Effect of Chromium on Nitrogen Solubility in Liquid Fe–Cr Alloys Containing 30 mass% Cr

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The nitrogen solubility in liquid Fe–Cr alloys has been measured by the gas–liquid metal equilibration technique in the temperature range from 1873 to 1973 K. The nitrogen dissolution follows the Sieverts' law for liquid Fe–Cr alloys containing chromium up to 30 mass%. Chromium increased the nitrogen solubility linearly at Cr content less than 3 mass%, and the second-order effect of Cr on nitrogen solubility was apparent at higher Cr content. Using Wagner's formalism, the first- and second-order interaction parameters between chromium and nitrogen were determined from the equilibrium relation between chromium and nitrogen contents in liquid Fe–Cr–N alloys as a function of temperature:

$$\log f_N^{\text{Cr}} = (-147.8/T + 0.019) \cdot [\% \text{Cr}] + (-2.58/T + 0.0021) \cdot [\% \text{Cr}]^2 \quad (0 < \text{mass}\% \text{Cr} < 30)$$

KEY WORDS: nitrogen solubility; Fe–Cr alloy; nitrogen; chromium; interaction parameters.

1. Introduction

Nitrogen control in high chromium stainless steels is of great importance not only to produce low nitrogen stainless steels but also to control the precipitation of TiN inclusions during casting which can help the formation of equi-axed cast structure.^{1–3)} For an example, the nitrogen control range for the Ti-stabilized high chromium ferritic stainless steel is 60–80 mass ppm, and there will be a trend towards more stringent nitrogen specifications in those steel grades to control product quality. In order to control the nitrogen content in ferritic stainless steels of various chromium contents, it is important to have accurate thermodynamic data of Fe–Cr–N system at steelmaking temperature.

The nitrogen solubility in Fe–Cr alloy melts has been measured by the Sieverts method^{4–8)} and the sampling method^{9,10)} for a wide range of chromium content. It is well known that the nitrogen solubility is significantly increased by the addition of chromium in liquid iron. However, there is still uncertainty in the first- and the second-order effect of chromium on the activity coefficient of nitrogen due to the limited experimental data in a low chromium range less than 10 mass% Cr in liquid iron. Also, the temperature effect on the chromium effect on nitrogen in Fe–Cr–N melts is not well known.

In the present study, the effect of chromium on nitrogen solubility in liquid Fe–Cr alloys was determined in the temperature range of 1873 to 1973 K by the gas–liquid metal equilibration technique (sampling method) utilizing a high frequency induction furnace. The effect of nitrogen partial pressures on the nitrogen solubility was tested to see if the Sieverts' law is obeyed in liquid Fe–Cr alloys up to

30 mass% Cr content. Using Wagner's formalism,¹¹⁾ the experimental results were thermodynamically analyzed to determine the first- and the second-order interaction parameters between chromium and nitrogen in liquid iron as a function of temperature.

2. Experimental Procedures

Five hundred grams of high purity electrolytic iron contained in an Al₂O₃ crucible (OD: 56 mm, ID: 50 mm, H: 96 mm) was melted using a 15 kW/30 kHz high frequency induction furnace as shown in Fig. 1. The melt temperature was directly measured by the thermocouple immersed in the melt, and the temperature was accurately controlled

Fig. 1. A schematic diagram of experimental system.

within 2 K during experiment by the PID controller of the induction furnace. Descriptions of experimental apparatus and procedures are available elsewhere.^{12,13)}

After controlling the melt temperature to a desired value, Ar–10% H_2 gas was blown onto the melt for 2 h to deoxidize the iron melt. The oxygen content in the melt decreased to a value less than 20 mass ppm by this method. Then the gas was switched to a mixture of desired nitrogen partial pressure ($P_{N_2}=0.015\text{--}0.97\text{ atm}$) by mixing Ar–10% H_2 and N_2 gases or using a N_2 –3% H_2 gas. The total flow rate of gas mixture was controlled by a mass flow controller in the range of 1 000 to 2000 mL/min depending on the nitrogen partial pressures in the gas.

Strong agitation of the melt by an induction stirring resulted in a fast attainment of equilibrium nitrogen solubility in liquid iron within an hour at a given nitrogen partial pressure. After confirming the equilibrium nitrogen solubility in pure liquid iron by the sampling and analysis, pellets of chromium (99.9 mass% purity) were added into liquid iron through an 18 mm ID quartz tube. After each chromium addition, a new nitrogen solubility equilibrium was attained within 1 h. This was confirmed by samplings and *in situ* analysis after the chromium addition. Chromium additions and samplings were repeated up to 3 mass% Cr and 30 mass% Cr in liquid iron in separate experiments.

