitrogen pressure at various temperatures, the interaction parameters between nitrogen and nitrogen at various temperatures can be analyzed. The nitrogen solubility in molten Ni-35Cr alloy system obviously deviated from the Sieverts' law and decreased with the increase of temperature. $\log f_{N,High} - \log f_{N,0.1MPa}$ and $[\text{pct N}]_{High} - [\text{pct N}]_{0.1MPa}$ at various temperatures can be described by linear relationship, and the slope value of the straight line equaled to e_N^N.

The interaction parameter of nitrogen on itself at various temperatures can be expressed as follows:

$$e_{N,1823K}^N = 0.1054 \quad [11]$$

$$e_{N,1873K}^N = 0.1234 \quad [12]$$

$$e_{N,1923K}^N = 0.1428 \quad [13]$$

Therefore, the temperature function of e_N^N can be expressed as

$$e_N^N = 0.8234 - 1309.64/T \quad [14]$$

At present, there are just few studies on the nitrogen solubility of Ni-based alloys under high pressure. Kowand and Speidel[29] obtained the value of e_N^N at 1823 K to correct the nitrogen solubility model of molten Ni-Cr system under nitrogen pressure up to 6.0 MPa. There are some differences between the value of e_N^N obtained in the literature ($e_{N,1823K}^N = 0.280$) and present study (Eqs. [11] through [14]), which can be attributed to the difference in sampling method.

B. *Interaction Parameters in Molten Ni-Cr and Ni-Mo Systems*

Figure 5 shows the variation of the nitrogen solubility with temperature in molten Ni-Cr system at 0.1 MPa nitrogen pressure. The nitrogen solubility of molten Ni-Cr alloy system increased with the chromium content. With the chromium content less than 5 wt pct, the solubility of nitrogen in molten Ni-Cr system increased with temperature. In contrast, the solubility of nitrogen in molten Ni-Cr system decreased with increasing temperature when the chromium content was 15 to 35 wt pct.

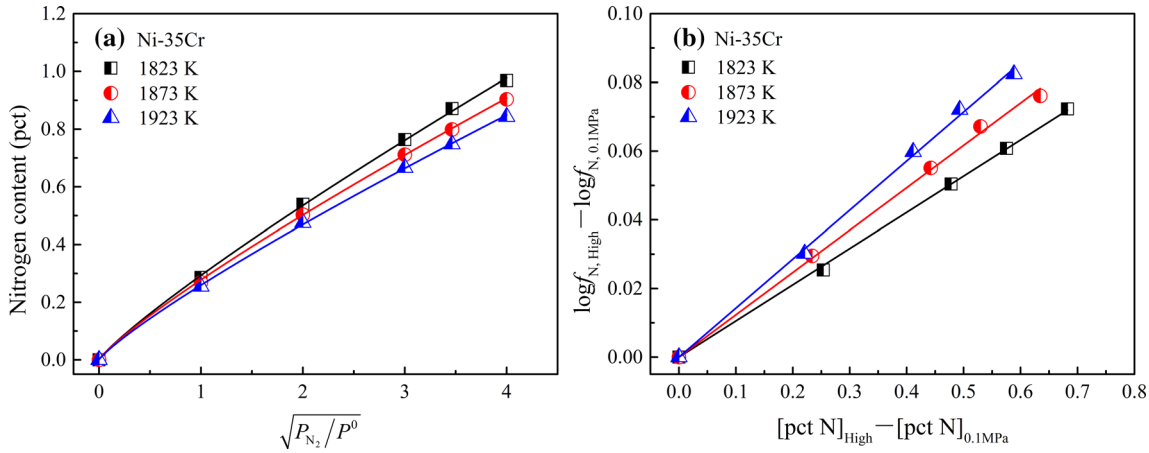

Fig. 4—(*a*) Variation of the nitrogen solubility in molten Ni-35Cr alloy with the square root of nitrogen pressure at various temperatures; (*b*) variation of the $\log f_{N,High} - \log f_{N,0.1MPa}$ in molten Ni-35Cr alloy with the $[\text{pct N}]_{High} - [\text{pct N}]_{0.1MPa}$ at various temperatures.

