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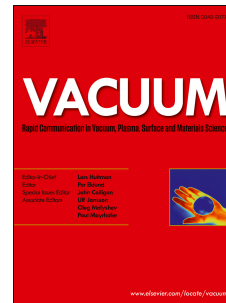
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Solubility Limit of Nitrogen in Fe-Cr-C-N Alloy Melt under Reduced N₂ Partial Pressure

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Abstract:

The N solubility in Fe-Cr-C-N melt was measured by the addition of Cr and C in liquid iron using the metal/gas equilibration technique at 1600 °C under a reduced N₂ partial pressure. Cr increased the N solubility by the attraction force between Cr and N, while C showed the opposite effect on N in liquid iron. The present experimental results were thermodynamically analyzed by Wagner's interaction parameter formalism. The existence of the simultaneous effect of Cr and C on the N solubility was confirmed, which was determined as the second-order cross-product parameter of Cr and C on N in liquid iron. This parameter set in the multicomponent Fe-Cr-C-N system can be used to predict the solubility limit of N in the degassing process of stainless steelmaking.

Keywords: ferritic stainless steel, N solubility, Fe-Cr-C-N system, Wagner's interaction parameter formalism

Degassing technology is crucial for the production of low C and N ferritic stainless steel having high formability as well as excellent corrosion resistance. The C content dissolved during an Electrical Arc Furnace (EAF) melting can be preferentially removed from Fe-Cr melts by Argon Oxygen Decarburization (AOD) process [1]. The blowing of Ar with O₂ gas enhances the decarburization reaction by diluting the CO partial pressure on the melt surface. Further decarburization can be achieved under vacuum because Vacuum Oxygen Decarburization (VOD) process can reach even lower total pressure than the CO partial pressure obtained in the AOD process [2]. The vacuum treatment during the VOD process additionally results in the removal of N from the stainless steel melt when the total pressure in the system is lower than the equilibrium N₂ partial pressure exerted by the N content in the melt [3]. The N solubility in liquid iron depends on N₂ partial pressure at the melt surface, melt composition, and temperature. Therefore, to accurately predict the refining limit of N during the vacuum decarburization processes of stainless steelmaking, it is critical to understand the thermodynamic behavior of N in Fe-Cr-C melts under reduced pressures.

In the authors' recent studies, the effects of Cr and C on N in liquid iron have been determined by measuring the N solubility in Fe-Cr-N [4] and Fe-C-N melts [5], respectively, at the various N₂ partial pressures and temperatures. However, the studies on the N behavior in Fe-Cr-C-N melt are very scarce until now [6]. In the Fe-Cr-C-N system, Cr has different affinities with C and N in liquid iron, and the interaction between C and N exhibits a strong repulsive force in liquid iron [5]. The experimental results were thermodynamically analyzed by Wagner's interaction parameter formalism [7]. In the multicomponent systems containing C [8, 9] in liquid iron, it has been found that the simultaneous effect of C and other alloying elements on N was significant, and it can affect the N solubility. In order to clarify such complex relations among Cr, C, and N in liquid iron, in the present study, the N solubility was measured with increasing Cr and C in liquid iron under the reduced N₂ partial pressure.

