1. Introduction

In the high nitrogen steel making process, addition of chromium and manganese is a common technique for elevating nitrogen solubility in the molten steel. However, the amounts of these alloying elements are sometimes restricted depending on steel grades. At an atmospheric pressure, nitrogen content of martensitic stainless or tool steels is approximately 0.15 mass% at highest1) and nitrogen solubility of ordinary austenitic stainless steel seems to be below 0.70 mass%.2) It is possible to manufacture high nitrogen steel without excessive chromium or manganese addition by using a pressurized electro-slag remelting furnace3,4) or a pressure induction melting furnace.5) However, nitrogen addition into molten steel by the nitrogen gas injection method of the practical ladle refining process involves a very complex mechanism, because the thermal and pressure conditions around the nitrogen gas bubbles change continuously in molten steel. Even if high nitrogen steel is manufactured under pressurized gas conditions, excessive addition of nitrogen to the molten steel causes porosities inside of the steel ingot. In the process of making high nitrogen steels, precise control of nitrogen content is required to obtain the desired properties.

Pressure conditions as well as alloy composition are very important for the kinetics of the nitrogen absorption and desorption reactions in molten steels. The relationship between the rates of nitrogen absorption/desorption and pressure conditions under a vacuum atmosphere has been investigated.6) However, theoretical confirmation is not enough to allow a commercial manufacturing process under a pressurized atmosphere. The purpose of the present work is to investigate the effects of nitrogen partial pressure and total pressure on the rate constants of nitrogen absorption and desorption in high-Cr molten steels under a pressurized atmosphere. The experiments of the nitrogen absorption were not long enough in the previous study7) to fully analyze the kinetics of mass transfer of nitrogen into the steels. Therefore, this study aims to kinetically clarify nitrogen absorption/desorption behaviors by carrying out additional experiments. For this purpose, the rates of nitrogen absorption and desorption reactions with a nitrogen/argon gas mixture were studied by the sampling method using a pressurized directional solidification furnace. Furthermore, the experimental results were analyzed by the mixed-control rate model.

2. Experimental Procedures

Figure 1 shows a schematic illustration of the pressurized directional solidification furnace. The furnace used in this study is capable of running both fundamental steel refining experiments and solidification experiments. The apparatus consists of a reaction tube made of alumina, a tungsten heater furnace covered with a pressure vessel, with a sam-
pling system attached to the pressure vessel. In the nitrogen absorption/desorption experiment, the molten steel was sampled several times using the sampling system.

The base alloy, 3.0 kg in weight, was set in the alumina crucible (65 mm in diameter and 150 mm in length). The furnace was degassed to 30 Pa using a vacuum pump, and then the nitrogen/argon gas mixture was introduced into the furnace so as to achieve a certain partial pressure for each gas. The flow rates of the gases were maintained during the melt experiment at a constant value between 1 and 5 L/min. With the molten steel temperature at 1 823 ± 20 K, the sampler, which was made of carbon steel, was inserted from the upper pressure vessel and collected the molten sample at the designated time.

In the nitrogen absorption experiments, nitrogen gas was induced into the furnace within 30 minutes after the base alloy was melted under an argon gas atmosphere. On the other hand, in the nitrogen desorption experiments, the molten steel was kept at a 0.50 MPa nitrogen partial pressure condition for 60 minutes after the base alloy was melted under a pure nitrogen gas atmosphere. The gas mixture condition in the pressure vessel was then controlled within 30 minutes. The start time was defined as the timing that the nitrogen-argon gas mixture condition was reached to designate pressure.

Table 1 shows the chemical composition of the tested steel. The nitrogen-free base alloy ingots were prepared before the nitrogen absorption/desorption experiments using a vacuum induction furnace, and then forged and cut to φ50 mm×L200 mm. The oxygen content of the tested steel was below 0.008 mass%. The sulfur content was below 0.001 mass%. The nitrogen content of the sample solidified in the carbon steel sampler was determined by the inert gas transportation fusion thermal conductivity method.

