Measurement of Nitrogen Dissolution Rate into Molten Alloys by Isotope Exchange Technique

Kazuki MORITA,^{*a)} Hideki ONO,^{a)} and Nobuo SANO^{a)}

(Received September 8, 1998; Accepted November 18, 1998)

An isotope exchange technique is introduced as a method for measuring the nitrogen dissolution rate into molten metal, and the results [H. Ono *et al.*, *Metall. Mater. Trans. B*, **26**, 991 (1995); *ibid.*, **27**, 848 (1996)] (refs. 1 and 2) for molten iron-M (M: Ti, Zr, V, Cr, O, Se, and Te) alloys at temperatures from 1873 to 2023 K are summarized.

The rate of nitrogen dissolution into molten iron is shown to increase by adding an element with a stronger affinity for nitrogen than Fe, such as Ti, Zr, V, and Cr. Among these elements, Ti increases the reaction rate most strongly and the rate constant for an Fe-0.08 mass pct Ti alloy is 1.5 times as large as that for pure iron at 1873 K. On the other hand, the addition of surface active elements, such as O, Se, and Te, retards the nitrogen dissolution into molten iron, and the degree of the retarding effect is in the order of Te, Se, and O.

For the addition of non-surface active elements, the correlation of rate constant with thermodynamic interaction parameter with nitrogen has been observed, and this effect is discussed in terms of the change in the activity of the vacant site on the surface of the molten alloy. In case of the addition of surface active elements, the adsorption coefficients of each element are estimated by fitting the concentration dependence of the nitrogen dissolution rate constant. It can be suggested that surface active elements and nitrogen are adsorbed on the same site at the interface and that the dissociation reaction of nitrogen molecule on the site represented by the equation, $N_2^g + \square = 2N^{ad}$, is the rate determining on the assumption that all sites at the metal surface have a uniform adsorption energy for each solute.

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. Hence, evaluation of the rate of nitrogen dissolution into molten iron is indispensable for efficient control of its nitrogen content, and many kinetic studies have been conducted. Nitrogen dissolution is known to have three steps, a mass transfer in molten iron, a chemical reaction at the surface and a mass transfer in the gas phase, respectively. Most of the researches have been performed by the sampling method in which it is difficult to focus only on the chemical reaction rate especially when the concentration of surface active elements are low. In order to know the maximum rate of nitrogen removal, it is important to investigate the rate constant of the chemical reaction and the pertinent effects of added elements.

An isotope exchange technique has an advantage in that the dissolution rate can be measured without any influence of liquid phase mass transfer. This measurement technique has been developed by Belton's group,^{3, 4)} and a few studies on the effect of surface active elements^{4, 7)} have been carried out.

We have also employed the technique in which the rate of change in the ratio of $^{30}N_2/^{28}N_2$ is monitored, and the effects of non-surface active elements on the nitrogen dissolution rate into molten iron alloys as well as those of surface active ones are summarized in the present study. The mechanisms of the effects of such elements on the reaction rate are discussed through

correlations with thermodynamic and physical properties.

2. Experimental

Since nitrogen dissolves into molten iron according to reaction (1), the rate of nitrogen dissolution, v (mol/cm²·s), is expressed by Eq. (2).

$$N_2(\text{gas}) = 2\bar{N} \text{ (in Fe)} \quad (1)$$

$$v = kP_{N_2} \quad (2)$$

where P_{N_2} (atm) is the partial pressure of nitrogen and k (mol/cm²·s·atm) is the rate constant of nitrogen dissolution reactions. Since three types of N_2 gas molecules, $^{28}N_2$, $^{29}N_2$, and $^{30}N_2$, exist in the gas phase, the following reactions can be considered as the nitrogen dissolution processes.