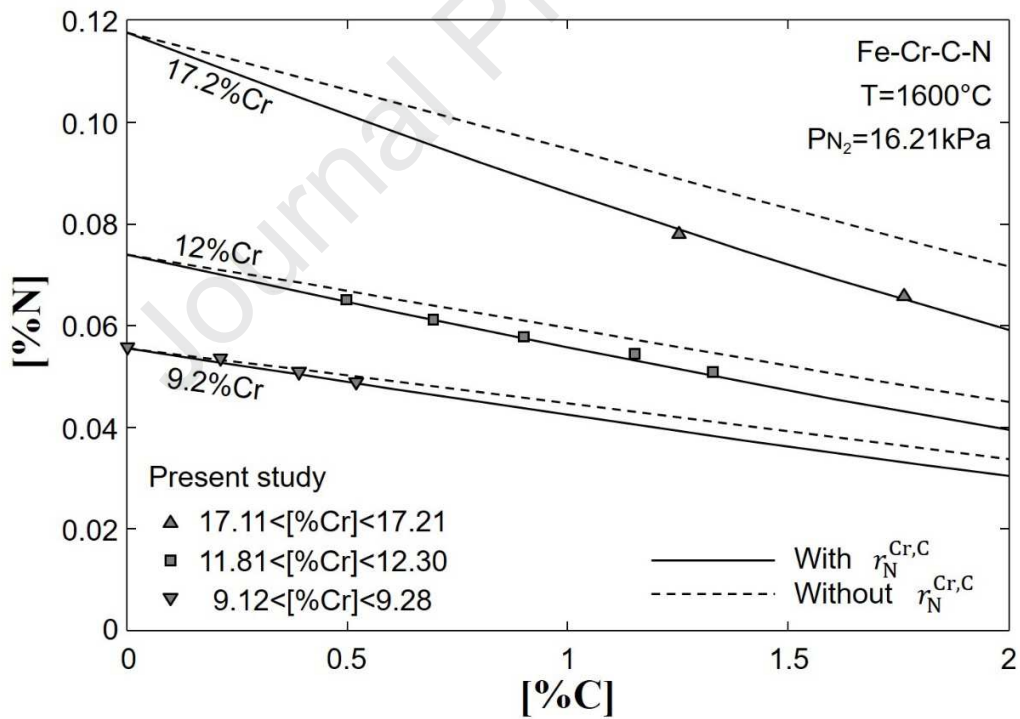
The N solubility in the Fe-Cr-C-N melt was measured by the sampling method under the reduced N₂ partial pressure of 16.21 kPa at 1600 °C. Five hundred grams of electrolytic Fe (99.99 %purity) and Cr shot (99.95 %purity) were melted in an Al₂O₃ crucible (outer diameter (OD): 56 mm, inner diameter (ID): 50 mm, height (H): 96 mm) using a high-frequency induction

furnace (15 kW/30 kHz). The melt temperature was directly measured by immersing the R-type (Pt/Pt-13 mass% Rh) thermocouple sheathed with the closed one end alumina tube (OD 6 mm). After melting, the initial O content in the Fe-Cr melt was forcibly controlled below 40 mass ppm by blowing Ar-10 vol%H₂ gas onto the melt surface at a high flow rate of 2 L/min for 4 hours. Then, N₂ gas was mixed with the Ar-10 vol%H₂ to have a reduced N₂ partial pressure. The flow rate of the gas mixture was adjusted to 1 L/min by a mass flow controller. Then, the variation of the N content in the melt was measured by the addition of the Cr shots and graphite powder (99.9995 %purity). The addition of Cr and graphite was repeated up to the desired composition of 18 wt%Cr and 2 %C relative to the total weight of melt. After each addition, the melt was equilibrated with the gas mixture for 1 hour and sampled using a 4 mm ID quartz tube connected to a syringe (10 mL) and quenched in ice water. The extracted pin samples were cut and polished to remove the excess graphite or oxide layer formed during solidification. The equilibrium N content was attained within 1 hour, which was confirmed by the *in-situ* analysis using the nitrogen analyzer (LECO TC-600) with an accuracy of ± 2 mass ppm. The C content was analyzed by the C/S analyzer (Eltra CS-800) within an error range of 1 %. The Cr content was analyzed by the Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES, SPECTRO ARCOS). 0.2 g of the metallic samples was dissolved in hydrochloric acid (1:1 HCL) and transferred to the measuring flask (100 mL). The standard solution containing the same amount of Fe (2000 mass ppm) was used to avoid any ionic interference effect during the analysis. The analytical limit of Cr in the metal sample was 5 ± 1 mass ppm.

The experimental results of the N solubility in Fe-Cr-C-N melt were summarized in Table 1. The variation of measured N solubility result by the addition of graphite and Cr under the reduced N₂ partial pressure of 16.21 kPa at 1600 °C was also plotted as shown in Fig. 1. The graphite was first added up to 0.52 wt% in Fe-9.23 wt%Cr melt, and then the Cr content was increased to 12.13 wt% by the addition of Cr shots. Such sequential additions of the C and Cr sources were repeated up to 17.11 wt%Cr and 1.74 wt%C as shown in the figure. The N solubility linearly decreased with the addition of graphite, while the Cr addition significantly increased the N solubility.

Table 1. Experimental results of N solubility in Fe-Cr-C melts.

