Interfacial Kinetics of Nitrogen with Molten Iron Containing Sulfur

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The effect of sulfur on the interfacial reaction rates of nitrogen dissolution into molten iron has been investigated at 1823 K using an isotope-exchange technique. In addition, surface activities of the vacant sites and the sites occupied by sulfur have been proposed to predict the interfacial reaction rates and to clarify the rate-determining step of nitrogen dissolution into molten iron using the sulfur adsorption that had been obtained in our previous study. It was found that the experimental results were in good accordance with the predicted values for adsorbed N2 dissociation control rather than those for N2 adsorption control in the low sulfur activity region, yielding that the dissociation of nitrogen molecule into atoms at the surface is the rate-determining step of the interfacial reaction of nitrogen dissolution into molten iron. However, with increasing sulfur content, the experimental results showed higher values than the predicted ones assuming that reactions only occur at vacant sites. In the high sulfur content region, it was considered that reactions at occupied sites might occur. Accordingly, the total interfacial reaction rate constant (mol/cm2 sec atm) of nitrogen dissolution could be expressed as

\[ k = 6.2 \times 10^{-5} a^2 + 4.0 \times 10^{-7} a^2 + 7.0 \times 10^{-6} a a. \]

KEY WORDS: isotope exchange; nitrogen dissolution; surface active element; adsorption; surface activity; rate-determining step.

1. Introduction

It is known that surface active elements such as oxygen and sulfur in molten iron lower the rates of interfacial chemical reactions of nitrogen gas with molten iron by occupying reaction sites when the mass transfers in the gas phase and molten iron are fast enough.1–9) Therefore, in order to know the maximum rate of nitrogen removal in steelmaking processes, it is important to understand the reaction mechanism of the interfacial chemical reaction of nitrogen gas with molten iron and the effect of surface active elements on the reaction.

In order to evaluate the interfacial chemical reaction rates and to decide a rate-determining step, a classical site blockage model has been applied by a number of investigators.1–9) The site blockage model assumes that surface active elements occupy the reaction sites and reaction only occurs on the vacant sites. Then, the reaction rates are expected to be proportional to the fraction of the vacant sites. This site blockage model has been combined with a simple ideal Langmuir adsorption isotherm, and expressed by Eq. (1).

\[ \frac{\theta_i}{(1-\theta_i) a_i} = K_i \] ...............................(1)

where \( \theta_i \) is the fraction of surface sites which are occupied by surface active element \( i \), \( a_i \) is the activity of solute \( i \) with respect to 1 mass% as standard state and \( K_i \) is the ideal adsorption coefficient of \( i \). It is usually assumed that the number of the total reaction sites is constant as \( I_0 \) (adsorption of \( i \) at saturation), and then the surface fraction of the site occupied by \( i (\theta_i) \) may be introduced by \( I_i / I_0 \) (adsorption of \( i / \)adsorption of \( i \) at saturation). Here \( I_i \) is defined as the concentration of \( i \) at the surface monolayer (mol/m2).

The interfacial chemical reaction between nitrogen gas and molten iron can be divided into two elementary steps represented by Eqs. (2) and (3), where \( \text{N}_2(g) \), \( \text{N}_2^{ad} \), \( v \) and \( \text{N}_2^{ad} \) denote nitrogen gas molecule in the gas phase, a site occupied by nitrogen gas molecule, a vacant site and a site occupied by nitrogen on the metal surface, respectively.

\[ \text{N}_2(g) + v = \text{N}_2^{ad} \] .................................(2)
\[ \text{N}_2^{ad} + v = 2\text{N}_2^{ad} \] .................................(3)

Fruehan and Martonik,1) Ban-ya et al.,2) Byrne and Belton3) and Glaws and Fruehan4) asserted that Eq. (2) would be the rate-determining step. On the other hand, Harashima et al.,5) Ono et al.,5b) Nagasaka6) and Jun et al.6) suggested that the Eq. (3) would be the rate-determining step. However, the reaction mechanism has not been fully understood yet.