### Table 1. Chemical composition of tested steel (mass%).

| C  | Si  | Mn  | Ni  | Cr  | Mo  | V   | Nb  | Co  | N   |
|----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| 0.04| 0.10| 0.10| 3.37| 10.97| 1.88| 0.60| 0.04| 3.92| 0.003|

3. Experimental Results

The variations of nitrogen content with time in the nitrogen absorption/desorption experiments are shown in Figs. 2–4 together with the results of previous work\(^7\) and Figs. 5, 6, respectively.
Fig. 6. Variation of nitrogen content with time in nitrogen desorption experiment in various total pressure conditions.

As for the nitrogen absorption experiments, the practical molten steel temperatures were from 1 800 K to 1 840 K. It can be seen that nitrogen content increases with time. It is noted that the data obtained under 0.1, 0.3, and 0.5 MPa in nitrogen partial pressures are plotted on the parabolic lines in spite of the different total pressure. As described later in detail, the lines shown in Figs 2–6 are those calculated by regression method with solving the rate constants of mass transfer of nitrogen at each step. These phenomena suggest that the total pressure has less influence on the nitrogen absorption reaction of molten steel under a pressurized atmosphere than does the nitrogen partial pressure. In every nitrogen partial pressure conditions, the increment of the nitrogen absorption rate became extremely small approximately over 4 000 seconds.

Figure 5 shows the variation of nitrogen content with time in the nitrogen desorption experiment for various nitrogen partial pressure conditions. In these nitrogen desorption experiments, the total pressure was fixed at 0.50 MPa. The decrement of the nitrogen desorption rate became small over 4 000 seconds for all the nitrogen partial pressure conditions.

The variation of nitrogen content with time in the nitrogen desorption experiment for various total pressure conditions is shown in Fig. 6. In these experiments, argon gas was introduced into the furnace to make various total pressures, immediately after the nitrogen partial pressure attained 0.50 MPa to 0.20 MPa. As shown in Fig. 6, the decrement of the nitrogen desorption rate became small over 5 000 seconds for all the total pressure conditions.

4. Discussion

Nitrogen dissolves in liquid iron or molten steel according to the following reaction:

\[ \frac{1}{2} N_2 (g) \rightleftharpoons 2N \] .......................................................... (1)

for which the equilibrium constant \( K_{N2} \) is given by:

\[ K_{N2} = \frac{a_N}{(PN_2)^{1/2}} = \frac{f_N}{(PN_2)^{1/2}} \] .......................................................... (2)

where \( a_N \) is the activity of nitrogen in the molten steel taking dilute solution as standard state, \( f_N \) is the activity coefficient of the nitrogen in molten steel, \( [%N] \) is the nitrogen content in the molten steel (mass%), and \( PN_2 \) is the nitrogen partial pressure (Pa).

Nitrogen dissolution reaction in liquid iron obeys Sieverts’ law in the case that nitrogen content in liquid phase is below 0.60 mass%.

Furthermore, equilibrium nitrogen solubility in molten steel can be calculated using the following equation considering the first and second order interaction parameters:

\[ \log K_{N2} = -518/T - 1.063 - \sum \left( e_N^M \left[\%M\right] + r_N^M \left[\%M\right]^2 \right) \] .......................................................... (3)

where \( T \) is the temperature (K), \( e_N^M \) is the first order interaction parameter of alloying element M, \( r_N^M \) is the second order interaction parameter of alloying element M, \( [%M] \) is the alloying element M content (mass%).

It is well known that the process of nitrogen absorption and desorption from molten steel consists of the following three steps: transport of nitrogen atoms from the bulk liquid to the interface (liquid phase mass transfer), chemical reaction at the interface, and transport of nitrogen molecules from the interface to the bulk gas (gas phase mass transfer). As for nitrogen absorption, the steps opposite to the above take place. Considering these mechanisms, the rate of the nitrogen absorption and desorption reactions is expressed in Eq. (4).\(^{6,9} \) Furthermore, the variation of the nitrogen content of the molten steel with time can be written as Eq. (5).\(^{6} \)

\[ n_{N2} = k_w A \left( [\%N] - [\%N]^* \right) \rho_F / 100M_{N2} \]

\[ = k_w A \left( [\%N]^2 - K_{N2}^2 P_{N2}^2 \right) \rho_F / 100M_{N2} \] .......................................................... (4)