System	Temp. (°C)	p_{N_2} (kPa)	[%Cr]	[%C]	[%N]	[%O]
Fe-Cr-C-N	1600	16.21	9.23	0	0.0556	0.0042
			9.19	0.21	0.0534	0.0026
			9.28	0.39	0.0508	0.0021
			9.12	0.52	0.0487	0.0019
			12.13	0.50	0.0651	0.0014
			12.06	0.70	0.0612	0.0015
			12.29	0.90	0.0577	0.0024
			12.30	1.15	0.0543	0.0027
			11.81	1.33	0.0507	0.0017
			17.21	1.25	0.0781	0.0019
			17.11	1.74	0.0659	0.0048

Fig. 1. Comparison between the present experimental data and calculated N solubility in Fe-Cr-C-N melt under 16.21 kPa at 1600 °C with/without considering the $r_N^{Cr,C}$ value.

The N solubility data measured in the present study can be thermodynamically analyzed based on the following N dissolution reaction:



$$K_{\text{N}} = \frac{h_{\text{N}}}{P_{\text{N}_2}^{1/2}} = \frac{f_{\text{N}}[\% \text{N}]}{P_{\text{N}_2}^{1/2}} \quad (2)$$

where K_{N} is the equilibrium constant of the reaction, and P_{N_2} is the controlled N_2 partial pressure in atm unit. h_{N} , f_{N} , and $[\% \text{N}]$ are the Henrian activity, Henrian activity coefficient, and the equilibrium concentration of N in wt%, respectively. The value of $\log K_{\text{N}}$ ($= -188/T - 1.25$) determined by Pehlke and Elliott [10] was adopted in the present study.

In the multicomponent Fe-Cr-C-N system, the f_{N} can be expressed as the following relations using Wagner's formalism [7]:

$$\begin{aligned} \log f_{\text{N}} &= \log K_{\text{N}} - \log[\% \text{N}] + \frac{1}{2} \log P_{\text{N}_2} \\ &= e_{\text{N}}^{\text{Cr}}[\% \text{Cr}] + r_{\text{N}}^{\text{Cr}}[\% \text{Cr}]^2 + e_{\text{N}}^{\text{C}}[\% \text{C}] + r_{\text{N}}^{\text{C}}[\% \text{C}]^2 + r_{\text{N}}^{\text{Cr,C}}[\% \text{Cr}][\% \text{C}] \end{aligned} \quad (3)$$

where e_{N}^i and r_{N}^i are the first- and second-order interaction parameters of i on N in liquid iron in mass%. In the Fe-N system, it is well known that the N solubility is directly proportional to the square root of N_2 partial pressure, $P_{\text{N}_2}^{1/2}$ as reported by Sievert *et al.* [11]. Such relation has been described as "Sieverts' law". When the dissolution of a gaseous element, i in liquid alloys obeys the Sieverts' law, the first- and second-order self-interaction parameters, e_i^i and r_i^i can be neglected. Therefore, in the present experimental condition, the self-interaction between N atoms in liquid iron was considered negligibly small, and the e_{N}^{N} and r_{N}^{N} values were assumed as zero.

On the other hand, Cr and C have significant interaction with N in liquid iron. As shown in Fig. 2, Cr decreases the $\log f_N$ value (attraction), while C increases it (repulsion) in liquid iron. In the authors' recent study [4], the first- and second-order interaction parameters of Cr on N, e_N^{Cr} and r_N^{Cr} , were determined by measuring the N solubility in liquid Fe-Cr alloys over the wide Cr concentration range up to 30 wt% under various N_2 partial pressures from 1.52 to 98.29 kPa. The temperature dependence was observed for both e_N^{Cr} and r_N^{Cr} values as $-147.8/T+0.019$ and $-2.58/T+0.0021$, respectively, at 1600-1700 °C. In the Fe-C-N system [5], the interaction parameters of C on N, e_N^C and r_N^C , were determined as 0.08 and 0.014, respectively, from the dilute C concentration to the graphite saturated condition. The e_N^C and r_N^C values were not dependent on the temperature at 1300-1600 °C [12]. The interaction parameter values in Fe-Cr-N and Fe-C-N systems determined over the wide range of melt composition, temperatures, and N_2 partial pressures [4,5] were adopted in the present study.

