Effect of Surface Concentration of Allo"ying Elements on Nitrogen Dissolution Rate in Molten Iron Alloys

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The effects of allo"ying elements, such as Mn, Cu and Mo, on the rate of nitrogen dissolution in the molten iron alloys are investigated by an isotope exchange technique at 1 973 K. The rate constant of nitrogen dissolution increases with increasing the content of Mn or Mo, which has stronger affinity with nitrogen than iron. On the other hand, the rate constant decreases with increasing the Cu content, which has a repulsive force against nitrogen in iron. The mole fractions of the allo"ying elements in the surface phase are estimated, and the reaction mechanism is discussed by investigating the dependence of the rate constant on the mole fraction in the surface phase. The effect of allo"ying elements on the nitrogen dissolution rate depends on the affinity of the solute element with nitrogen in molten iron and the mole fraction in the surface phase.

KEY WORDS: nitrogen dissolution; isotope exchange; surface concentration; Butler’s equation.

1. Introduction

Nitrogen dissolves into molten iron during its refining processes and even a small amount of nitrogen in steel causes harmful effects on the mechanical properties. Accordingly, it is important to evaluate the nitrogen dissolution rate in molten iron and many kinetic studies have been carried out.1–11 One of the rate-limiting steps of nitrogen dissolution in molten iron is considered to be the adsorption and/or the dissociation of nitrogen at the metal surface. Several kinetic studies of investigating the effects of the allo"ying elements have been carried out. For example, by one of the present authors and others,8 the effects of Ti, Zr, V and Cr on the rate were previously investigated by an isotope exchange technique. It is found that those elements, which have stronger affinity with nitrogen than iron, increase the rate, and the reason was explained by an increase of the activity of the vacant site at the metal surface. Subsequently, Morita et al.11 investigated the effects of Al, Si and B on the rate. It is shown that these elements decrease the rate because of the repulsive force against nitrogen in iron. In these studies, the effects of the allo"ying elements are investigated based on the relation between the rate constant and the bulk concentration of the solute elements in molten iron. On the other hand, it is expected that the effects of the allo"ying elements on the rate can be related to the mole fractions of the solute elements in a surface phase more closely, because the adsorption and the dissociation of nitrogen occur at the metal surface. In the present study, the mole fractions of the allo"ying elements in the surface phase are estimated from Butler’s equation12 by the method proposed by Tanaka et al.13–16 and the elements, the mole fractions in the surface phase of which are largely different from those in the bulk phase, namely manganese, copper and molybdenum, are selected as the allo"ying elements. The nitrogen dissolution rates in the molten iron–M (M: Mn, Cu and Mo) alloys have been measured by the isotope exchange technique at 1 973 K. The reaction mechanism is discussed by investigating the dependence of the rate constant on the mole fraction in the surface phase.

2. Calculation of Surface Concentration of Liquid Alloys

The mole fractions of the solute elements in a surface phase are estimated from Butler’s equation12 for the surface tension of binary liquid alloy by the method proposed by Tanaka et al.13–16 at 1 973 K. The procedure is briefly described here. Butler’s equation for the surface tension σ of any A–B binary liquid alloy can be expressed as

\[ \sigma = \sigma_A^+ \frac{RT}{A_A} \ln \left( \frac{1 - N_B^S}{1 - N_B^B} \right) + \frac{1}{A_A} \sigma_{E,S}^A(T, N_B^S) - \frac{1}{A_B} \sigma_{E,B}^S(T, N_B^S) \]

\[ \sigma = \sigma_B^- \frac{RT}{A_B} \ln \left( \frac{N_A^S}{N_A^B} \right) + \frac{1}{A_B} \sigma_{E,B}^B(T, N_B^B) \]

\[ \sigma = \sigma_A^+ + \sigma_B^- \]

where \( R \) denotes the gas constant (J/(mol · K)), \( T \) the absolute temperature (K), \( \sigma_X \) the surface tension of pure liquid X (N/m), and \( A_X \) the molar surface area in a monolayer of pure liquid X (X=A or B) (m²/mol). \( A_X \) can be obtained from

\[ A_X = LN_0^{1/3} r_X^{2/3} \]

where \( r_X \) is the radius of the solute element X.
where \( N_i \) is Avogadro’s number, and \( V_X \) is the molar volume of pure liquid \( X \) (m\(^3\)/mol). \( L \) in Eq. (2) is usually set to be 1.091 for liquid metals, assuming close-packed structures.\(^{17} \)