\[ = k_w A \frac{P}{RT} \ln \frac{P - P_{N2}^*}{P - P_{N2}} - d[\%N]/dt = n_{N2} (100M_{N2})/W_m \] .......................................................... (5)

where \( n_{N2} \) is the molar flux of nitrogen (mol·s\(^{-1}\)), \( A \) is the interfacial area between the gas and the molten steel (m\(^2\)), \( \rho_F \) is the density of the liquid iron (kg·m\(^{-3}\)), \( M_{N2} \) is the molecular weight of the nitrogen gas (kg·mol\(^{-1}\)), \( W_m \) is the weight of the molten steel (kg), \( k_w \) is the mass transfer coefficient in the liquid phase (m·s\(^{-1}\)), \( k_r \) is the rate constant for the chemical reaction at the gas/liquid interface (m·mass%·s\(^{-1}\)), \( k_{g*} \) is the mass transfer coefficient in the gas phase (m·s\(^{-1}\)), \( [\%N]^* \) is the nitrogen content at the gas/liquid interface (mass%), \( P \) is the total pressure (Pa), \( P_{N2}^* \) is the nitrogen partial pressure at the gas/liquid interface (Pa), \( R \) is the gas constant. The mass transfer coefficients and the rate constant can be estimated from Eqs. (4) and (5). In the present work, the geometric cross-section of the Al\(_2\)O\(_3\) crucible was adopted as the interfacial area between the gas and the molten steel. Furthermore, the time variations of the nitrogen content at each step were obtained by rearranging Eqs. (4) and (5). Three variables, \( k_w, k_r, k_{g*} \) in which the deviation between the time variation curve and the experimental data became minimum were determined in this study.

In a nitrogen desorption experiment under a vacuum atmosphere, Mukawa et al. reported that the value of \( k_{g*} \) satisfied the relation of the following equation:\(^{6,10} \)

\[ k_{g*} = D_{Ar-N2}/\delta \] .......................................................... (6)

where \( D_{Ar-N2} \) is the binary diffusion coefficient of the nitrogen.
gen-argon gas mixture (m² s⁻¹), and δ is the thickness of the boundary layer in the gas phase (m). Here, the distance from the upper side of the crucible to molten steel surface was applied as the δ value⁴¹ estimated approximately as 0.035 m.

The binary diffusion coefficient of binary gas systems can be calculated using the Chapman-Enskog method¹²,¹³ as follows:

\[ D_{ij} = 1.8583 \times 10^{-3} \left( \frac{T^*}{P \Omega_d} \right)^{1/2} \]  

where \( M \) is the molecular weight of the gas (g), \( \sigma \) is the collision diameter¹⁴ (10⁻¹⁰ m), given by \( \sigma_{ij} = (\sigma_i + \sigma_j)/2 \). The collision integral \( \Omega_d \) is expressed as follows:

\[
\Omega_d = \frac{1.06036}{\left( T^* \right)^{0.15616}} + \frac{0.19300}{\exp\left( 0.47635 \cdot T^* \right)} + \frac{1.03587}{\exp\left( 1.52996 \cdot T^* \right)} + \frac{1.76474}{\exp\left( 3.89411 \cdot T^* \right)} \]  

where \( T^* \) is the dimensionless temperature, given by \( T = k_B T / e_j \), \( e_j \) is the Lennard-Jones parameter (K), and \( k_B \) is Boltzmann’s constant, given by \( e_j = (e_j, e_j) \)¹². The parameters for calculation of the binary diffusion coefficient are shown in Table 2. The binary diffusion coefficient was estimated to be 4.0531 × 10⁻⁵ m² s⁻¹. Substituting the above values to Eq. (6), the mass transfer coefficient in the gas phase was calculated as the value between 0.001 and 0.01.

According to the three researches,¹⁵–¹⁷ the formulae for the rate constants of the chemical reaction at the gas/liquid interface under a pressurized atmosphere are suggested as follows accounting for the surface-active elements:

\[ k_r = 0.974 \times f_s^2 \left( 1 + 28.4 \left[ \%O \right] + 5.34 \left[ \%S \right] \right)^2 \]  

\[ k_r = 3.16 \left( 1 + 286 \left[ \%O \right] + 108 \left[ \%S \right] / 2 \right) \]  

\[ k_r = 15.0 \times f_s^2 \left( 1 + 161 \left[ \%O \right] + 63.4 \left[ \%S \right] \right)^2 \]  

where \([\%O]\) is the oxygen content (mass%), and \([\%S]\) is the sulfur content (mass%).

