Effect of Niobium on Nitrogen Solubility in High Chromium Steel

Sang-Beom LEE, Myung-Chae JUNG,1) Hyoseok SONG1) and Chang-Hee RHEE

Pohang University of Science and Technology, San 31, Hyoja-Dong, Nam-Gu, Pohang, 790-784, Republic of Korea.
1) POSCO, #5, Dongchon-Dong, Nam-Gu, Pohang, Republic of Korea.

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1. Introduction

Ferritic stainless steel gained higher demand recently due to its low cost and high mechanical performance. For the production of high purity steel such as ferritic stainless steel, nitrogen removal is very important. Normally, niobium is alloyed to fix carbon and nitrogen to prevent chromium nitride or carbide formation in ferritic stainless steels. The effects of niobium on nitrogen in high chromium stainless steel are determined by thermodynamic behaviors of nitrogen in Fe–Cr–Nb alloy, the experimental data on nitrogen solubility in the high chromium steel containing niobium, however, are scarce.

Since there are few experimental studies on the Fe–Cr–Nb alloy system, thermodynamic data on binary alloy systems (Fe–Cr and Fe–Nb) have been used to predict the behavior of nitrogen. The interaction parameters of alloying elements on nitrogen in liquid Fe–Cr alloys containing niobium have been determined. The equilibrium nitrogen solubility in the liquid iron alloy was measured by metal–gas equilibrium technique under 0.04 to 1.0 atm of nitrogen atmosphere at 1 823 to 1 923K. Nitrogen solubility in Fe–Cr–Nb melts obeyed Sieverts’ law for all compositions studied in present study. The results obtained are summarized as follows;

(1) The solubility of nitrogen markedly increased with increasing chromium and niobium. The interaction parameters in liquid iron alloys containing 10–18% of Cr and 0.2–2% of Nb are obtained.

(2) The solubility of nitrogen was lower at a higher temperature in Fe–Cr melts in this study.

(3) Test results indicated that it is not likely to form niobium nitride in Fe–Cr–Nb–N alloys and it was confirmed by EDS.

KEY WORDS: nitrogen; chromium; niobium; solubility; interaction parameter; activity coefficient.

2. Experiments

Master alloys were prepared by melting the appropriate amount of iron, chromium and niobium in alumina crucibles using vacuum induction furnace. The chemical compositions of alloys and pure iron used in the experiments are given in Table 1.

Experimental apparatus used to measure the nitrogen solubility in liquid metal is schematically shown in Fig. 1. A resistance furnace was used for heating and an alumina tube (70 mm ID×1.2 m L) was used as a reaction tube. The tube was closed by top and bottom end fittings. An alumina crucible (18 mm ID×40 mm L) was used for melting of samples and this crucible was held in an alumina holding crucible (50 mm ID×100 mm L). The temperature of the hot zone was measured with a thermocouple (Pt–30%Rh/Pt–6%Rh). When furnace heated up to the desired temperature, the crucible filled with the sample was slowly lowered from the top of the reaction tube to the hot zone and placed on the support.

The inside of the tube was then flushed continuously with flowing Ar gas containing 2% H2 gas for purging. After completely melt down of the sample, Ar and N2 gas mixture was introduced; the ratio of which is changed to control the nitrogen partial pressure. The gases were purified by passing through a magnesium chip and dehydrating agent columns. Flow rate of gas mixture was controlled by mass flow controller.

Since nitrogen solubility in molten alloy is a function of temperature, the partial pressure of nitrogen and the chemical composition of alloy, experiments were carried out in the following way.

Table 1. Chemical compositions of alloy and pure iron used in experiments.

|       | C   | Cr  | Nb  | O   | N   | Fe   |
|-------|-----|-----|-----|-----|-----|------|
| Fe-Cr | 0.005 | 18.55 | -   | 0.002 | 0.002 | Bal.  |
| Fe-Nb | 0.014 | 18.5 | 4.92 | 0.0005 | 0.005 | Bal.  |
| Pure iron | - | - | - | - | - | 99.95 |
the range: 10–18% chromium, 0.2–5.0% niobium and 0.2–1.0 \( \sqrt{P_{N_2}} \) at 1 823 to 1 923K. The nitrogen content was determined by Nitrogen/Oxygen Analyzer, which measures nitrogen and oxygen in a sample simultaneously using thermal conductivity and infrared absorption, respectively. Chromium and niobium contents were analyzed by the Inductively Coupled Plasma Emission Spectrometry. The cross-section of a sample was observed with Energy Dispersive Spectrometer. The experimental results are given in Table 2.