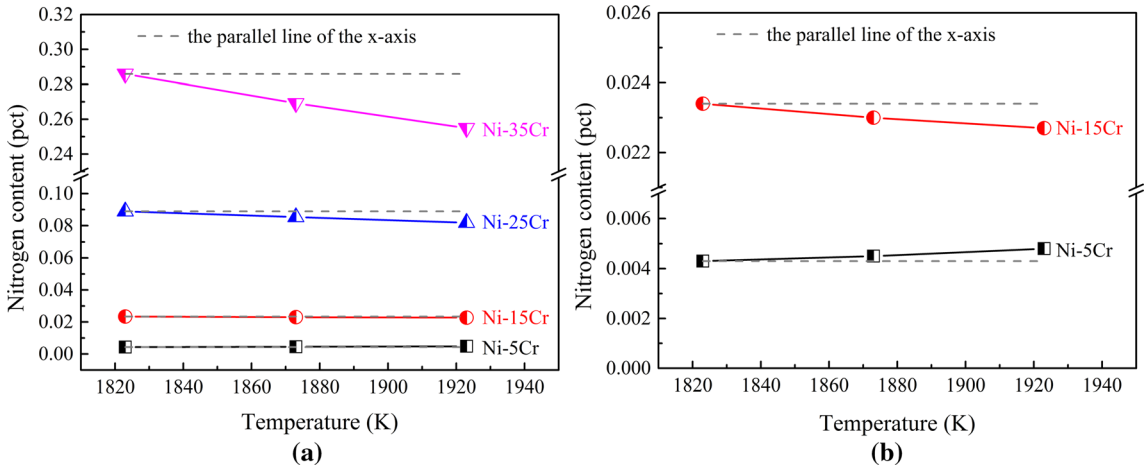

Fig. 5—Variation of the nitrogen solubility with temperature in molten Ni-Cr system: (*a*) Ni-5Cr, Ni-15Cr, Ni-25Cr, and Ni-35Cr; (*b*) the partial enlarged view of (a).

For the molten Ni-Cr binary system, the logarithm of the nitrogen activity coefficient is expressed as

$$\log f_N = e_N^N[\text{pct N}] + e_N^{Cr}[\text{pct Cr}] + r_N^{Cr}[\text{pct Cr}]^2. \quad [15]$$

The relationship between the logarithm of the nitrogen activity coefficient and the chromium content is expressed as

$$\log f_N - e_N^N[\text{pct N}] = e_N^{Cr}[\text{pct Cr}] + r_N^{Cr}[\text{pct Cr}]^2. \quad [16]$$

Figure 6 shows the variation of the $\log f_N - e_N^N[\text{pct N}]$ in molten Ni-Cr system with the chromium content at 0.1 MPa nitrogen pressure and various temperatures. $\log f_N - e_N^N[\text{pct N}]$ was not linearly related to chromium content, which proved the presence of the second-order interaction parameter. Therefore, the relationship between $\log f_N - e_N^N[\text{pct N}]$ and chromium content at each temperature needs to be represented by e_N^{Cr} and r_N^{Cr}. The e_N^{Cr} and r_N^{Cr} at various temperatures are expressed as follows:

$$e_{N,1823K}^{Cr} = -0.0888,\ r_{N,1823K}^{Cr} = 6.54 \times 10^{-4} \quad [17]$$

$$e_{N,1873K}^{Cr} = -0.0862,\ r_{N,1873K}^{Cr} = 6.20 \times 10^{-4} \quad [18]$$

$$e_{N,1923K}^{Cr} = -0.0839,\ r_{N,1923K}^{Cr} = 5.94 \times 10^{-4} \quad [19]$$

Therefore, the temperature functions of e_N^{Cr} and r_N^{Cr} can be obtained, respectively:

$$e_N^{Cr} = 0.0055 - 171.85/T \quad [20]$$

$$r_N^{Cr} = -0.00050 + 2.102/T \quad [21]$$

Herrera-Trejo and Ablitzer[26] carried out the nitrogen dissolution equilibrium experiments of molten Ni-Cr system (Cr content: 0 to 35.7 wt pct) by Sieverts' method, and obtained e_N^{Cr} and r_N^{Cr} at 1873 K. Table I