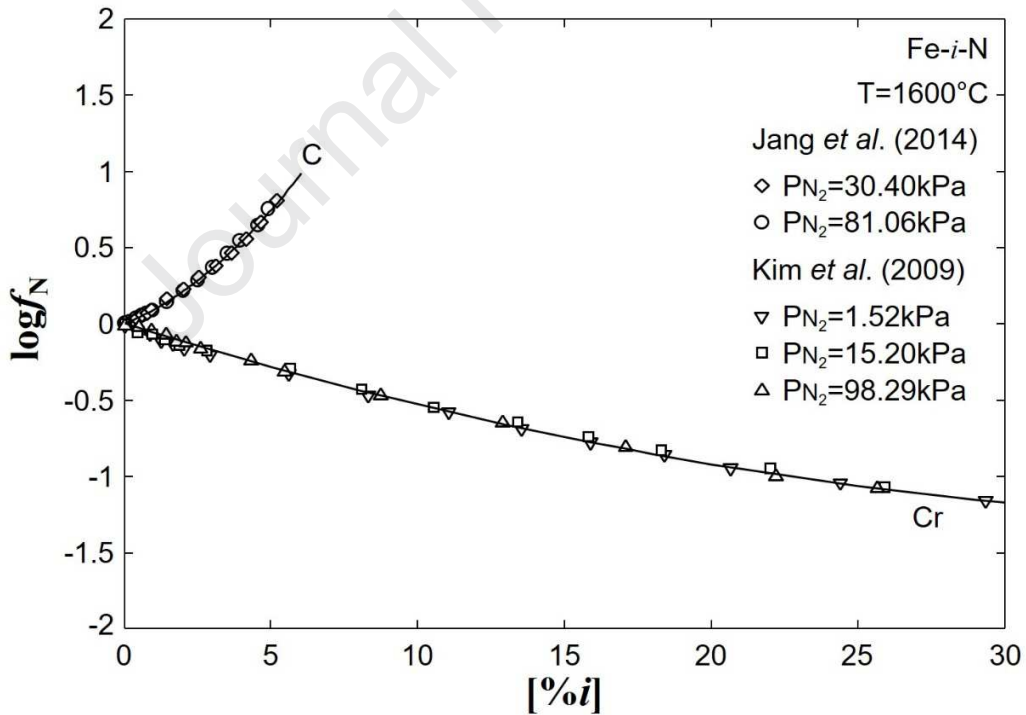


Fig. 2. Effects of Cr and C on the activity coefficient of N in liquid iron at 1600 °C. [4,5]

In Figure 1, the N solubility data in Fe-Cr-C-N melt measured in the present study are shown together with the calculated solubility lines using Eqs. (1) through (3). The dashed solubility lines were calculated without considering the simultaneous effect of Cr and C on N in liquid iron, $r_N^{Cr,C}$, and they show higher values compared to the measured N solubility. The difference between the measured and calculated N solubility values becomes more significant at higher Cr and C concentrations. This result indicates that the cross-product effect of Cr and C on N in liquid iron is very important to determine in predicting the N solubility in the Fe-Cr-C-N system.

As can be seen in Eq. (3), the $r_N^{Cr,C}$ value is the coefficient of the cross-product of Cr and C, [%Cr][%C]. Hence, rearranging Eq. (3), the second-order cross-product parameter can be determined by the following equation:

$$\log f_N - (e_N^{Cr}[\%Cr] + r_N^{Cr}[\%Cr]^2 + e_N^C[\%C] + r_N^C[\%C]^2) = r_N^{Cr,C}[\%Cr][\%C] \quad (4)$$

The left-hand side parameters of Eq. (4) are the known values such as the analyzed Cr and C contents, interaction parameters determined in the Fe-Cr-N and Fe-C-N systems, and calculated $\log f_N$ value from $\log K_N$, P_{N_2} and the N content of the melt. They were plotted against [%Cr][%C], as shown in Fig. 3. The data points show an excellent linear relationship. Thus the $r_N^{Cr,C}$ value can be determined from the slope of the data by the linear regression analysis. The $r_N^{Cr,C}$ value was determined as 0.0024 at 1600 °C.

Therefore, the N solubility can be calculated by the following relation based on Eq. (3) as functions of melt temperature, composition and N_2 partial pressure at the melt surface for the Fe-Cr-C-N system:

$$\log[\%N] = \frac{-188}{T} - 1.25 + \frac{1}{2} \log P_{N_2} - \left(\frac{-147.8}{T} + 0.019 \right) [\%Cr] - \left(\frac{-2.58}{T} + 0.0021 \right) [\%Cr]^2 - 0.08[\%C] - 0.014[\%C]^2 - 0.0024[\%Cr][\%C] \quad (5)$$

As can be seen in Fig. 1, the experimental results of the N solubility were reproduced very well by considering the $r_N^{Cr,C}$ value (solid lines).