\( N_X^S \) and \( N_X^B \) in Eq. (1) are mole fractions of a component \( X \) in a surface phase and a bulk phase, respectively; \( G_X^{SE}(T, N_X^S) \) is the partial excess Gibbs energy of \( X \) in the surface phase as a function of \( T \) and \( N_X^S \). \( G_X^{SE}(T, N_X^B) \) is the partial excess Gibbs energy of \( X \) in the bulk phase as a function of \( T \) and \( N_X^B \). Equation (1) can be solved from the relationship between excess Gibbs energy in bulk and surface phases as follows. Since \( G_X^{SE}(T, N_X^B) \) in Eq. (1) can be obtained directly from thermodynamic databases, we only need the additional information on \( G_X^{SE}(T, N_X^S) \) in the surface phase. The various authors proposed the models for \( G_X^{SE}(T, N_X^S) \), which can be summarized as follows:

\[
G_X^{SE}(T, N_X^S) = \beta_{MX}^{mix} G_X^{SE}(T, N_X^B) \quad \text{...........}(3)
\]

where \( \beta_{MX}^{mix} \) is a parameter corresponding to the ratio of the concentration number in the surface phase \( Z^S \) to that in the bulk phase \( Z^B \). In addition to the \( Z^S/2 \) value, by taking the relaxation of surface structure into consideration, the suitable value for \( \beta_{MX}^{mix} \) in Eq. (3) is determined to be 0.83 for liquid metals by Tanaka et al.\(^{15–16} \) Accordingly, the surface concentration of liquid alloys, as well as the surface tension, can be calculated by the following procedure:

1. Set temperature \( T \) and composition \( N_X^S \) of an alloy.
2. Insert the values for surface tension \( \sigma \), molar volume \( V_X \) of pure liquid substances at the chosen temperature in Eqs. (1) and (2).
3. Determine excess Gibbs energies in the bulk phase at the chosen temperature and composition, and substitute them in Eq. (1).
4. The two equations on the right-hand side of Eq. (1) become an equation with unknown \( N_X^B \). This equation is solved for \( N_X^B \). Moreover, by substituting the derived \( N_X^B \) value into the first equation of the right-hand side of Eq. (1), the surface tension \( \sigma \) of the liquid alloy can be also calculated.

The mole fraction of each component element in a surface phase for binary iron alloy was estimated using thermodynamic data\(^{13,18,19} \) at 1973 K. The results are shown in Fig. 1. The mole fractions of manganese and copper are found to be higher in the surface phase. On the other hand, the mole fractions of tungsten and molybdenum are lower in the surface phase. In order to investigate the effect of surface concentration of alloying elements on nitrogen dissolution rate, manganese, copper and molybdenum were selected as the alloying elements.