3. Results and Discussion

For the nitrogen dissolution reaction in molten iron,

\[
\frac{1}{2} \text{N}_2(g) = \text{N} \quad \text{(1)}
\]

the equilibrium constant is expressed by Eq. (2).

\[
K = \frac{a_N}{\sqrt{P_{N_2}}} = f_N \frac{[\text{wt}\% \text{N}]}{\sqrt{P_{N_2}}} \quad \text{(2)}
\]

where, \( a_N \) and \( f_N \) are the activity and the activity coefficient of nitrogen, respectively, \([\text{wt}\% \text{N}]\) is weight percent of nitrogen content in molten iron and \( P_{N_2} \) is the partial pressure of nitrogen in atmosphere. Activity coefficient of nitrogen in Fe–Cr–Nb alloy system is expressed by following equation:

\[
\log f_N = \log f_N^{\text{pure iron}} + e_N \frac{[\text{wt}\% \text{N}]}{\sqrt{P_{N_2}}} + e_{\text{Cr}} \frac{[\text{wt}\% \text{Cr}]}{\sqrt{P_{N_2}}} + e_{\text{Nb}} \frac{[\text{wt}\% \text{Nb}]}{\sqrt{P_{N_2}}} + \frac{r_N}{\sqrt{P_{N_2}}} \frac{[\text{wt}\% \text{N}]}{\sqrt{P_{N_2}}} \frac{[\text{wt}\% \text{Cr}]}{\sqrt{P_{N_2}}} \frac{[\text{wt}\% \text{Nb}]}{\sqrt{P_{N_2}}} \quad \text{(3)}
\]

where \( e_i \) and \( r_i \) represent the first and second order self-interaction parameter of a component \( i \) and \( e_i^j \) and \( r_i^j \) represent the first and second order interaction parameter between \( i \) and \( j \) (the effect of \( j \) on \( i \)), respectively. The activity coefficients contain the cross-product second order parameters (\( r_i^j \) and \( r_j^i \)) as well as the squared second order parameters (\( r_i^j \)). If \( f_N^{\text{pure iron}}, e_N, e_{\text{Cr}}, e_{\text{Nb}} \) in Fe–Cr–Nb system are 1, 0 and 0, respectively, \( \log f_N \) can be reduced as follows:

\[
\log f_N = e_{\text{Cr}} \frac{[\text{wt}\% \text{Cr}]}{\sqrt{P_{N_2}}} + e_{\text{Nb}} \frac{[\text{wt}\% \text{Nb}]}{\sqrt{P_{N_2}}} + \frac{r_N}{\sqrt{P_{N_2}}} \frac{[\text{wt}\% \text{N}]}{\sqrt{P_{N_2}}} \frac{[\text{wt}\% \text{Cr}]}{\sqrt{P_{N_2}}} \frac{[\text{wt}\% \text{Nb}]}{\sqrt{P_{N_2}}} \quad \text{(4)}
\]

On the other hand, since the activity coefficient of nitrogen in pure iron relative to 1 wt% standard state, activity coefficient of nitrogen in molten alloy can be expressed as follows:

\[
\log f_N = \log f_N^{\text{pure iron}} + \log \frac{[\text{wt}\% \text{N}]}{[\text{wt}\% \text{N}]} \quad \text{(5)}
\]

where, nitrogen solubility in pure iron is known as 0.045%. Therefore, activity coefficient of nitrogen in alloy can be obtained from the experimental result for Fe–Cr–Nb alloy system.

In order to determine the time for the equilibrium of dissolution reaction of nitrogen between gas and molten steel of Fe–Cr–Nb system, preliminary experiments were carried out under the conditions of 1 atm nitrogen atmosphere for Fe–18%Cr–5%Nb system and 0.04 atm nitrogen atmosphere for Fe–18%Cr–0.6%Nb system, respectively at 1 873K. It was confirmed that the systems for 1 atm and 0.04 atm nitrogen were equilibrated approximately within 8 h and 12 h, respectively as shown in Fig. 2. The experiments were carried out for 16 h. It was found that nitrogen dissolution reaction obeys the Siverts’ law from the linear relationship between nitrogen contents in molten steel of Fe–18%Cr–0.6%Nb system and the values of square root of the partial pressure of nitrogen gas in atmosphere at 1 823 to 1 923 K as shown in Fig. 3.
3.1. Nitrogen Solubility in Fe–Cr–Nb Alloy

Nitrogen solubility with respect to niobium content in Fe–18%Cr–Nb system under 1 atm nitrogen gas atmosphere was measured at various temperatures as shown in Fig. 4. Nitrogen solubility increases rapidly with increasing niobium content. By comparing this result with the reported data as shown in Fig. 5, the values obtained in present study is in good agreement with the values reported by Turnock and Pehlke2) and Pehlke and Elliott.1) In this figure the line of Ishii et al.3) and Morita et al.4) which is recalculated in this study using the first order interaction parameter between chromium and nitrogen, \( e_{\text{Cr}}^{\text{N}} (\frac{-0.046}{H_{1002}}) \) of Fe–Cr binary system reported by Ishii et al.3) and that between niobium and nitrogen, \( e_{\text{Nb}}^{\text{N}} (\frac{-0.086}{H_{1002}}) \) of Fe–Nb binary system reported by Morita et al.4) is higher than the others determined in the ternary system of Fe–Cr–Nb at the higher content of niobium.