The metal sample of about 10 g was extracted by a 4 mm ID quartz tube connected to a syringe (10 mL), and it was quenched rapidly in water. One of the main concerns in the measurement of equilibrium nitrogen solubility in liquid Fe–Cr alloy by the sampling method was how to retain the dissolved nitrogen in metals during sampling procedure. A separate test was conducted to see if any delay in quenching would result in a substantial error in determining soluble nitrogen contents. The result showed that quenching the metal samples in water within 3 s did not invalidate the results as confirmed in our previous study.¹³⁾

The metal samples were carefully cut for the chemical analysis. The nitrogen and oxygen contents in the metal sample were measured by the inert gas fusion-infrared absorptiometry technique with an accuracy of ± 1 mass ppm. For the analysis of chromium, the metal sample (0.2 g) was dissolved in 20 mL of HCl (1+1) in a glass beaker of 50 mL capacity heated in a water bath for 2 h. Chromium dissolved in the sample solution was then analyzed by the ICP-AES using the appropriate standard solutions containing the similar amount of Fe as in the sample solutions. The accuracy of Cr analysis in metal sample was 5 ± 1 mass ppm.

3. Results and Discussion

The dissolution of nitrogen in liquid iron alloys can be written as

$$\Delta G_1^\circ = 3\,598 + 23.89T \quad \text{J/mol}^{14)}$$

$$K_1 = \frac{f_N[\%N]}{P_{N_2}^{1/2}} \quad \dots\dots\dots(2)$$

Fig. 2. Effect of Cr additions on nitrogen solubility in liquid iron at 1 873 K.

where K_1 is the equilibrium constant for Reaction (1) and, f_N is the activity coefficient of nitrogen in 1 mass% standard state in liquid iron.

Using Wagner's formalism,¹¹⁾ the equilibrium constant of above reaction can be rewritten as the following relation using the interaction parameters:

$$\begin{aligned} \log K_1 &= \log f_N + \log[\%N] - \frac{1}{2} \log P_{N_2} \\ &= e_N^N[\%N] + r_N^N[\%N]^2 + e_N^{Cr}[\%Cr] + r_N^{Cr}[\%Cr]^2 \\ &\quad + \log[\%N] - \frac{1}{2} \log P_{N_2} \dots\dots\dots(3) \end{aligned}$$

where e_N^i and r_N^i are the first- and the second-order interaction parameters of elements on nitrogen in liquid Fe–Cr–N alloy, respectively. As mentioned earlier, the oxygen content was very low in the melt and the effect of oxygen on nitrogen was assumed to be negligible. The first- and the second-order self interaction parameters of N, e_N^N and r_N^N , respectively, are known to be zero at nitrogen content up to 0.045 mass% in liquid iron at 1 879 K.⁵⁾

The activity coefficient of chromium on nitrogen, f_N^{Cr} can be then defined as

$$\begin{aligned} \log f_N^{Cr} &= e_N^{Cr}[\%Cr] + r_N^{Cr}[\%Cr]^2 \\ &= \log K_1 - \log[\%N] + \frac{1}{2} \log P_{N_2} \dots\dots\dots(4) \end{aligned}$$

Figure 2 shows the nitrogen solubility of liquid iron containing chromium up to 3 mass% under nitrogen partial pressures of 0.015, 0.15 and 0.97 atm at 1 873 K. Chromium increased the nitrogen solubility in Fe–Cr melt linearly at all nitrogen partial pressures. Figure 3 shows the values of $\log f_N^{Cr}$ plotted vs. chromium concentration in mass% in liquid iron using the relation expressed by Eq. (4). The data determined at different nitrogen partial pressures show an excellent linear relationship. As shown in the figure, the relation between the $\log f_N^{Cr}$ values and chromium content was not affected by the nitrogen partial pressure. In other words, the Sieverts' law of nitrogen dissolution was obeyed, that is, the values of e_N^N and r_N^N in Eq. (3) can be considered as zero. The first-order interaction parameter, e_N^{Cr} can be determined as -0.06 at 1 873 K by a linear regression analysis of data in Fig. 3.

Fig. 3. Effect of Cr on the activity coefficient of nitrogen in liquid iron at 1873 K.

Fig. 4. Nitrogen solubility in liquid Fe-Cr alloys under various nitrogen partial pressures at 1873 K.