In present work, the oxygen content of the tested steel was below 0.008 mass%. The sulfur content was below 0.001 mass%. The accuracy of numerical analysis results were discussed using the calculated values by Eqs. (9)–(11).

The rate constants obtained by numerical analysis in the nitrogen absorption experiment are shown in Table 3. The drawn curves in Figs. 5 and 6 are the calculated results by Eq. (6). On the other hand, the rate constants for the chemical reaction at the gas/liquid interface were estimated at over 0.006 by Eqs. (9)–(11). This value was slightly higher than that of the present study as seen in Tables 3 and 4. It suggests that the oxygen and sulfur contents in the molten steel are not enough to explain the chemical condition at gas/liquid interface under a pressurized atmosphere.

Mukawa et al. discussed the effects of the total pressure on the mass transfer resistance under a vacuum atmosphere⁶ demonstrating that gas phase mass transfer resistance became higher under the higher total pressure conditions. As understood in Table 4, the \( k_r \) and \( k_m \) values are obviously affected by the total pressure while the \( k_o \) values are as 0.0030 m·mass%·s⁻¹ under every gas pressure condition. On the other hand, it was found that the mass transfer coefficient in the gas phase decreased with the increase of total pressure. The mass transfer coefficient in molten steel was reported as 0.0009 m·s⁻¹ by Mukawa et al. under a vacuum atmosphere⁶ in good agreement with our data.

Table 3 clearly shows that the \( k_o \) is the only value affected by the total pressure while the \( k_r \) and \( k_m \) value are not. This can imply that the gas phase mass transfer dominates the overall reaction rate for absorption of nitrogen into the molten steel under a pressurized atmosphere.

The rate constants obtained by numerical analysis in the nitrogen desorption experiment are shown in Table 4. The drawn curves in Figs. 5 and 6 are the calculated results by using the rate constants listed in Table 4. It should be noted that the mass transfer coefficients in the liquid phase were the same as the value of 0.0009 m·s⁻¹ obtained from the nitrogen absorption experiments. In contrast, it is considered that the rate constants for the chemical reaction at the gas/liquid interface and the mass transfer coefficient in the gas phase depend on the gas pressure condition.

As shown in Tables 3 and 4, the mass transfer coefficient in the gas phase obtained by the absorption/desorption experiments were between 0.0005 and 0.008, which were close to the values calculated by Eq. (6). On the other hand, the rate constants for the chemical reaction at the gas/liquid interface were estimated at over 0.006 by Eqs. (9)–(11).

This value was slightly higher than that of the present study as seen in Tables 3 and 4. It suggests that the oxygen and sulfur contents in the molten steel are not enough to explain the chemical condition at gas/liquid interface under a pressurized atmosphere.

Mukawa et al. discussed the effects of the total pressure on the mass transfer resistance under a vacuum atmosphere⁶ demonstrating that gas phase mass transfer resistance became higher under the higher total pressure conditions. As understood in Table 4, the \( k_r \) and \( k_m \) values are obviously affected by the total pressure while the \( k_o \) values are

| Table 2. Parameters for Chapman-Enskog equation. |
|-----------------------------------------------|
| Molecule (i,j) | \( \sigma (\text{Å}) \) | \( e/k_B (\text{K}) \) |
| N₂ | 3.798 | 71.4 |
| Ar | 3.542 | 93.3 |

| Table 3. Obtained rate constants from nitrogen absorption experiment. |
|-----------------------------------------------|
| Nitrogen partial pressure (MPa) | Total pressure (MPa) | \( k_r \) (m·s⁻¹) | \( k_m \) (m·mass%·s⁻¹) | \( k_o \) (m·mass%·s⁻¹) |
|-----------------------------------------------|
| 0.10 | 0.20 | 0.0060 | 0.0030 | 0.0009 |
| 0.30 | 0.55 | 0.0025 | 0.0030 | 0.0009 |
| 0.50 | 0.60 | 0.0013 | 0.0030 | 0.0009 |