3. Experimental

An alumina crucible (26 mm O.D., 20 mm I.D.), in which high-purity electrolytic iron ([mass ppm S]=7, [mass ppm P]=3) and M [M: Mn (purity 99.95%), Cu (purity 99.0%) or Mo (purity 99.9%)] totally weighing 60 g were contained, was settled in a transparent quartz reaction chamber (65 mm O.D., 62 mm I.D.) and inductively heated up to 1873 K in an Ar–H\(_2\) mixture. The iron sample was held for 1 to 2 h in the Ar–H\(_2\) mixture and was sufficiently deoxidized at 1873 K. Then, the iron sample was cooled rapidly. Using the prepared samples, the measurements were carried out as follows: The alumina crucible containing the metal sample was inserted into the transparent quartz reaction chamber and inductively heated up to 1973 K in a hydrogen. The temperature on the metal surface was monitored by a dual wavelength infrared pyrometer, and adjusted manually within an error of \( \pm 3 \) K. After reaching the experimental temperature, the ingoing gases were changed to a H\(_2\)–N\(_2\) mixture, and the measurement of the nitrogen dissolution rate in the molten iron alloy was started. The nitrogen in the ingoing gas contains about 1 mol% nitrogen isotope, \(^3\)\(^{15}\)N\(_2\). The total gas flow rate was preliminary determined to be 1 000 cm\(^3\)/min (s.t.p.) (\( F_{H_2} = 950, \ V \approx 50 \) cm\(^3\)/min (s.t.p.)). In the total gas flow rate of 1 000 cm\(^3\)/min (s.t.p.), the measured rate constant is not dependent on the gas flow rate; the effect of the gas phase mass transfer on the rate can be considered negligibly small. The tip of the gas inlet tube (15 mm O.D., 11 mm I.D.) was located at 5 mm above the metal surface and the gas mixture was blown onto the metal surface. A quadrupole mass spectrometer was used to measure the fractions of isotope nitrogen in the ingoing and the outgoing gases, \(^3\)\(^{15}\)F\(_i\) and \(^3\)\(^{15}\)F\(_f\), through a quartz capillary tube (0.375 mm O.D., 0.075 mm I.D.). The measurement was finished when the fraction of \(^3\)\(^{15}\)N\(_2\) in the total nitrogen (\(^3\)\(^{15}\)N\(_2\) + \(^3\)\(^{14}\)N\(_2\) + \(^3\)\(^{15}\)N\(_2\)) in the outgoing gas showed a constant value, which suggests the achievement of nitrogen equilibrium between gas and metal phases. The oxygen and nitrogen contents of the samples were analyzed after each experiment. The oxygen contents of the samples were in the range of 7 to 20 [mass ppm].

The derivation of the equation for calculating a rate constant has been given elsewhere\(^3,7,8,11\). Therefore, the summary is briefly described here. By considering a mass balance of \(^{30}\)N\(_2\), the following equation holds on the assumption that the fraction of \(^{30}\)N\(_2\) in the total absorbed nitrogen is equal to that in the ingoing nitrogen:

\[
\frac{P_{N_2} F}{RT} \left( F_{^{30}F} - F_{^{30}F} \right) = A \left( F_{^{30}F} - F_{^{30}F} \right) \quad \text{...........}(4)
\]

where \( A \) denotes the surface area of molten metal (cm\(^2\)), \( F_{^{30}F} \) the equilibrium fraction of \(^{30}\)N\(_2\), \( F_{^{30}F} \) and \( F_{^{30}F} \) the frac-
tions of $^{30}\text{N}_2$ in the ingoing and outgoing gases, respectively, $P_{\text{N}_2}$ the partial pressure of nitrogen (atm), $R$ the gas constant ($=82.1$ $(\text{cm}^3\cdot\text{atm}/\text{K}\cdot\text{mol})$), $T$ the temperature of gas (K), and $V$ the volume flow rate $(\text{cm}^3/\text{s})$. Since nitrogen dissolves in the molten iron alloy according to Eq. (5), the rate of nitrogen dissolution $v$ $[\text{mol}/(\text{cm}^2\cdot\text{s})]$, which is a first order with respect to the partial pressure of nitrogen, is expressed by Eq. (6),

$$\text{N}_2(\text{g})=2\text{N} \text{ (in iron alloy)} \quad (5)$$

$$v=kP_{\text{N}_2} \quad (6)$$

where $k$ is the rate constant of nitrogen dissolution $[\text{mol}/(\text{cm}^2\cdot\text{s}\cdot\text{atm})]$. The substitution of Eq. (6) into Eq. (4) gives the rate constant as follows:

$$k=\frac{P}{ART} \cdot \frac{30F_i-30F_e}{30F_i-30F_{\text{al}}}, \quad (7)$$

4. Results and Discussion

The dependence of the rate constant of nitrogen dissolution on manganese concentration at $1973\,\text{K}$ is depicted in Fig. 2 by plotting the rate constant against the mole fraction of manganese in the surface phase. The corresponding mole fraction in the bulk phase is described on the upper horizontal line in Fig. 2. Similarly, the dependences of the rate constant of nitrogen dissolution on mole fractions of copper and molybdenum at $1973\,\text{K}$ are shown in Figs. 3 and 4, respectively. It is found that the rate constant of nitrogen dissolution increases with increasing manganese or molybdenum content, and the effect of manganese on increasing the rate is larger than that of molybdenum. On the other hand, copper decreases the rate constant of nitrogen dissolution. The solid and dashed lines in Figs. 2 through 4 are drawn on the basis of the proposed models in the present study, which will be discussed later. The effects of aluminum, silicon and boron on the rate of nitrogen dissolution were investigated by Morita et al.\textsuperscript{11} The mole fractions of aluminum and silicon out of these elements are higher in the surface phase than in the bulk, as shown in Fig. 1. The mole fractions of aluminum and silicon in the surface phase were calculated for their experimental data, and the rate constants were replotted against the mole fractions in the surface phase. The dependences of the rate constant of nitrogen dissolution on the mole fractions of aluminum and silicon in the surface phase are shown in Figs. 5 and 6, respectively. The corresponding mole fractions in the bulk phase are also described in Figs. 5 and 6 at the upper horizontal lines. The solid and dashed lines in Figs. 5 and 6 are also drawn on the basis of the proposed models in the present study, as well as those in Figs. 2 through 4.

The reaction of nitrogen dissolution in molten iron alloy is described by Eq. (5), which can be divided into the following two steps:

$$\text{N}_2(\text{g})+2\square=2\square \quad (8)$$

$$2\square=2\text{N}+2\square \quad (9)$$
where $\square$ and $\text{N}$ denote a vacant site on the metal surface and a site occupied by a nitrogen atom, respectively. Moreover, Eq. (8) can be divided into the following two steps:

$$N_2(g) + \square = \text{N} \quad \cdots \quad (10)$$

$$\text{N} + \square = 2\text{N} \quad \cdots \quad (11)$$

where $\text{N}$ denotes a site occupied by a nitrogen molecule. In these equations, for example, when the reaction (11), namely the dissociation of nitrogen molecule at the surface site, is a rate-determining step and the reaction (10), namely the dissolution of nitrogen, is a rate-determining step, the rate equation for Eq. (11) can be described as

$$v = k_{11}a^2 \text{N}^2 = k_{11}k_{10}a^2P_{N_2} \quad \cdots \quad (12)$$

where $k_{11}$ is the forward rate constant for Eq. (11) and $K_{10}$ is the equilibrium constant for Eq. (10). Combination of Eqs. (6) and (12) leads to the rate constant, $k$, as follows:

$$k = k_{11}K_{10}a^2 \quad \cdots \quad (13)$$

When the reaction of Eq. (9), namely the dissolution of nitrogen in the iron alloy, is a rate-determining step, the rate constant, $k$, has the same dependence of being proportional to the second power of the activity of vacant site, $a$, as shown in Eq. (13). However, in the isotope-exchange method, Eq. (9) can be considered to be in a virtually equilibrium state in principle and it is not necessary to take this case into account. On the other hand, when Eq. (10), namely the adsorption of nitrogen molecule at the surface site, is a rate-determining step, the following rate constant equation can be derived,

$$k = k_{10}a^2 \quad \cdots \quad (14)$$

where $k_{10}$ denotes the forward rate constant for Eq. (10). In this case, the rate constant is proportional to $a$. It can be found from Eq. (13) or (14) that there is an influence of the alloying elements on the dissolution rate of nitrogen because the activity of the vacant site is affected by them. Here, the activity of the vacant site, $a$, is a measure that how fast nitrogen adsorbs and dissociates at each adsorption site yielded by iron or alloying element, and it represents the reactivity of the adsorption site by converting the variation of the reaction rate at each adsorption site to the apparent number of the adsorption site yielded by iron. Accordingly, it does not mean that the number of the adsorption site changes with the content of alloying element, in actual. Under the assumption that the activity of the vacant site, $a$, at the metal surface directly corresponds to the mole fractions of the component elements at the surface, the activity of the vacant site may be expressed as follows:

$$a = \theta_\text{Fe} + \theta_\text{X} \quad \cdots \quad (15)$$

where $\theta_\text{Fe}$ and $\theta_\text{X}$ denote the mole fractions of iron and alloying element, $X$, at the surface, respectively, and $\gamma$ the activity coefficient of the vacant site yielded by $X$, relative to that yielded by iron. The substitution of Eq. (15) into Eqs. (13) and (14) gives the following equations:

$$k = k_{11}K_{10}(\theta_\text{Fe} + \gamma\theta_\text{X})^2 \quad \cdots \quad (16)$$

$$k = k_{10}(\theta_\text{Fe} + \gamma\theta_\text{X}) \quad \cdots \quad (17)$$

In case that no surface active elements, such as oxygen and sulfur, cover the metal surface, namely perfectly clean surface, it holds that $\theta_\text{Fe} + \theta_\text{X} = 1$. Therefore, the above equations can be converted as follows:

$$k = k_{11}K_{10}(1 - (1 - \gamma)\theta_\text{X})^2 \quad \cdots \quad (18)$$

$$k = k_{10}(1 - (1 - \gamma)\theta_\text{X}) \quad \cdots \quad (19)$$

The solid and the dashed lines in Figs. 2 through 6 are described by fitting the experimental results to Eqs. (18) and (19) and by determining the $\gamma$ values, respectively (Model 1: Eq. (18), Model 2: Eq. (19)). The determined $\gamma$ values for Models 1 and 2, respectively, are shown in Table 1 for each element. As to the $\gamma$ value, it can be expected to take a positive value from its definition. However, the derived $\gamma$ values are found to be negative for Cu, Al and Si from
Langmuir-type ideal adsorption isotherm, the adsorption
by oxygen, is estimated as follows. Assuming a
is found that the
face active elements is very sensitive even if the contents
are low and the accurate estimation is very difficult; it is
very important to estimate the site coverage by the surface
active elements in order to determine the γ value accurately.
As to the validity of application of the two model, in the
previous study, Model 1 is concluded to be more valid be-
cause the value for the adsorption coefficient of oxygen de-

erived from Model 1 rather than that from Model 2 is in
good agreement with that estimated from depression of sur-
fact tension. In the present study, Model 1 is also con-
dered to be more valid, because the solid curve is found to
represent the variation of the rate constant with the content
of the alloying element more closely, as shown in Fig. 6,
and the derived γ values for Model 1 seem to be more suit-
able than those for Model 2. From these point of view, it
can be concluded that the dissociation reaction of nitrogen
molecule at the surface site, which is represented by Eq.
(11), is the rate-determining step.

The derived γ values for Model 1 at [mass% O]=0.0020
are plotted against the interaction parameters of the added
elements with nitrogen in molten iron, ε_{i₁} at 1873 K in
Fig. 7. The linear relationship is found between the γ values
and the interaction parameters; the γ value is larger for the
element with stronger affinity with nitrogen. The effects
of the alloying elements on the rate of nitrogen dissolution
are summarized in Table 1. The activity coefficient of the
vacant site yielded by the solute element relative to that yielded by iron at 1973 K.