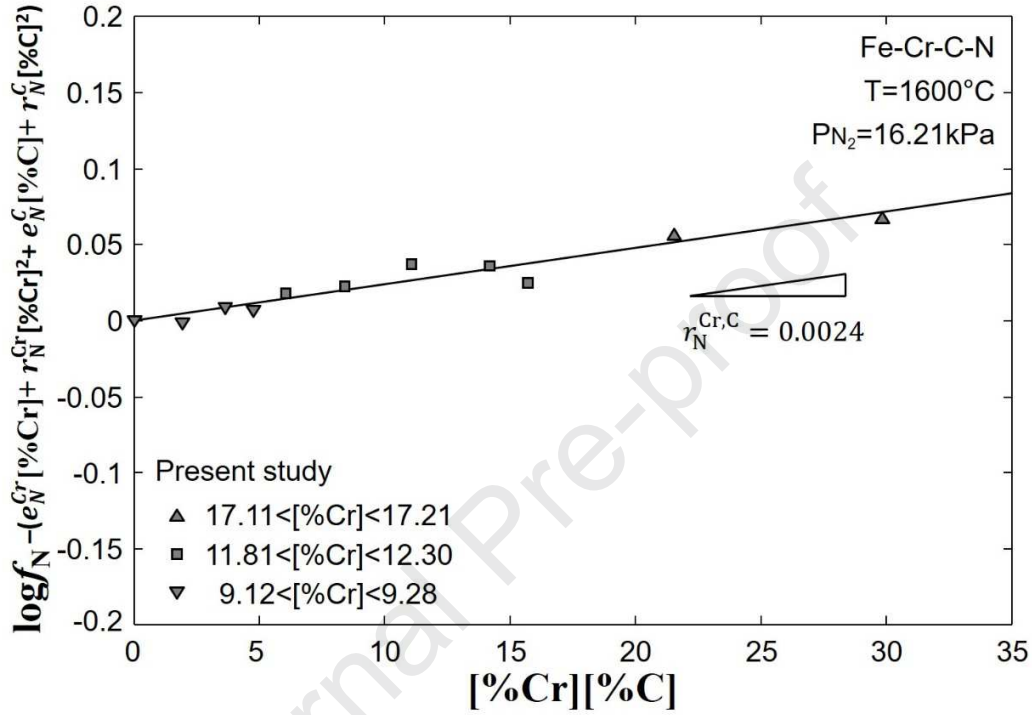


Fig. 3. Relation of Eq. (4) to determine the $r_N^{Cr,C}$ value in Fe-Cr-C-N melt.

In order to check the validity of interaction parameters used and determined in the present study, Figure 4 compares the predicted N solubility with available experimental data in the literature and the present experimental results for Fe-Cr-C-N melt. As sub-systems for Fe-Cr-Ni-Mo-Mn-C duplex stainless steels, Anson *et al.* [6] measured the N solubility in Fe-20 wt%Cr-N and Fe-20 wt%Cr-C-N melts under 101.325 kPa N_2 partial pressure at 1550-1650 °C. Their N solubility data and the present results measured under the reduced P_{N_2} of 16.21 kPa show an excellent correlation with the predicted N solubility up to 0.3 wt%N. However, at higher N solubility, Anson *et al.*'s data show lower values than the predicted ones. The author's recent study [4] indicated that a loss of soluble N content could be expected during the sampling and quenching process by the supersaturation of N and the formation of N_2 bubbles in the metal sample.

Therefore, the N equilibration under reduced P_{N_2} with the rapid quenching was effective in keeping the soluble N content in the melt. Kim *et al.* [4] and Ishii *et al.* [13] have measured the N solubility in the Fe-Cr-N system by the rapid quenching technique under the wide range of N_2 partial pressures at 1.52-98.29 and 4.17-99.40 kPa, respectively. Their results show an excellent agreement with the predicted solubility as shown in Fig. 4. Anson *et al.* [6] also determined the interaction parameters of various alloying elements on nitrogen in Fe-20 wt%Cr-*i*-N melt from their experimental data using the same interaction parameter formalism for the prediction of N solubility in duplex stainless steels. Therefore, their parameters can be used only for Fe-20 wt%Cr melt at fixed Cr content.