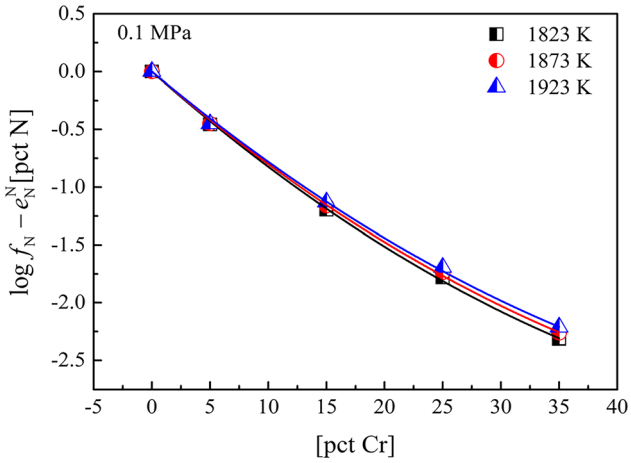

Fig. 6—Variation of the $\log f_N - e_N^N[\text{pct N}]$ in molten Ni-Cr system with the chromium content at 0.1 MPa nitrogen pressure and various temperatures.

collects the interaction parameters of chromium on nitrogen in present study and various literatures. It can be found that their interaction parameters are very close to the present study. Figure 7 shows the good agreement between the nitrogen solubility measurements and the predicted values of the present study, and the comparison of the measurements for the Ni-Cr system with the predictions of various literature models at various nitrogen pressures. As shown in Figure 7(a), since the interaction of nitrogen on itself was not considered, the calculated values of the model established by Herrera-Trejo and Ablitzer[26] were larger than the measured values in the present study, and the deviation increased with chromium content. The Sieverts' method is inherently inaccurate because the metal vapor in the reaction system can react with the nitrogen atmosphere to form stable nitrides, or nitrogen can be adsorbed on the deposit. The above effects are more pronounced for melts with high content of alloy elements, and appear as increased nitrogen dissolution.[23] It is accepted that the solubility of nitrogen measured by the Sieverts' method

Table I. The interaction parameters of chromium on nitrogen in present study and various literatures

Author	Year	Temp. (K)	P_{N_2} (MPa)	e_N^{Cr}	r_N^{Cr}
Herrera-Trejo and Ablitzer[26]	1997	1873	0.1	− 0.0856	5.00×10^{-4}
Kowanda and Speidel[27]	2000	1823	0.1	− 0.0952	7.00×10^{-4}
			1.0	− 0.1047	9.00×10^{-4}
			2.5	− 0.1073	1.00×10^{-3}
			6.0	− 0.0759	6.00×10^{-4}
Abdulrahman and Hendry[33]	2001	1873	0.1	− 0.0766	—
Kowanda and Speidel[29]	2003	1823	0.1 to 6.0	− 0.0952	7.00×10^{-4}
Present study	2022	1823	0.1 to 1.6	− 0.0888	6.54×10^{-4}
		1873		− 0.0862	6.20×10^{-4}
		1923		− 0.0839	5.94×10^{-4}

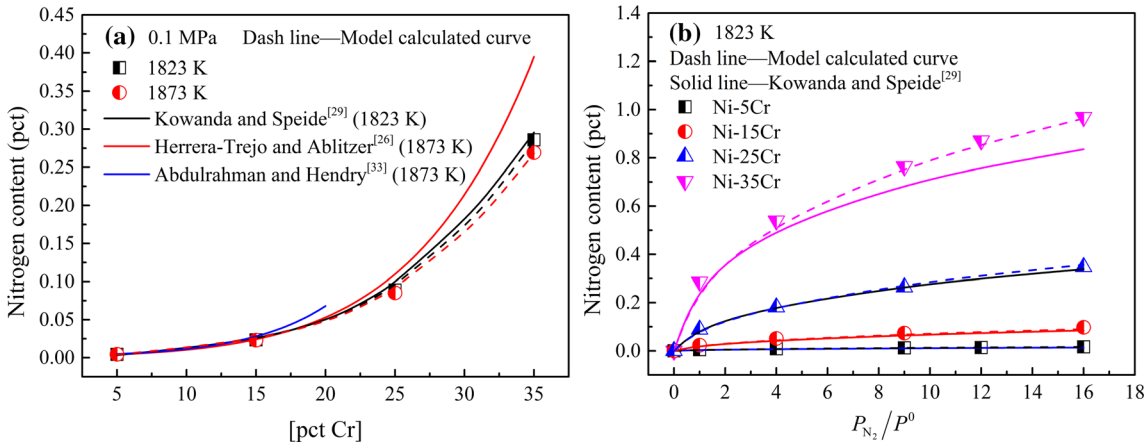

Fig. 7—(*a*) Variation of the nitrogen solubility in molten Ni-Cr system with the chromium content at 0.1 MPa nitrogen pressure and various temperatures; (*b*) variation of the nitrogen solubility in molten Ni-Cr system with the nitrogen pressure at 1823 K.

was larger than the actual value,[22–24] which may be the reason for the larger value predicted by their nitrogen solubility models.