Sulfur adsorption is a good example to examine the rate-determining step. There have been several researches on the sulfur adsorption in the temperature range between 1823 and 1873 K. Ban-ya et al.2) and Byrne and Belton3) showed that the ideal adsorption coefficient of sulfur would be 130–140 when Eq. (2) is the rate-determining step. On the other hand, Ban-ya et al.2) and Harashima et al.3) showed that the ideal adsorption coefficient of sulfur would be 7–63 when Eq. (3) is the rate-determining step. The depression of the surface tension of molten iron by sulfur may be an-
other source of quantitative information on the adsorption isotherm.\(^9\) The ideal adsorption coefficient of sulfur obtained by surface tension measurements ranges from 185\(^{10}\) to 365,\(^{11}\) which values are much higher than those obtained in kinetic studies of nitrogen reactions with molten iron. Recently, the authors\(^{12}\) have suggested a non-ideal sulfur adsorption model. It was found that even though a simple ideal adsorption model expressed by Szyzkowski equation can show the surface tension within experimental errors, the ideal adsorption isotherm may not express the sulfur adsorption properly. Therefore, it is considered that the interfacial chemical reaction rates should be examined based on the non-ideal adsorption isotherm.

In addition, Byrne and Belton,\(^3\) Glaws and Fruehan\(^4\) and Tsukihashi and Fruehan\(^13\) found a residual rate in a high sulfur activity region where the surface is almost saturated with sulfur. This behavior was also found in the Fe–Se and Fe–Te systems by Ono et al.\(^6\) Hence, N\(_2\) dissociation reactions may occur on the sites occupied by surface active elements in such a high activity region.

In the present study, the effect of sulfur on the interfacial reaction rates of nitrogen dissolution into molten iron has been investigated at 1823 K using an isotope-exchange technique, which has an advantage in that the dissolution rate can be measured without any influence of liquid phase mass transfer. Then, an attempt has been made to predict the interfacial reaction rates and to clarify the rate-determining step of the interfacial reaction of nitrogen dissolution into molten iron based on the non-ideal sulfur adsorption isotherm on molten iron.

2. Experimental

The rate of nitrogen dissolution in molten iron by the overall reaction (4) has been found to be first order with respect to the pressure of nitrogen by Fruehan and Martonik\(^1\) and Kobayashi et al.\(^14\)

\[ N_2(gas) = 2N(in \text{Fe}) \]  

Thus, the rates of nitrogen dissolution, \(v\) (mol/cm\(^2\) sec), may be written as

\[ v = kP_{N_2} \]  

where \(k\) (mol/cm\(^2\) sec atm) is the rate constant of nitrogen dissolution. The rate constant equation introduced by Ono et al.\(^{15}\) is represented by Eq. (6).

\[ k = \frac{\bar{V}}{ART} \frac{30 \ F_i - 30 \ F_{eq}}{30 \ F_i - 30 \ F_{eq}} \]  

where \(A\) (cm\(^2\)) is the surface area of molten metal, \(\bar{V}\) (cm\(^3\)/sec) is the volume flow rate, \(T\) (K) is the temperature of gas, \(R\) (82.1 cm\(^3\) atm/K mol) is the gas constant, \(30 \ F_{eq}\) is the equilibrium fraction of \(30 \ N_2\), and \(30 \ F_i\) and \(30 \ F_{eq}\) are the fractions of \(30 \ N_2\) in the ingoing and outgoing gases, respectively. (See Ref. 15 for details.)

The experimental apparatus is shown in Fig. 1. An alumina crucible (I.D.: 22 mm) containing about 25 g of metal was inserted into a transparent quartz reaction tube and inductively heated in an argon and hydrogen gas mixture. When the sample was melted at 1823 K, Fe–1mass%S alloy or FeS was added in order to control the sulfur content, and then a gas mixture of H\(_2\)–H\(_2\)S–Ar(P(H\(_2\)S)/P(H\(_2\)) = 0–0.000147) was introduced to maintain the desired sulfur activity in the sample at a flow rate of 900 ml/min STP.