| [mass ppm O] | Model 1 | Model 2 | Model 1 | Model 2 |
|--------------|---------|---------|---------|---------|
| γ            |         |         |         |         |
|              | φ        | φ       | K_{O₁}a_{O₁} | K_{O₁}[mass% O] |

where K_{O₁}, a_{O₁} and [mass% O] denote the adsorption coefficient of oxygen on the iron surface, oxygen activity in the iron relative to 1 mass% solution and oxygen content of the metal (mass%), respectively. By one of the authors and others, the value for K_{O₁} was previously derived from the dependence of the rate constant of nitrogen dissolution in molten iron on oxygen concentration by the isotope exchange technique. The K_{O₁} values were determined to be 144 and 258 for Models 1 and 2, respectively, at 1973 K. By substituting these values in Eq. (23), the φ was calculated at [mass% O]=0.0020. Using the calculated φ for each model, which is shown in Table 1, γ was estimated again by fitting the experimental results to Eqs. (20) and (21). The derived γ values are also shown in Table 1. It is found that the γ values approach unity by taking the surface site coverage by oxygen into account, and the γ value for aluminum changes from negative to positive in Model 1. However, the γ values for copper and silicon are still negative. This may be because the site coverage by the surface active elements is very sensitive even if the contents are low and the accurate estimation is very difficult; it is very important to estimate the site coverage by the surface active elements in order to determine the γ value accurately. As to the validity of application of the two model, in the previous study, Model 1 is concluded to be more valid because the value for the adsorption coefficient of oxygen derived from Model 1 rather than that from Model 2 is in good agreement with that estimated from depression of surface tension. In the present study, Model 1 is also considered to be more valid, because the solid curve is found to represent the variation of the rate constant with the content of the alloying element more closely, as shown in Fig. 6, and the derived γ values for Model 1 seem to be more suitable than those for Model 2. From these point of view, it can be concluded that the dissociation reaction of nitrogen molecule at the surface site, which is represented by Eq. (11), is the rate-determining step.

The derived γ values for Model 1 at [mass% O]=0.0020 are plotted against the interaction parameters of the added elements with nitrogen in molten iron, ε_{i₁} at 1873 K in Fig. 7. The linear relationship is found between the γ values and the interaction parameters; the γ value is larger for the element with stronger affinity with nitrogen. The effects of the alloying elements on the rate of nitrogen dissolution are summarized in Fig. 8 together with the other data conducted by a similar method. The dissolution rate constant is demonstrated as a reduced value, where k_{pure iron} denotes the one for pure iron. The effects are investigated based on the bulk concentration in Fig. 8, because the thermodynamic data are unavailable for the several alloying elements, in calculating the surface concentration. The slopes of the lines in Fig. 8 are compared with the interaction parameters between nitrogen and the very elements in molten iron, ε_{i₁} at 1873 K. The relationship is shown in Fig. 9; it is qualitatively found that the elements with stronger affinity with nitrogen than iron (the interaction parameter is negative) have a stronger effect of promoting the nitrogen dissolution rate and those with stronger repulsive force against nitrogen (the interaction parameter is positive) have a stronger effect of retarding the rate.

Table 1. The activity coefficient of the vacant site yielded by the solute element relative to that yielded by iron at 1973 K.
5. Conclusions

The mole fractions of Mn, Cu and Mo in a surface phase are estimated to be much different from those in a bulk phase. Based on these surface mole fractions, the effect of alloying elements on the rate of nitrogen dissolution have been investigated by an isotope exchange technique at 1973 K. The results are summarized as follows:

1. A model, which represents the effect of the alloying element on the rate of nitrogen dissolution, is proposed by investigating the dependence of the rate constants on the mole fractions of the alloying elements in the surface phase. The experimental results were analyzed by the model, and the rate-determining step is considered to be the dissociation reaction of nitrogen molecule at the surface site represented as follows:

\[ \text{N}_2 + \square = 2\text{N} \]

2. The rate constant of nitrogen dissolution increases with increasing the content of Mn or Mo, which has stronger affinity with nitrogen than iron. On the other hand, the rate constant decreases with increasing the Cu content, and Cu has a repulsive force against nitrogen in iron.

3. The effect of alloying elements on the rate of nitrogen dissolution is investigated based on the activity coefficient of the vacant site, \( \gamma \). The \( \gamma \) values are linearly related with the interaction parameters of the added elements with nitrogen in molten iron, \( e_{Ni} \). The effect of alloying elements on the rate of nitrogen dissolution depends on the affinity of the solute element with nitrogen in molten iron and the mole fraction in the surface phase.

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