Similarly, Abdulrahman and Hendry[33] also used the Sieverts' method to research the solubility of nitrogen in molten Ni-Cr systems (Cr content: 0 to 20 wt pct), and obtained e_N^{Cr} to describe the solubility of nitrogen. According to Figure 6, when the chromium content did not exceed 20 wt pct, the nitrogen activity coefficient can be approximately described by the first-order interaction parameter. As the chromium content further increased, both first- and second-order interaction parameters were required simultaneously to describe the activity coefficient of nitrogen in the molten Ni-Cr system. Meanwhile, the interaction parameter of nitrogen on itself was considered in the present study, and thus the measured value of e_N^{Cr} was smaller. As shown in Figure 7(a), the predicted values of the nitrogen solubility model established by Abdulrahman and Hendry[33] are larger than that in the present study. They used the Sieverts' method for nitrogen solubility study, which may be the reason for the larger predicted values of the model.[22–24]

Similar to the present study, Kowanda and Speidel[27] used the sampling method to study the solubility of nitrogen in molten Ni-Cr system under high nitrogen pressures. Although the relationship between nitrogen solubility and nitrogen pressure was found to deviate from Sieverts' law, the interaction of nitrogen on itself was not initially considered. Instead, by regression analysis of nitrogen solubility data at each nitrogen pressure, e_N^{Cr} and r_N^{Cr} corresponding to each nitrogen pressure were obtained. In the subsequent study, Kowanda and Speidel[29] discovered and obtained the interaction of nitrogen on itself, and subsequently obtained the interaction parameters of chromium on nitrogen to predict the nitrogen solubility of molten Ni-Cr system at various nitrogen pressures (Table I). The interaction of nitrogen on itself is larger than the present study, and the interaction of chromium on nitrogen is smaller than the present study. As shown in Figure 7, their valued of model prediction mostly agree with the measurements in the present study, except that the predicted values for the molten Ni-35Cr system are relatively small and become more significant with increasing nitrogen pressure.[29]

Figure 8 shows the variation of the nitrogen solubility with the temperature in molten Ni-Mo system at 0.1 MPa nitrogen pressure. For molten Ni-Mo system, the solubility of nitrogen increased with increasing temperature and molybdenum content.

For the molten Ni-Mo binary system, the logarithm of the nitrogen activity coefficient is expressed as

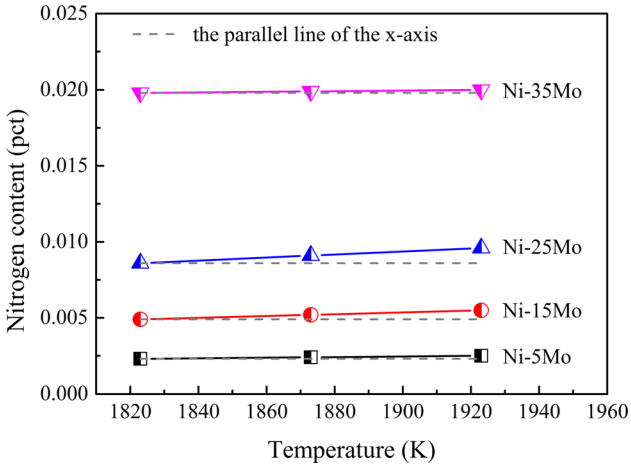

Fig. 8—Variation of the nitrogen solubility with the temperature in molten Ni-Mo system.

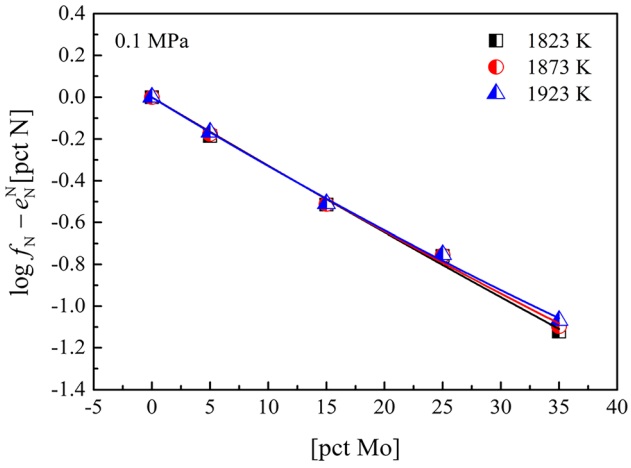

Fig. 9—Variation of the $\log f_N - e_N^N$[pct N] in molten Ni-Mo system with the molybdenum content at 0.1 MPa nitrogen pressure and various temperatures.