The sample temperature was monitored by a dual wavelength infrared pyrometer and controlled manually within ±10 K. After holding about 1 h, the distance between the metal surface and the tip of the gas blowing lance was adjusted to be 5 mm, and then nitrogen gas containing 1.23 at% nitrogen isotope (\(^{30}N_2\)) was introduced at a flow rate of 100 ml/min STP, i.e., the total gas flow rate was 1000 ml/min STP. Compositions of gas mixtures of ingoing and outgoing gases were analyzed with a mass spectrometer (ANELVA, TE-360B). In most experiments, with a gas mixture at a total flow rate of 1000 ml/min STP, the gas mass transfer could be negligibly small in our experimental geometry based on the previous work.\(^{15}\)

The sample metal was analyzed after each experiment for oxygen, sulfur and carbon by LECO analyzers. Oxygen and sulfur contents are 0.0010–0.0020 mass% and 0.0025–0.0593 and 2 mass%, respectively. Some experiments were conducted with samples containing about 3–5 mass% carbon.

3. Results

The effect of sulfur content on the rate constant of nitrogen dissolution into molten iron is shown in Fig. 2. It is found that rate constants for Fe–S alloys is apparently higher than those for Fe–C–S alloys at the same sulfur content. However, when they are plotted as a function of sulfur activity in the bulk phase, they became the same namely the role of carbon is just to enhance the activity of sulfur as pointed out by Tsukihashi and Fruehan\(^{13}\) (Fig. 3). Here, the standard state of sulfur is 1 mass% in molten iron. Other reported values mostly measured with an isotope exchange technique in the temperature range of 1823–1873 K are also shown in Fig. 3 together with the present data. For the rate of nitrogen desorption under reduced pressure at
1 873 K by Harashima et al.,\textsuperscript{5)} the rate constant of nitrogen dissolution was calculated and plotted in Fig. 3 using the equilibrium constant of reaction (4) as shown by Eq. (7).\textsuperscript{16}

\[ \log K_4 = -\frac{1036}{T} - 2.126 \] ............................(7)

The present experimental results are in reasonable accordance with reported values when \( a_S < 0.03 \), but slightly lower than those of Harashima et al.\textsuperscript{3,5} and Nagasaka\textsuperscript{7} when \( a_S < 0.03 \). The difference is considered as a result of the temperature difference by 50 K. From the experimental results, it is obvious that the rate constant decreases considerably with increasing the activity of sulfur in the bulk phase even in the low sulfur activity region, which supports that the effect of gas phase mass transfer was negligible in the present experimental condition. Moreover, in the region where the surface of molten iron is believed to be saturated with sulfur, it is found that the reaction rate is not zero, but close to a constant value. The rate constant of nitrogen dissolution at very high sulfur activity (\( a_S = 1.58 \)) was \( 5.0 \times 10^{-7} \) mol/cm\(^2\) sec atm in this study, which is very close to the values of 3.2–6.5 \( \times 10^{-7} \) mol/cm\(^2\) sec atm after Byrne and Belton\textsuperscript{3} (\( a_S = 0.66 \)), Glaws and Fruehan\textsuperscript{4} (\( a_S = 0.2–0.5 \)) and Nagasaka\textsuperscript{7} (\( a_S = 0.7 \)). It may be more reasonable to assume that some reactions might occur even on the sites occupied by sulfur.

4. Discussion
4.1. Activity of the Reaction Site
The authors\textsuperscript{12} have suggested a non-ideal adsorption model to evaluate surface tension and adsorption for molten Fe–S alloys based on Butler’s equation considering the differences in size and interaction of adsorbed atoms. Thus, we may consider that the activity of the reaction sites for nitrogen adsorption is not equal to the surface concentration of the vacant sites. If we assume that the number of total reaction sites in unit area is constant, \( T_S^\infty \) (sulfur adsorption at saturation), then the surface fraction \( \theta_S \) can be introduced by \( T_S^\infty / T_S^\theta \) as suggested in an ideal adsorption model. In general, the chemical equilibrium between the sites occupied by sulfur and the vacant sites can be expressed by

\[ \frac{\gamma_\psi \theta_S}{\gamma_v (1 - \theta_v) a_S} = K_S \] ............................(8)

where \( \gamma_v \) and \( \gamma_\psi \) are the activity coefficients of the vacant sites and the sites occupied by sulfur, respectively.