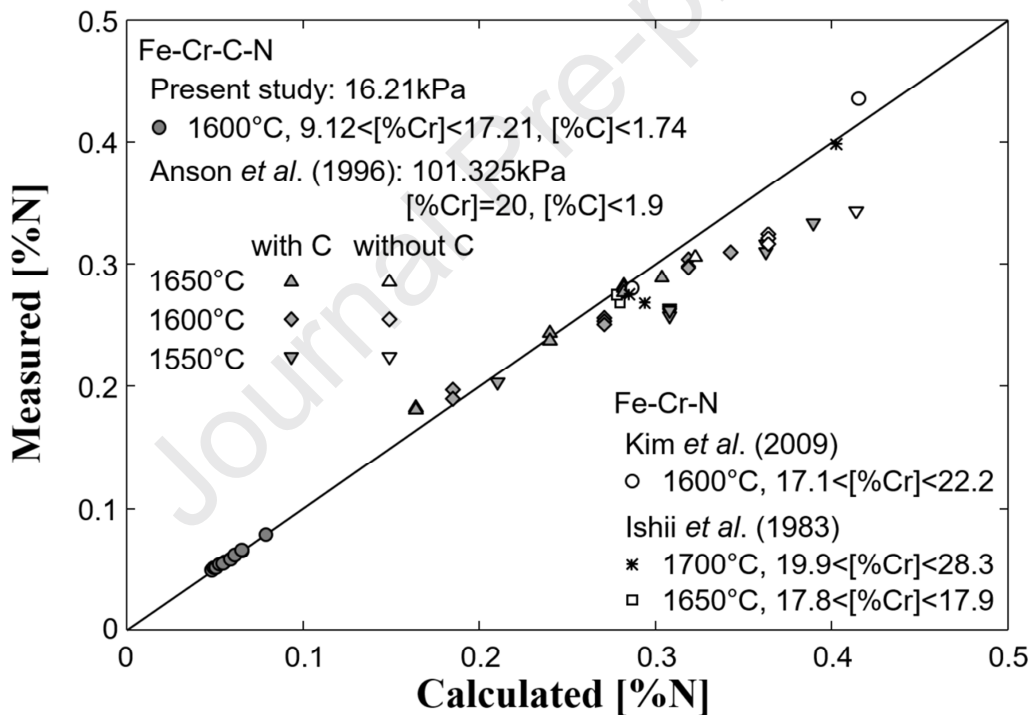


Fig. 4. Correlation between calculated and measured N solubility in Fe-Cr-C-N melt [4,6,13].

In the present study, the cross-product effect of Cr and C on N in liquid iron was determined by measuring the N solubility in Fe-Cr-C-N melt under the reduced N_2 partial pressure at 1600 °C. The simultaneous effect of Cr and C on N identified in the present study can be used to predict

the solubility limit of N in liquid stainless steel over the wide range of Cr and C content under various N₂ partial pressures from atmospheric to low vacuum pressures. The activity coefficient of N in Fe-Cr-C-N melt can be expressed as:

$$\log f_{\text{N}} = \left(\frac{-147.8}{T} + 0.019 \right) [\% \text{Cr}] + \left(\frac{-2.58}{T} + 0.0021 \right) [\% \text{Cr}]^2 + 0.08 [\% \text{C}] + 0.014 [\% \text{C}]^2 + 0.0024 [\% \text{Cr}] [\% \text{C}]$$

$$(\text{Cr} \leq 28.3 \%, \text{C} \leq 1.74 \%, P_{\text{N}_2} \leq 101.325 \text{ kPa})$$

Acknowledgements

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Figure captions:

Fig. 1. Comparison between the present experimental data and calculated N solubility in Fe-Cr-C-N melt under 16.21 kPa at 1600 °C with/without considering the $\gamma_{\text{N}}^{\text{Cr,C}}$ value.

Fig. 2. Effects of Cr and C on the activity coefficient of N in liquid iron at 1600 °C. [4,5]

Fig. 3. Relation of Eq. (4) to determine the $\gamma_{\text{N}}^{\text{Cr,C}}$ value in Fe-Cr-C-N melt.

Fig. 4. Correlation between calculated and measured N solubility in Fe-Cr-C-N melt [4,6,13].

Table captions:

Table 1. Experimental results of N solubility in Fe-Cr-C melts.

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1. Cr exhibits a strong attraction with N in liquid iron, while C shows the opposite tendency.
2. The simultaneous effect of Cr and C on the N solubility in Fe-Cr-C-N melt was found.
3. The second-order cross-product parameter of Cr and C on N in liquid iron was determined using Wagner's formalism.

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Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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