$$\log f_N = e_N^N[\text{pct N}] + e_N^{Mo}[\text{pct Mo}] + r_N^{Mo}[\text{pct Mo}]^2 . \quad [22]$$

The relationship between the logarithm of the nitrogen activity coefficient and the molybdenum content is expressed as

$$\log f_N - e_N^N[\text{pct N}] = e_N^{Mo}[\text{pct Mo}] + r_N^{Mo}[\text{pct Mo}]^2 . \quad [23]$$

Figure 9 shows the variation of the $\log f_N - e_N^N$[pct N] in molten Ni-Mo system with the molybdenum content at 0.1 MPa nitrogen pressure and various temperatures. It indicates that the $\log f_N - e_N^N$[pct N] was not linearly related to molybdenum content, which proved the presence of the second-order interaction parameter. Therefore, the relationship between $\log f_N - e_N^N$[pct N] and molybdenum content at each temperature needs to be represented by e_N^{Mo} and r_N^{Mo}.

e_N^{Mo} and r_N^{Mo} at various temperatures are expressed as follows:

$$e_{N,1823K}^{Mo} = -0.0332,\ r_{N,1823K}^{Mo} = 1.10 \times 10^{-4} \quad [24]$$

$$e_{N,1873K}^{Mo} = -0.0336,\ r_{N,1873K}^{Mo} = 1.40 \times 10^{-4} \quad [25]$$

$$e_{N,1923K}^{Mo} = -0.0340,\ r_{N,1923K}^{Mo} = 1.68 \times 10^{-4} \quad [26]$$

Therefore, the temperature functions of e_N^{Mo} and r_N^{Mo} can be obtained, respectively:

$$e_N^{Mo} = -0.0491 + 29.09/T \quad [27]$$

$$r_N^{Mo} = 0.00130 - 2.302/T \quad [28]$$

Figure 10 shows the good agreement between the measured nitrogen solubility and the predicted values of the present study, and the comparison of the measurements for the Ni-Mo system with the predictions of Kowanda and Speidel's model at various nitrogen pressures[29] Kowanda and Speidel[29] studied the nitrogen solubility of molten Ni-Mo system at 1823 K and nitrogen pressure up to 4.0 MPa, and obtained $e_{N,1823K}^{Mo} = -0.0560$ and $r_{N,1823K}^{Mo} = 5.00 \times 10^{-4}$. Considering the interaction of each element on nitrogen, e_N^{Mo} obtained by Kowanda and Speidel[29] was much smaller than that measured in the present study, while e_N^N was relatively larger. It can be seen that the model established by Kowanda and Speidel[29] can also well predict the nitrogen solubility in the present study, but there was a certain deviation for the molten Ni-25Mo system.

C. *Interaction Parameters in Molten Ni-Cr-Mo System*

Figure 11 shows the variation of the nitrogen solubility with the temperature in molten Ni-Cr-Mo system at 0.1 MPa nitrogen pressure. The nitrogen solubility decreased with temperature and increased with chromium and molybdenum contents. According to Eq. [6], for the molten Ni-Cr-Mo system, $r_N^{Cr,Mo}$ can be expressed as

$$\begin{aligned}\log f_N &- e_N^N[\text{pct N}] - e_N^{Cr}[\text{pct Cr}] \\ &- r_N^{Cr}[\text{pct Cr}]^2 - e_N^{Mo}[\text{pct Mo}] - r_N^{Mo}[\text{pct Mo}]^2 \\ &= r_N^{Cr,Mo}[\text{pct Cr}][\text{pct Mo}] \end{aligned} \quad [29]$$