\( T_S^\infty \) was given as a function of sulfur content in our previous study.\textsuperscript{12} Using these data, \( \theta_S/(1 - \theta_v) a_S \) can be plotted as a function of \( \theta_S \) or \( a_S \). Figure 4 shows the plot of \( \theta_S/(1 - \theta_v) a_S \) as a function of \( \theta_S \). In an ideal adsorption isotherm, the activity coefficients \( \gamma_\psi \) and \( \gamma_v \) of Eq. (8) would be unity, and \( K_S \) would be constant across the concentration range. In Fig. 4, it is found that the value of \( \theta_S/(1 - \theta_v) a_S \) is almost constant up to \( \theta_S = 0.03 \), but gradually increased and shows maximum value of 297 at \( \theta_S = 0.77 \), and then decreased rapidly. Therefore, the adsorption of sulfur cannot be expressed by a simple ideal adsorption isotherm across the concentration range if the sulfur saturation is taken as the standard state. The activity coefficient of occupied sites is considered to be constant (\( \gamma_\psi = 26 \)) and that of vacant sites to be unity in the region of dilute solution in the surface. Accordingly, we can obtain a constant value of
In order to derive the activity coefficient of reaction sites across the concentration range, we define $M$ as the ratio of $g_v/g_q$, and $g_q$ as $g_q^0/g_q$. Then,

$$\ln M = \ln \gamma_v - \ln \gamma_q$$

Equation (9) is differentiated to give

$$d\ln M = d\ln \gamma_v - d\ln \gamma_q$$

From Gibbs–Duhem relation,

$$(1 - \theta_\beta)d\ln \gamma_v + \theta_\beta d\ln \gamma_q = 0$$

Substitution in Eq. (10) gives

$$\ln \gamma_v = \int_{\theta_\beta = 0}^{\theta_\beta} \left( \frac{d\ln M}{d\theta_\beta} \right) d\theta_\beta$$

Using Eq. (12), we can calculate the activity coefficient of vacant sites at $\theta_\beta = \theta_\beta$. The value of $\ln \gamma_v$ will be the area between $\theta_\beta = 0$ and $\theta_\beta = \theta_\beta$ in Fig. 5. Then, $\gamma_q$ can be obtained by Eq. (13),

$$\gamma_q = \frac{\gamma_v}{M} = \gamma_q^0 \frac{\gamma_v}{\gamma_q^0 M}$$

where $\gamma_q$ is one when $\theta_\beta$ approaches one. In this calculation, the value of $\gamma_q^0$ is estimated as 2.95, yielding the sulfur adsorption coefficient, $K_S$, as 171.

The resulting activities of the vacant sites and the occupied sites in the surface of molten Fe–S alloys are shown in Figs. 6 and 7 as functions of $\theta_\beta$ and $a_S$, respectively. The activity of the vacant sites decreases with increasing sulfur activity in the bulk phase, whereas that of the occupied sites increases.

### 4.2. Rate Constant

In order to derive a rate constant for the interfacial reaction, we may separate the activity region into three. (Region I: low sulfur activity, Region II: intermediate and Region III: high sulfur activity.) In Region I, reactions on the vacant sites are assumed to prevail. Then, as suggested by Ono et al.\(^{19}\) the rate constants can be given by Eq. (14) or (15) corresponding to the rate-determining step of Eq. (2) or (3).

$$k = k_\alpha a_\theta = k'_\alpha a_\theta$$

$$k = k_\beta a_\theta = k'_\beta a_\theta^2$$

where $k'_\alpha$ is the rate constant on the free vacant sites for pure iron and $K_\alpha$ is the equilibrium constant of Eq. (2).

In Region III, it is assumed that almost all the sites are occupied by sulfur. Then, there can be no possibility other than the following reactions,

$$\text{N}_2 + \theta = \text{N}_2^{\text{ad on } \theta}$$

$$\text{N}_2^{\text{ad on } \theta} + \theta = 2\text{N}^{\text{ad on } \theta}$$

where $\text{N}_2^{\text{ad on } \theta}$ and $\text{N}_2^{\text{ad on } \theta}$ denote nitrogen gas molecule on a site occupied by sulfur, a site occupied by sulfur and nitrogen on a site occupied by sulfur, respectively. Then, the rate constants for Eqs. (16) and (17) will be Eqs. (18) and (19), respectively

$$k = k_1a_\theta = k'_1a_\theta$$

$$k = k_2a_\theta = k'_2a_\theta^2$$

Fig. 6. Surface activity of the vacant site and the occupied site of molten Fe–S alloy as a function of $\theta_\beta$. Fig. 7. Dependence of concentration and activity of the occupied sites and the vacant sites on the sulfur activity in the bulk phase at 1823 K.
where $k'$ is the rate constant on the sites occupied by sulfur and $K_{16}$ is the equilibrium constant of Eq. (16).