| Table 4. Obtained rate constants from nitrogen desorption experiment. |
|-----------------------------------------------|
| Nitrogen partial pressure (MPa) | Total pressure (MPa) | \( k_r \) (m·s⁻¹) | \( k_m \) (m·mass%·s⁻¹) | \( k_o \) (m·mass%·s⁻¹) |
|-----------------------------------------------|
| 0.10 | 0.50 | 0.0080 | 0.0030 | 0.0009 |
| 0.20 | 0.50 | 0.0050 | 0.0010 | 0.0009 |
| 0.30 | 0.50 | 0.0010 | 0.0005 | 0.0009 |
| 0.20 | 0.70 | 0.0005 | 0.0010 | 0.0009 |
| 0.20 | 1.00 | 0.0013 | 0.0010 | 0.0009 |
Fig. 7. Relationship between nitrogen partial pressure and rate constant for chemical reaction in gas/liquid interface.

Fig. 8. Relationship between total pressure and mass transfer coefficient in gas phase.

not. This can imply that the gas phase mass transfer and chemical reaction rate at the gas/liquid interface dominate the overall reaction rate for desorption of nitrogen from the molten steel under a pressurized atmosphere.

The relationship between the nitrogen partial pressure and the rate constant for the chemical reaction at the gas/liquid interface is shown in Fig. 7 indicating that the rate constant decreases with increasing of nitrogen partial pressure. It is well known that nitrogen is a surface-active element same as oxygen and sulfur. The rate constant for the chemical reaction at the gas/liquid interface in low carbon steel is proposed as the following expression:  

\[ k_i = k_{0i} f_n \left( 1 + \kappa_0 a_0 + \kappa_S a_S + \kappa_N a_N \right) \]  \hspace{1cm} (12)

where \( k_{0i} \) is the rate constant for the chemical reaction in pure iron (m·mass%−1·s−1), \( \kappa \) is the adsorption equilibrium constant of \( i \) species, \( a_i \) is the activity of \( i \) species, and \( a_N \) is the activity of nitrogen at the gas/liquid interface. Sufficiently low oxygen and sulfur contents of the present steel are guessed that the nitrogen activity in Eq. (12) dominates the rate constant for the chemical reaction at the gas/liquid interface. Therefore, it is considered that the nitrogen activity increases with the increase of nitrogen partial pressure. As a result, the rate constant for the chemical reaction is lower under higher nitrogen partial pressure conditions. The chemical reaction at the gas/liquid interface has significant influence on the nitrogen desorption rate under a pressurized atmosphere.

Figure 8 shows the relationship between the total pressure and the mass transfer coefficient in the gas phase. The calculated results from Eq. (6) at 1823 K are shown along with the experimental results of Mukawa et al. The tendency of the mass transfer coefficient in the gas phase of this study is similar to those of Mukawa et al. The reason why, the larger experimental error is seen in this study, is the thermal convection in the pressure vessel.

As shown in Fig. 8, the experimental error of nitrogen desorption was larger than that of nitrogen absorption. It is guessed that the sudden gas temperature and convection condition change inside the furnace occurred for the nitrogen gas decompression and the argon gas compression operation at start period of the nitrogen desorption experiments.

5. Conclusions

In this study, the rates of nitrogen addition and removal with a nitrogen/argon gas mixture were studied by the sampling method using a pressurized directional solidification furnace. The effects of the nitrogen partial pressure and the total pressure on the rate constant of nitrogen absorption and desorption in high-Cr molten steel under a pressurized atmosphere was investigated. The obtained results can be summarized as follows:

(1) In the nitrogen absorption reaction, the mass transfer coefficient in the liquid phase of high-Cr molten steel at 1823 K was estimated at approximately 0.0009 m·s−1.

(2) Because the nitrogen partial pressure dependence of the estimated rate constant for the chemical reaction was confirmed in this study, we can conclude that the chemical reaction at the gas/liquid interface has a significant influence on the nitrogen desorption rate under a pressurized atmosphere.

(3) The total pressure dependence of the mass transfer coefficient in the gas phase was confirmed. From these results, it can be seen that the effect of the gas phase mass transfer would be dominant on the nitrogen absorption/desorption reaction under a pressurized atmosphere.

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