3.2. Interaction Parameter, \( e_{\text{Nb}}^{\text{N}} \)

Nitrogen solubility under 1 atm of nitrogen in the range of 10–18% chromium contents at 1 873 K in Fig. 6 indicates that nitrogen solubility increases with increasing chromium content, and for given chromium content, it is a linear function of niobium content. The activity coefficient of nitrogen as a function of Nb content in Fig. 7 indicates that a linear relationship between the activity coefficient of nitrogen in logarithmic scale and niobium content exists. The effects of niobium on the activity coefficient of nitrogen can be determined by the first order term from the slope of line for each chromium content.

10% Cr: \( e_{\text{Nb}}^{\text{N}} = -0.066 \)........................(6)

15% Cr: \( e_{\text{Nb}}^{\text{N}} = -0.056 \)........................(7)

18% Cr: \( e_{\text{Nb}}^{\text{N}} = -0.051 \)........................(8)

The negative values of interaction parameters mean that niobium is the attractive element to nitrogen.

The effects of chromium on the relationship between niobium and nitrogen were quantitatively determined by the relationship between interaction parameter, \( e_{\text{Nb}}^{\text{N}} \) and chromium content as shown in Fig. 8. The second order interaction
parameter, \( r_{Cr,Nb} \), which represents the effects of chromium and niobium on nitrogen, was determined from the slope of the line in the figure and determined as follows:

\[
\frac{\partial^2 \log f_N}{\partial (%Cr) \partial (%Nb)} = r_{Cr,Nb} = 0.0018 \pm 0.00014 \quad (9)
\]

Although each element of chromium and niobium increases nitrogen solubility, the positive value of \( r_{Cr,Nb} \) would mean that chromium and niobium decreases the activity of each other, resulting in smaller nitrogen solubility. This may explain that the line calculated using the data of binary system in Fig. 5 is higher than those determined in the ternary system of Fe–Cr–Nb at the higher content of niobium.

Consequently, the relationship between interaction parameter, \( e_{N,Nb} \) and chromium content can be expressed to be:

\[
\frac{\partial \log f_N}{\partial (%Nb)} = e_{N,Nb} = 0.0018 \pm 0.00014 [\%Cr]
\]

\[
-0.084(\pm 0.0020) \quad (10)
\]

where the value of the intercept of y-axis, \(-0.084\pm0.0020\) is the extrapolated value of \( e_{N,Nb} \) to \([\%Cr]=0\), which is the effect of niobium on nitrogen in the binary system of Fe–Nb. It can be compared with other reported data as shown in Table 3.

### 3.3 Interaction Parameter, \( e_{Cr} \)

The activity coefficient of nitrogen (\( f_N \)) with respect to chromium content in the range of 0.2–2% of niobium content under 1 atm of nitrogen gas at 1873K in Fig. 9 indicates that the activity coefficient of nitrogen decreases with increasing chromium content and also with increasing niobium content. There is a linear relationship between chromium content and the activity coefficient of nitrogen in logarithmic scale, from which it is expected that activity coefficient of nitrogen can be expressed by the first order interaction parameter between chromium and nitrogen for the constant up to 2.0% niobium content. Each slope of the lines represents the first order interaction parameter between chromium and nitrogen with niobium content.

\[
0.2\% Nb: \quad e_{Cr}^{0.2\%} = -0.037 \quad (11)
\]

\[
0.6\% Nb: \quad e_{Cr}^{0.6\%} = -0.036 \quad (12)
\]

\[
1.0\% Nb: \quad e_{Cr}^{1.0\%} = -0.035 \quad (13)
\]

\[
2.0\% Nb: \quad e_{Cr}^{2.0\%} = -0.034 \quad (14)
\]

The negative values of interaction parameters mean that chromium tends to form compound with nitrogen, that is, nitrogen solubility increases with increasing chromium content. The interaction between chromium and niobium results in decreasing the absolute value of the interaction parameter with increase of niobium content.

The interaction parameters obtained above are plotted over niobium contents in Fig. 10, where the second order interaction parameter, \( r_{N,Nb,Cr} \) is shown as the same slope of the line in Fig. 8 assuming the mathematical formula:

\[
\frac{\partial^2 \log f_N}{\partial (%Cr) \partial (%Nb)} = \frac{\partial^2 \log f_N}{\partial (%Cr) \partial (%Nb)} = r_{N,Nb,Cr} = 0.0018 \quad (15)
\]

to have \( r_{Cr,Nb} = r_{N,Nb,Cr} = 0.0018 \).