In Region II, other than the simultaneous reactions (2), (3), (16) and (17), adsorbed nitrogen gas molecule can be dissociated into both reaction sites as shown by Eqs. (20) and (21).

\[ \text{N}_2 \text{ad} + \theta = \text{N}^{ad} + \text{N}_2^{ad, on \theta} \] \hspace{1cm} (20)
\[ \text{N}_2 \text{ad}^{on \theta} + \nu = \text{N}^{ad} + \text{N}_2^{ad, on \theta} \] \hspace{1cm} (21)

The rate constants for Eqs. (20) and (21) are given as Eqs. (22) and (23), respectively.

\[ k = k_{20}K_{20}a_\text{fe}a_\text{g} \] \hspace{1cm} (22)
\[ k = k_{21}K_{10}a_\text{fe}a_\text{g} \] \hspace{1cm} (23)

Since reactions (20) and (21) may occur simultaneously,

\[ k = k_{20}K_{20}a_\text{fe}a_\text{g} + k_{21}K_{10}a_\text{fe}a_\text{g} = k'a_\text{fe}a_\text{g} \] \hspace{1cm} (24)

Consequently, if the nitrogen gas molecule adsorption such as Eqs. (2) and (16) is the rate-determining step, then the total rate constant will be expressed by Eq. (25).

\[ k = k''a_\text{fe} + k'a_\text{fe}a_\text{g} \] \hspace{1cm} (25)

On the other hand, if the nitrogen gas molecule dissociation on the surface such as Eqs. (2), (17) and (21) is the rate-determining step, then the total rate constant will be expressed by Eq. (26).

\[ k = k''a_\text{fe}^2 + k''a_\text{fe}^2 + k'a_\text{fe}a_\text{g} \] \hspace{1cm} (26)

### 4.3. Rate Determining Step

Due to the simple reaction mechanism, Region I is considered to be proper to decide the rate-determining step. In order to predict the rate constant in Region I, the rate constant for pure iron, $k^o$, is necessary. The surface active elements in the surface of molten iron are considered to show the highest activity region of the present study, the effect of oxygen might become negligible. Therefore, it is possible to derive the rate constant $k$ as a function of sulfur activity in the bulk phase for Eqs. (14) and (15). In Fig. 3, the predicted values by Eqs. (14) and (15) are shown with experimental results. It is obvious that the predicted line by Eq. (14) is much higher, but that by Eq. (15) is close to the experimental values. Accordingly, it may be concluded that the dissociation of adsorbed nitrogen molecule into atoms expressed by Eq. (3) is more reasonable as a rate-determining step.

There are several researches to measure the rate constant for high purity iron containing less than 20 ppm oxygen without sulfur. Using these data, it is considered that $k^o$ can be obtained by Eq. (27) if Eq. (2) is the rate-determining step, while by Eq. (28) if Eq. (3) is the rate-determining step as suggested by Ono et al. for ideal adsorption isotherm.

\[ \frac{1}{k} = \frac{1}{k^o} + \frac{K_{0}/\gamma^o_\text{fe}}{k^o}a_\text{fe} \] \hspace{1cm} (27)
\[ \frac{1}{\sqrt{k}} = \frac{1}{\sqrt{k^o}} + \frac{K_{0}/\gamma^o_\text{fe}}{\sqrt{k^o}}a_\text{fe} \] \hspace{1cm} (28)

If we plot the value of $1/k$ or $1/k^{1/2}$ as a function of $a_\text{fe}$, then from the intercept with a vertical axis, we can obtain the value of $k^o$ as shown in Fig. 8. Here rate constants for high purity iron containing low level of oxygen are re-estimated by Eq. (29) considering the effect of the gas phase mass transfer expressed by Eq. (30) after Kikuchi et al.