Considering a mass balance of $^{30}N_2$, Eq. (6) holds on the assumption that the composition of absorbed gas is not affected by desorbed gas, and the fraction of $^{30}N_2$ in the total absorbed nitrogen equals that in the ingoing nitrogen.

$$P_{N_2}V(^{30}F_i - ^{30}F_f)/RT = Av(^{30}F_i - ^{30}F_f) \quad (6)$$

where A (cm²) is the surface area of molten metal, V (cm³/s) is the volume flow rate, T (K) is the temperature of gas, R (82.1 (cm³·atm/K·mol)) is the gas constant, $^{30}F_{eq}$ is the equilibrium fraction of $^{30}N_2$, $^{30}F_i$, and $^{30}F_f$ are the fractions of $^{30}N_2$ in the ingoing and outgoing gases, respectively. Incorporating Eq. (2) into Eq. (6), the rate constant is represented by Eq. (7).

$$k = V(^{30}F_i - ^{30}F_f)/ART(^{30}F_i - ^{30}F_{eq}) \quad (7)$$

On the other hand, the rate constant equation introduced by Byrne and Belton was derived by assuming the complete mixing of gas at a metal surface and is represented by Eq. (8).

$$k = -V \ln \{ (^{30}F_f - ^{30}F_{eq}) / (^{30}F_i - ^{30}F_{eq}) \} / ART \quad (8)$$

^{*a)} Department of Metallurgy, Graduate School of Engineering, The University of Tokyo (7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan) (E-mail: morita@wood2.mm.t.u-tokyo.ac.jp)

Equation (7) gives a smaller value for the rate constant than Eq. (8) and its difference can be ignored when the difference between ^{30}Fi and ^{30}Ff is small.

An alumina crucible containing 30 g of metal samples was inserted into a transparent quartz reaction chamber and inductively heated. The experimental temperature was manually controlled between 1823 K and 2023 K within the accuracy of ± 3 K, monitored by a dual wavelength infrared pyrometer sighted onto the metal. The total gas flow rate was mainly 900 mL/min STP and changed from 700 to 900 mL/min STP for the experiments of non-surface active elements addition. Preceding the investigation of the effect of added elements, the rates of nitrogen dissolution into pure iron were measured at temperatures ranging from 1823 to 2023 K, and the subsequent experimental conditions, such as gas flow rate, were determined from their results. Figure 1 shows the dependence of the rate constant for high-purity iron on total volume flow rate $V_{\text{N}_2+\text{H}_2}$ at 1923, 1973, and 2023 K, which were investigated by changing nitrogen flow rate at a constant hydrogen flow rate, 500 cm³/min STP. At lower flow rates, smaller rate constants are observed because of insufficient supply of gases onto the metal surface. Accordingly, to eliminate the effect of gaseous mass transport, we need to measure at high flow rates, which give a constant value for the rate constant. From Fig. 1, the total flow rate of 900 cm³/min STP is shown to be enough to give a constant value for the rate constant. Based on these results and the fact that the rate constant is not dependent on nitrogen flow rate but on total flow rate,⁹⁾ subsequent measurements for non-surface active elements addition were made at total flow rate of 900 cm³/min STP ($V_{\text{N}_2}=200$ cm³/min STP, $V_{\text{H}_2}=700$ cm³/min STP). For the experiments of non-surface active elements addition, the total gas flow rate was changed from 200 to 900 mL/min STP since the reaction rates were slower.

A quadrupole type mass spectrometer (ANELVA, TE-360B) was used to measure ^{30}Ff and ^{30}Feq of the sample gas through a quartz capillary (0.35 mm o.d., 0.25 mm i.d., 1500 mm length).

Details on the preparation and analysis of the iron-M alloys are described elsewhere by the present authors.^{1), 2)}

Fig. 1. Dependence of the rate constant for pure iron on flow rate at 1923, 1973, and 2023 K.