Figure 12 shows the variation of the left-hand side of Eq. [29] with the [pct Cr][pct Mo] at 0.1 MPa nitrogen pressure and various temperatures. The left-hand side of Eq. [29] had a linear relationship with [pct Cr][pct Mo], and $r_N^{Cr,Mo}$ equaled the slope value of the straight line. The temperature function of $r_N^{Cr,Mo}$ can be determined as

$$r_N^{Cr,Mo} = 0.00129 - 1.609/T \quad [30]$$

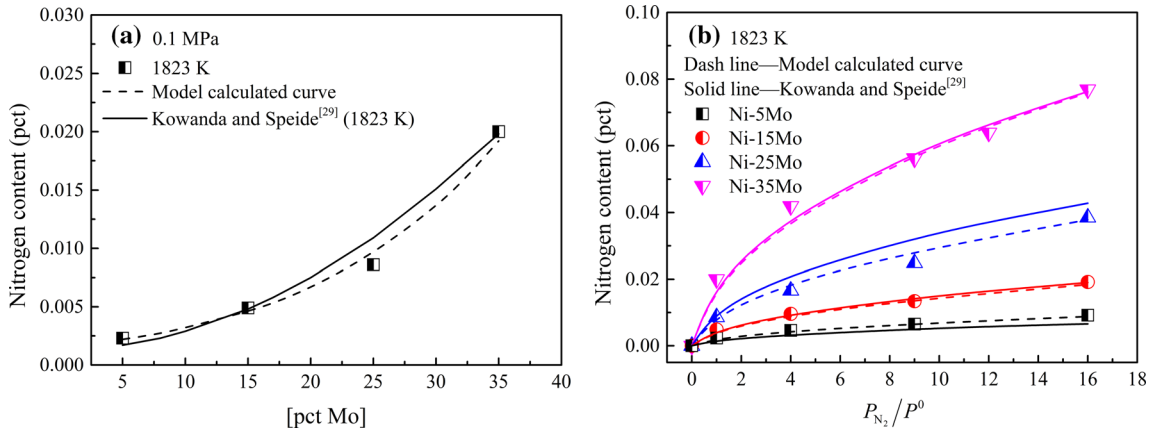

Fig. 10—(*a*) Variation of the nitrogen solubility in molten Ni-Mo system with the molybdenum content at 0.1 MPa nitrogen pressure and various temperatures; (*b*) variation of the nitrogen solubility in molten Ni-Mo system with the nitrogen pressure at 1823 K.

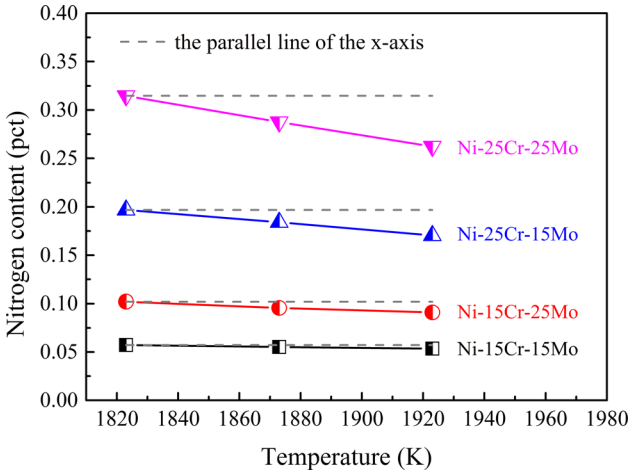

Fig. 11—Variation of the nitrogen solubility with the temperature in molten Ni-Cr-Mo system.

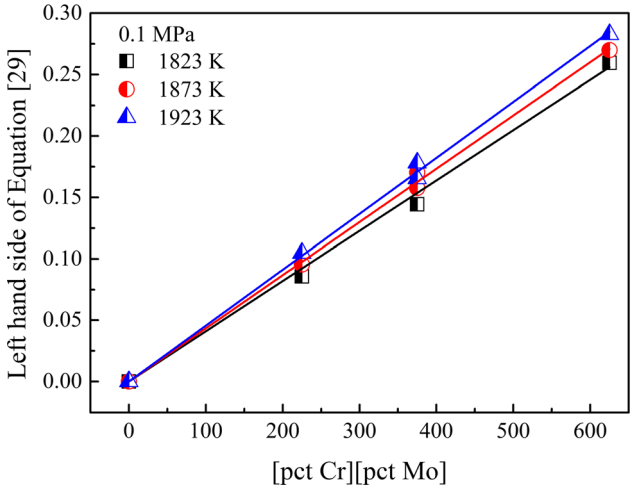

Fig. 12—Variation of the left-hand side of Eq. [29] with the [pct Cr][pct Mo] at 0.1 MPa nitrogen pressure and various temperatures.