Figure 4 shows the nitrogen solubility of liquid Fe-Cr alloys containing chromium up to 30 mass% under different nitrogen partial pressures at 1873 K. At chromium contents higher than 3 mass% in liquid iron, the effect of chromium on the nitrogen solubility was not linear, and the nitrogen solubility increased more rapidly with higher chromium content. Figure 5 shows the relation of f_N^{Cr} values vs. chromium concentration up to 30 mass% in liquid iron calculated using the same relation of Eq. (4). As shown in the figure, the f_N^{Cr} values determined at different nitrogen partial pressures of 0.015, 0.15 and 0.97 atm show an excellent correlation with chromium content in the melt. The relation was not affected by nitrogen partial pressures or nitrogen content in the melt. Therefore, it can be concluded that the Sieverts' law of nitrogen dissolution is obeyed in liquid Fe-Cr alloys containing chromium up to 30 mass%. The first- and second-order interaction parameters can be simultaneously determined as -0.06 and 0.0007 , respectively, at 1873 K by a regression analysis of data in Fig. 5.

$$\log f_N^{\text{Cr}} = -0.06[\% \text{Cr}] + 0.0007[\% \text{Cr}]^2 \quad \text{at } 1873 \text{ K} \dots (5)$$

Several groups including Humbert and Elliott,⁴⁾ Wada and Pehlke,⁸⁾ Blossey and Pehlke⁷⁾ and Ishii *et al.*^{9,10)} measured the nitrogen solubility in Fe-Cr melt at 1 atm nitrogen pressure using the Sieverts method⁴⁻⁸⁾ and the sampling method.^{9,10)} Table 1 summarizes the interaction parameter values of chromium on nitrogen in Fe-Cr melt reported by various authors. In Fig. 6, the $\log f_N^{\text{Cr}}$ values calculated at

Fig. 5. Relation of $\log f_N^{\text{Cr}}$ vs. [%Cr] in liquid Fe-Cr-N alloy at 1873 K.

1873 K from their experimental data^{4,8,9)} using the same equilibrium constant for the nitrogen dissolution reaction given by Eq. (1) are compared. The solid line shown in the figure is the relation of Eq. (5) determined in the present study. The dotted lines are the relations reported by previous workers.^{4,7-9)}

Humbert and Elliott⁴⁾ measured the nitrogen solubility in Fe-Cr melt using the Sieverts' method under 1 atm nitrogen pressure. They reported only the first-order parameter of e_N^{Cr} as -0.045 at 1873 K from the slope of their data up to 18.8 mass% Cr content as shown in Fig. 6. However, this value could not correlate the f_N^{Cr} values at higher chromium contents. Their data at high chromium content show a better correlation with the solid line obtained in the present study. Later Pehlke and his co-workers⁵⁻⁸⁾ have measured the nitrogen solubility in liquid Fe-Cr and Fe-Cr-Ni alloys in wide ranges of composition and temperature using the same experimental method. Pehlke and Elliott⁵⁾ reported the value of e_N^{Cr} as -0.045 at 1873 K in liquid Fe-Cr alloys containing up to 10 mass% Cr. Wada and Pehlke⁸⁾ reported the values of e_N^{Cr} and r_N^{Cr} as -0.046 and 0.00032 at 1873 K, respectively, from the nitrogen solubility data in liquid Fe-Cr-Ti alloys of only two compositions (10.2 and 30.2 mass% Cr).

Blossey and Pehlke⁷⁾ determined the values of e_N^{Cr} and r_N^{Cr} as -0.052 and 0.00054 at 1873 K, respectively, for Fe-Cr alloys containing up to 21 mass% Cr. Blossey *et al.*⁷⁾ pointed out that the experimental reproducibility was not excellent using the Sieverts' method under 1 atm nitrogen pressure. Humbert and Elliott⁴⁾ also pointed out that there was an inherent error of the Sieverts' method caused by the vaporization and subsequent condensation of metal in the cooler part of the reaction chamber, and the metallic vapor might react with the nitrogen atmosphere to form a stable nitride or the nitrogen may be adsorbed on the metallic deposit.

Ishii and Fuwa⁹⁾ used the sampling method utilizing an induction furnace to determine the nitrogen solubility in liquid Fe-Cr alloys under 1 atm nitrogen pressure in the temperature range from 1853 to 1953 K. They reported the value of e_N^{Cr} as -0.047 in liquid Fe-Cr alloys containing up to 9 mass% Cr. However, the temperature dependency of e_N^{Cr} values was not observed in their work. They measured the temperature of a Fe-Cr alloy melt by an optical pyrometer. The emissivity of infra-red rays from the melt surface

Table 1. Interaction parameters between Cr and N in Fe–Cr–N alloy melt at 1 873 K.

e_N^{Cr}	i_N^{Cr}	Temp. Range(K)	[%Cr] Range	P_{N_2} (atm)	Method	Ref.
-0.06 (-147.8/T+0.019)	0.0007 (-2.58/T+0.0021)	1873-1973	0 ~ 30	0.015 ~ 0.97	Sampling	Present Study
-0.045	0	1873	0 ~ 47.2	1	Sieverts	4)
-0.045	0	1873	0 ~ 10	1	Sieverts	5
-0.047	0.00017	1873	0 ~ 18	1	Sieverts	6
-0.052	0.00054	1873	0 ~ 21	1	Sieverts	7
-0.046 (-164/T+0.0415)	0.00032 (1.675/T-0.0006)	1823-2003	10.2, 30.2	1	Sieverts	8
-0.047	0	1853-1953	0 ~ 9	1	Sampling	9
-0.046 (-148/T+0.033)	0	1823-2023	0 ~ 15	1	Sampling	10
-0.046 (-148/T+0.033)	0.00030 (1.56/T-0.00053)	1923-2053	15 ~ 60	0.04 ~ 1	Sampling	10