\[ \frac{1}{k} = \frac{1}{k^o} - \frac{1}{k_g/RT} \] \hspace{1cm} (29)

\[ \text{Sh} = \left( \frac{k_g}{D} \right) = (0.27 \pm 0.07)(r_g/d)^{-1.5} \text{Re}^{0.76} \text{Sc}^{0.5} \] \hspace{1cm} (30)

where $k_g$ (cm/s), $D$ (cm$^2$/s), $r_g$ (cm) are the mass transfer coefficient of gas phase, the diameter of the gas blowing lance, the diffusion coefficient of the gas and the radius of alumina crucible, respectively. In the previous experimental condition, the Re number was 35–43 and the Sh number was 1.07–1.36, yielding $k_g/RT$ to be $1.50 - 1.91 \times 10^{-4}$ (mol/cm$^2$ sec atm). The chemical reaction rate constants ($k$) were higher than those of the overall reaction ($k_{\text{overall}}$) by 17–33% at 1823 and 1873 K (Table 1). The values of $k^o$ determined by Eqs. (27) and (28) show almost the same values as $6.53 \times 10^{-5}$ (mol/cm$^2$ sec atm) and $6.17 \times 10^{-5}$ (mol/cm$^2$ sec atm), respectively. Then, it is possible to derive the rate constant $k$ as a function of sulfur activity in the bulk phase for Eqs. (14) and (15). In Fig. 3, the predicted values by Eqs. (14) and (15) are shown with experimental results. It is obvious that the predicted line by Eq. (14) is much higher, but that by Eq. (15) is close to the experimental values. Accordingly, it may be concluded that the dissociation of adsorbed nitrogen molecule into atoms expressed by Eq. (3) is more reasonable as a rate-determining step.

### 4.4. Determination of Rate Parameters

Since Eq. (15) is only valid for a low sulfur activity region, the rate constant in a wide sulfur activity range should be predicted by Eq. (26), assuming that the dissociation of adsorbed nitrogen molecule into atoms is the rate-determining step. In Region I, the rate constant can be expressed by Eq. (31), because the activity of the occupied sites is negligibly smaller than that of the vacant sites or close to zero.

\[ k = k''a_\text{fe}^2 + k'a_\text{fe}^2 + k'a_\text{fe}a_\text{g} \]
\[ k = 6.17 \times 10^{-5} a_\text{fe}^2 \] (mol/cm$^2$ sec atm) \hspace{1cm} (31)

However, with increasing sulfur activity in the bulk phase the predicted line by Eq. (15) is lower than the experimental values.
results. If the surface of molten iron is almost fully covered by sulfur (Region III), the activity of the vacant site will be close to zero and that of the occupied site will be almost unity. Then, the rate constant will be expressed by Eq. (32).

\[ k = k' a_v^2 + k' a_q + k'' a_q a_v \]
\[ = k' a_v^2 = k' = 4.0 \times 10^{-7} \text{ (mol/cm}^2 \text{sec atm)} \]……(32)

Finally, the best fitting of Eq. (26) with the present experimental results and those of other researchers shown in Fig. 9 by a dashed line gives us the value of \( k' \) as \( 7.0 \times 10^{-6} \). According to the results, the total reaction rate constant is given as Eq. (33)

\[ k = 6.2 \times 10^{-4} a_v^2 + 4.0 \times 10^{-7} a_q + 7.0 \times 10^{-6} a_q a_v \text{ (mol/cm}^2 \text{sec atm)} \]……(33)

5. Conclusions

The effects of sulfur on the rate of nitrogen dissolution into molten iron have been investigated at 1 823 K by an isotope exchange technique, and compared with the model predicted by the non-ideal sulfur adsorption.

(1) The rate decreases with increasing activity of sulfur in the bulk phase, and closes to a constant value at high sulfur activity.

(2) The effect of carbon on the reaction rate is negligible.

(3) Surface activities of the vacant sites and the sites occupied by sulfur were suggested using the surface adsorption of sulfur that has been proposed in our previous study.

(4) Adsorption coefficient of sulfur, \( K_S \), is obtained as 171.

(5) According to the comparison between the experimental results and model predictions, the nitrogen dissociation is considered as a rate-determining step.

(6) The total interfacial reaction rates of nitrogen dissolution into molten iron can be deduced considering the reactions on the vacant sites and the sites occupied by sulfur.

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