Figure 13(a) shows the comparison between the measured values of nitrogen solubility in molten Ni-Cr-Mo system and the predicted values with or without $r_N^{Cr,Mo}$. The presence of $r_N^{Cr,Mo}$ makes the predictions of the model agree well with the measured values. With the increase of chromium and molybdenum contents, the $r_N^{Cr,Mo}$ has a greater impact on the prediction accuracy. The presence of $r_N^{Cr,Mo}$ is necessary to accurately predict nitrogen solubility in molten Ni-Cr-Mo system with high chromium and molybdenum contents.[19,20,31,32] As shown in Figure 13(b), even if the nitrogen pressure is as high as 1.6 MPa, the model of Ni-Cr-Mo alloy system with $r_N^{Cr,Mo}$ can still accurately predict the nitrogen solubility.

D. *Nitrogen Solubility Model of Molten Ni-Cr-Mo System*

On the basis of the above thermodynamic research, an accurate prediction model of nitrogen solubility in molten Ni-Cr-Mo system with high chromium and molybdenum contents was established, which is suitable for both atmospheric pressure and high nitrogen pressure. The nitrogen solubility model in molten Ni-Cr-Mo system is

$$\begin{aligned}\log[\text{pct N}] &= \frac{1}{2}\log\left(P_{N_2}/P^0\right) + \log K_N - \log f_N \\ &= \frac{1}{2}\log(P_{N_2}/P^0) - 1905.66/T - 1.779 \\ &\quad - ((0.8234 - 1309.64/T) \times [\text{pct N}] \\ &\quad + (0.0055 - 171.85/T) \times [\text{pct Cr}] \\ &\quad + (-0.00050 + 2.102/T) \times [\text{pct Cr}]^2 \\ &\quad + (-0.0491 + 29.09/T) \times [\text{pct Mo}] \\ &\quad + (0.00130 - 2.302/T) \times [\text{pct Mo}]^2 \\ &\quad + (0.00129 - 1.609/T) \times [\text{pct Cr}][\text{pct Mo}])\end{aligned} \quad [31]$$

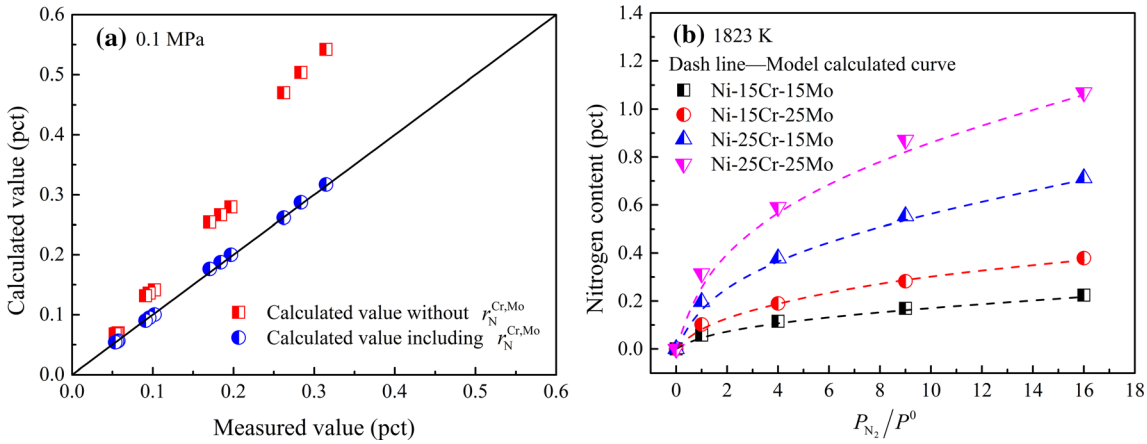

Fig. 13—(*a*) Comparison between the measured values of nitrogen solubility in molten Ni-Cr-Mo system and the predicted values with or without $r_N^{Cr,Mo}$; (*b*) variation of the nitrogen solubility in molten Ni-Cr-Mo system with the nitrogen pressure at 1823 K.