3. Results and Discussion

The dependence of the rate constant for pure iron on temperature is shown in Fig. 2 with the values reported by other researchers. Here, the values reported by Kobayashi *et al.*⁹⁾ with the same technique and Eq. (9) were recalculated using Eq. (8) and are plotted in Fig. 2. From the results of the rate of nitrogen desorption under reduced pressures by Harashima *et al.*⁹⁾ and Yamamoto,¹⁰⁾ the rate constants of nitrogen dissolution were calculated using the equilibrium constant of Eq. (1) and are also shown in Fig. 2. The rate constant obtained by the present work is in excellent agreement with those by Kobayashi *et al.* and Harashima *et al.*, and a linear relationship is obtained as Eq. (9).

$$\log k (\text{mol/cm}^2 \cdot \text{s} \cdot \text{atm}) = -3300/T - 2.76 \quad (1823 \text{ to } 2023 \text{ K}) \quad (9)$$

The value by Yamamoto is for molten iron containing 10 ppm of oxygen and 4 ppm of sulfur measured at a pressure of about 10^{-8} to 10^{-6} atm using an electron-beam melting technique. Although it is larger than that in the present work, the difference is too small to consider an alternative reaction mechanism.

Dependences of the rate constant on Ti, Zr, V, and Cr concentrations are shown in Figs. 3, 4, 5, and 6, respectively. Formation of nitride restricted the concentration of Ti, Zr, and V. As seen in the figures, the rate constant of nitrogen dissolution increases linearly by the addition of Ti, Zr, V, and Cr for each temperature.

Fig. 2. Dependence of the rate constant of nitrogen dissolution into pure iron on temperature.

Fig. 3. Dependence of the rate constant of nitrogen dissolution on titanium concentration.

Fig. 4. Dependence of the rate constant of nitrogen dissolution on zirconium concentration.

Fig. 5. Dependence of the rate constant of nitrogen dissolution on vanadium concentration.

Fig. 6. Dependence of the rate constant of nitrogen dissolution on chromium concentration.

Titanium increased the dissolution rate most effectively and the rate constant for an Fe-0.08 mass pct Ti alloy is about 1.5 times larger than that of pure iron at 1873 K.

In Fig. 6, the rate constant obtained by Glaws and Fruehan⁷⁾ is smaller than that of the present work probably due to the larger amount of sulfur concentration in their experiment since they described that their sulfur contents were below 50 ppm. Namely, when the present results are revised using the equation representing the effect of sulfur suggested by Ban-ya *et al.*,¹¹⁾ the rate constant for an iron including 50 ppm sulfur at 1873 K gives the value of 1.8×10^{-5} (mol/cm²·s·atm), which is in reasonable agreement with the value of Glaws *et al.*

In this work, the nitrogen dissociation rate at a bare metal surface was hardly contaminated by surface active elements because oxygen and sulfur contents of the metal were very low. Accordingly, we may consider that nitrogen adsorption and dissociation at an adsorption site surrounded by added elements, such as Ti, Zr, V, and Cr, are easier than at that surrounded by iron. This effect is included in the mechanism for nitrogen dissolution into molten iron alloy, as subsequently stated. The reaction for nitrogen dissolution into a metal is described by Eq. (1). Equation (2) can be divided into the two steps represented by Eqs. (10) and (11), where $\square$ and superscript *ad* denote a vacant site on the metal surface and the nitrogen adsorbed on the vacant site, respectively.

Assuming that the reaction represented by Eq. (10) is a rate determining step with the step given by Eq. (11) at virtual equilibrium, the rate equation for Eq. (10) can be described by Eq. (12) or (13).

$$v = k_0 P_{\text{N}_2} a_{\square}^2 \quad (12)$$

$$= k_0 P_{\text{N}_2} (K_{11} a_{\text{N}^{\text{ad}}}^2 / a_{\text{N}}^2) \quad (13)$$

where k_0 is the forward rate constant for Eq. (10) and K_{11} is the equilibrium constant for Eq. (11). Combining Eqs. (12) and (13) with Eq. (2), k is expressed by Eq. (14) or (15).

$$k = k_0 a_{\square}^2 \quad (14)$$

$$= k_0 (K_{11} a_{\text{N}^{\text{ad}}}^2 / a_{\text{N}}^2) \quad (15)$$

According to Eq. (15), alloying elements may affect the dissolution rate of nitrogen through affecting the activity of vacancy site relative to that of pure iron (a_{Fe}) at the metal surface.