Fig. 6. Relations of $\log f_N^{Cr}$ vs. [%Cr] in liquid Fe–Cr–N alloys measured by various authors at 1 873 K.

can vary with the melt composition, and this may cause an error in temperature measurement and control by the optical pyrometry. The $\log f_N^{Cr}$ values calculated from the experimental data by Ishii and Fuwa at 1853 K are also shown in Fig. 6. Their data show good agreement with the solid line determined in the present study in spite of the temperature difference by 20 K.

Figure 7 shows the nitrogen solubility of liquid Fe–Cr alloys containing chromium up to 27.5 mass% at nitrogen partial pressures of 0.02 and 0.03 atm at 1923 and 1973 K, respectively. Using the similar procedure, the values of $\log f_N^{Cr}$ were determined as a function of chromium concentration in liquid iron using the relation expressed by Eq. (4). **Figure 8** shows the values of $\log f_N^{Cr}$ plotted vs. chromium concentration up to 3 mass% in liquid iron at 1923 and 1973 K. The first-order interaction parameter, e_N^{Cr} values can be determined as -0.058 and -0.056 at 1923 and 1973 K, respectively by a linear regression analysis of data in Fig. 8. **Figure 9** shows the relation of $\log f_N^{Cr}$ values vs.

Fig. 7. Nitrogen solubility in liquid Fe–Cr alloy at 1923 and 1973 K.

chromium concentration up to 27.5 mass% in liquid iron at 1923 and 1973 K. The data obtained by Wada and Pehlke⁸⁾ and Ishii *et al.*¹⁰⁾ are also shown in the figure for comparison. The first- and second-order interaction parameters can be simultaneously determined from the following relations derived by a regression analysis of experimental data shown in Fig. 9.

$$\log f_N^{Cr} = -0.058[\%Cr] + 0.00073[\%Cr]^2 \quad \text{at } 1923 \text{ K} \quad \dots\dots\dots(6)$$

$$\log f_N^{Cr} = -0.056[\%Cr] + 0.00075[\%Cr]^2 \quad \text{at } 1973 \text{ K} \quad \dots\dots\dots(7)$$

Fig. 8. Effect of Cr on the activity coefficient of nitrogen in liquid iron at 1923 and 1973 K.

Fig. 9. Relations of $\log f_N^{\text{Cr}}$ vs. [%Cr] in liquid Fe–Cr–N alloys at 1923 and 1973 K.

Therefore, the temperature dependence of e_N^{Cr} and r_N^{Cr} values can be determined as $-147.8/T + 0.019$ and $-2.58/T + 0.0021$, respectively, in the temperature range from 1873 to 1973 K.

$$\log f_N^{\text{Cr}} = (-147.8/T + 0.019) \cdot [\% \text{Cr}] + (-2.58/T + 0.0021) \cdot [\% \text{Cr}]^2 \quad \text{.....(8)}$$

In the present study, variations of nitrogen partial pressure and chromium content in liquid iron over a wide range

and a direct measurement of melt temperature by the immersion of thermocouple enabled us to obtain more reliable information on thermodynamic relations between chromium and nitrogen in Fe–Cr–N melt as a function of temperature. The first-order e_N^{Cr} values determined in the present study appears to be more negative than the values reported by many investigators who assumed that the effect of Cr on nitrogen solubility was linear up to 10–15 mass% Cr. However, considering the second-order r_N^{Cr} values determined at higher Cr content, the present data can predict the nitrogen solubility more accurately in liquid Fe–Cr alloys over a wide range of composition. As shown in Figs. 6 and 9, the relations of $\log f_N^{\text{Cr}}$ values vs. chromium concentration in mass% in liquid iron determined in the present study at different temperatures correlate well with the experimental data determined by other investigators.

4. Conclusions

The nitrogen solubility in liquid Fe–Cr alloys has been measured in the temperature range from 1873 to 1973 K. The nitrogen dissolution follows the Sieverts' law in liquid Fe–Cr alloys containing chromium up to 30 mass%. The activity coefficient of nitrogen in liquid Fe–Cr–N alloys can be expressed as:

$$\log f_N^{\text{Cr}} = (-147.8/T + 0.019) \cdot [\% \text{Cr}] + (-2.58/T + 0.0021) \cdot [\% \text{Cr}]^2 \quad (0 < \text{mass}\% \text{Cr} < 30)$$

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