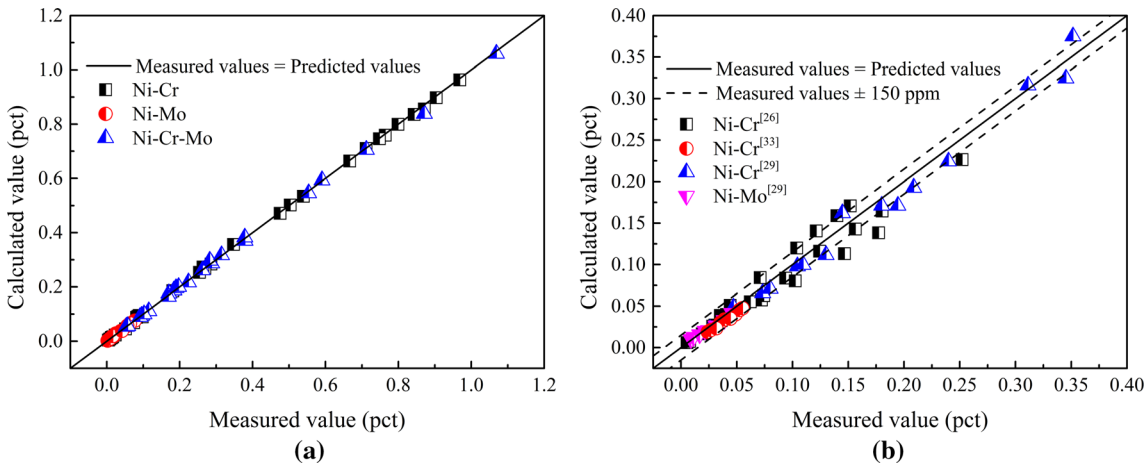

Fig. 14—Comparison between the measured values and the predicted values: (*a*) the data measured in the present study; (*b*) the data measured in the literature studies.

The comparison between the measured values and the predicted values is shown in Figure 14. Figure 14(a) shows that the model calculations are very consistent with the nitrogen solubility data measured in the present work. As shown in Figure 14(b), the model predictions for molten Ni-Cr system are somewhat different from Herrera-Trejo and Ablitzer's experimental values of nitrogen solubility,[26] and most of them are slightly smaller than the experimental values. Abdulrahman and Hendry[33] conducted the nitrogen solubility study in molten Ni-Cr system under 0.1 MPa nitrogen pressure. It can be found that their measured values are slightly larger than the predicted values of the model in the present study. As described in Section II on the study of the interaction parameters in molten Ni-Cr system, the reason for this phenomenon may be due to the Sieverts' method. The measured data obtained by Kowanda and Speidel[29] for the molten Ni-Cr system at nitrogen pressure up to 6.0 MPa agree well with nitrogen solubility predictions of the present model. Meanwhile, they also measured the nitrogen solubility of molten Ni-Mo system at 1823 K and nitrogen pressure up to 4.0 MPa. The model predictions in the present study still agree well with the measured nitrogen solubility for Ni-Mo system (Mo content: 0 to 40 wt pct). From the above comparison, the model established in present study has wide validity in a wide range of nitrogen pressure and alloy composition.

IV. CONCLUSIONS

The solubility of nitrogen in molten Ni, Ni-Cr, Ni-Mo, and Ni-Cr-Mo systems was investigated by sampling method at 1823 to 1923 K and nitrogen pressures up to 1.6 MPa. The main findings can be summarized as follows:

1. The interaction parameter of nitrogen on itself was measured as $e_N^N = 0.8234 - 1309.64/T$ to describe the deviation of nitrogen solubility from Sieverts' law.
2. For molten Ni-Cr and Ni-Mo systems with chromium or molybdenum content in the range of 5.0 to 35.0 wt pct, the interaction parameters of chromium and molybdenum on nitrogen were determined as

follows: $e_N^{Cr} = 0.0055 - 171.85/T$, $r_N^{Cr} = -0.00050 + 2.102/T$, $e_N^{Mo} = -0.0491 + 29.09/T$, $r_N^{Mo} = 0.00130 - 2.302/T$.

3. For molten Ni-Cr-Mo system, the second-order cross-interaction parameter of chromium with molybdenum on nitrogen was determined as $r_N^{Cr,Mo} = 0.00129 - 1.609/T$.
4. An accurate prediction model of nitrogen solubility in molten Ni-Cr-Mo system that is effective at normal pressure and high nitrogen pressure was established, and the model calculations were very consistent with the measured nitrogen solubility.

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CONFLICT OF INTEREST

On behalf of all authors, the corresponding author states that there is no conflict of interest.

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