The relationship between interaction parameter, \( e_{N,Nb} \) and
niobium content can be expressed to be:

$$\frac{\partial \log f_e}{\partial (\% \text{Cr})} = e_N^C = 0.0018 (\pm 0.00014) [\% \text{Nb}]$$

$$-0.037 (\pm 0.00036) \quad \ldots (16)$$

where the value of the intercept of $y$-axis, $-0.037 \pm 0.00036$ is the extrapolated value of $e_N^C$ to $[\% \text{Nb}] = 0$, which is the effect of chromium on nitrogen in the binary system of Fe–Cr. It can be compared with other reported data as shown in Table 3.

### 3.4. Temperature Dependence

In order to understand the effects of temperature on nitrogen solubility, the experimental data for 0.2–5% niobium content in Fe–18%Cr under 1 atm partial pressure of nitrogen gas, was estimated at 1 823 to 1 923K. The plot of these data in Fig. 11 results in following equations:

0.2 % Nb:  \( \log(\text{wt\%N}) = \frac{1540}{T} - 1.37 \quad \ldots (17) \)

0.6 % Nb:  \( \log(\text{wt\%N}) = \frac{1330}{T} - 1.24 \quad \ldots (18) \)

1.0 % Nb:  \( \log(\text{wt\%N}) = \frac{1000}{T} - 1.07 \quad \ldots (19) \)

2.0 % Nb:  \( \log(\text{wt\%N}) = \frac{1090}{T} - 1.05 \quad \ldots (20) \)

5.0 % Nb:  \( \log(\text{wt\%N}) = \frac{2360}{T} - 1.58 \quad \ldots (21) \)

These results indicate that the solubility of nitrogen in Fe–Cr–Nb melt decreases at a higher temperature, contrary to the effects of temperature as the solubility for pure iron or carbon steel. High temperature, therefore, would be beneficial for nitrogen removal in stainless steelmaking.

### 3.5. Niobium Nitride Precipitation

In order to control the behavior of non-metallic inclusions, thermodynamic data for the formation of compounds are required. Niobium nitride (NbN) would be only possible to form thermodynamically in the system considered in this study. The formation of niobium nitride (NbN) has been investigated in Fe–Cr–Nb alloy system at 1 873K in the present study.

The reaction for niobium nitride formation is expressed by following equations:

$$\text{Nb}(1\text{wt\%}) + \text{N}(1\text{wt\%}) = \text{NbN(s)} \quad \ldots (22)$$

$$\Delta G^\circ = -213 000 + 1037 (J) \quad \ldots (23)$$

where the value by Morita et al.\textsuperscript{6} is used as free enthalpy for the formation of niobium nitride.

Solubility product is obtained by the values of equilibrium constant $K$ and activity coefficients, $f_{\text{Nb}}$ and $f_{\text{N}}$ as follows:

$$[\% \text{Nb}] [\% \text{N}] = \frac{1}{K f_{\text{Nb}} f_{\text{N}}} \quad \ldots (25)$$

The experimental data are plotted in Fig. 12 where the calculated lines of solubility product with the value of $f_{\text{Nb}}$ (0.5 and 1.0) are shown. Experimental results lie under the calculated line with $f_{\text{Nb}} = 1$, indicating that NbN would not form under the test conditions. The analysis of the cross-section of the sample (Fe–18%Cr–5%Nb–0.44%N, 1 873 K) by Energy Dispersive Spectrometer did not show any niobium nitride (Fig. 13). However, more detailed observation such as TEM (Transmission Electron Microscopy)
work may be needed to analyze precipitation of niobium nitride compound.

4. Conclusions

Thermodynamic study of nitrogen solubility in Fe–Cr–Nb alloy was carried out using equilibrium between gas and liquid metal at temperature range of 1823–1923 K. The results may be summarized as follows:

(1) Nitrogen solubility obeys Siverts’ law in the range of 0–18% Cr and 0–5% Nb in Fe–Cr–Nb alloy system.

(2) Both chromium and niobium increase nitrogen solubility and niobium had larger effects on nitrogen solubility than chromium.

(3) Following interaction parameters were determined:

\[ e^N_{\text{Nb}} = 0.0018(\pm0.00014)[\%\text{Cr}] - 0.084(\pm0.0020) \]

\[ e^N_{\text{Cr}} = 0.0018(\pm0.00014)[\%\text{Nb}] - 0.037(-0.00036) \]

(4) Nitrogen solubility in Fe–Cr–Nb alloy system decreases with increasing temperature.

(5) Observation by EDS indicated that no niobium nitride precipitated within 5% of niobium content in Fe–18%Cr alloy.

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