Similarly, the results of a desorption rate study are discussed in the following. Assuming that the rate-determining step for desorption is the same as that for dissolution with Eq. (11) being at equilibrium, the desorption rate, v' , is expressed by Eq. (17), being proportional to the square of nitrogen concentration as seen in Eq. (18), where k' is the rate constant for the reverse reaction of Eq. (10) and f_{N} is the activity coefficient of nitrogen in molten iron. Hence, the rate constant k_d is represented by Eq. (19).

$$v' = k' a_{\text{N}^{\text{ad}}}^2 \quad (16)$$

$$= k' a_{\text{N}}^2 f_{\text{N}}^2 [\text{pct N}]^2 / K_{11} \quad (17)$$

$$= k_d [\text{pct N}]^2 \quad (18)$$

$$k_d = k' a_{\square}^2 f_{\text{N}}^2 / K_{11} \quad (19)$$

Using the relationships of Eqs. (20) and (21), Eq. (19) may be rewritten as Eq. (22).

$$k_0 / k' = K_{10} \quad (20)$$

$$K_{11} = K_{10} K_{11} \quad (21)$$

$$k_d = k_0 a_{\square}^2 f_{\text{N}}^2 / K_{11} \quad (22)$$

$$= k f_{\text{N}}^2 / K_{11} \quad (23)$$

According to Eq. (22), alloying elements should affect not only f_{N} but also $a_{\square}^2$ in the desorption rate studies. For this confirmation, the dissolution rate constant k was calculated from the data of the desorption rate constant for Fe-Cr alloys k_d measured by Ban-ya *et al.*,¹¹⁾ who employed the conventional method, using Eq. (23) with known K_{11} ¹²⁾ and f_{N} ¹³⁾ values. The calculated k values are also shown in Fig. 7 with the present data at 1873 K. The consistence of the results obtained by two entirely different experimental techniques indi-

cates that the proposed mechanism of the dissociation and adsorption of nitrogen is valid and they are rate-determined by Eq. (10).

As discussed above, the effect of added elements was put in order using the concept of the activity of vacant site. In Fig. 8, the effect of Ti, V, and Cr at 1873 K and Zr at 1923 K is shown by plotting k/k (pure iron) against their concentration. The effect of carbon by Tsukihashi and Fruehan⁶⁾ is also shown in Fig. 8. The slopes of the straight lines in Fig. 8 correspond to $a_V^2/(mass\ pct\ M)$ according to Eq. (14). These values are compared in Table 1 with the interaction parameters for the elements with nitrogen. Although the quantitative correlation cannot be observed and the data for interaction parameter are not very accurate, an element that has a stronger affinity for nitrogen generally tends to increase the nitrogen dissolution rate more effectively by increasing the activity of vacant site.

The effect of oxygen on the rate constant of nitrogen dissolution is shown in Fig. 9. Analyzed oxygen contents of the samples were used for plotting the present

Fig. 7. Comparison of the rate constant for Fe-Cr alloy with the desorption rate data at 1873 K.

Fig. 8. The effect of added elements on the rate constant of nitrogen dissolution.

Table 1. Interaction Parameters of Added Elements with Nitrogen and the Slopes of the Straight Lines Described in Fig. 8 for Each Element

Added elements	e_N (1873 K)	a_N^2 [% added elements]
Ti	-0.6	6.5
Zr	-0.63	0.58
V	-0.123	0.12
Cr	-0.046	0.016
C	0.13	0

data. The solid line was drawn on the basis of the equation representing the effect of surface active solute on the rate, which will be discussed below. The rate of nitrogen dissolution decreases by increasing oxygen content. The rate constant is about 1×10^{-5} mol/cm²·s·atm at 1973 K when the oxygen content is 0.010 mass pct.

From the results of the rate of nitrogen desorption under reduced pressures at 1873 K by Harashima *et al.*,⁹⁾ the rate constant of nitrogen dissolution was calculated and plotted in Fig. 9, using equilibrium constant of Eq. (1). Ban-ya *et al.*¹⁰⁾ obtained the dependence of a desorption rate constant on oxygen and sulfur contents of iron at 1873 K using the sampling method. The corresponding rate constant equation of nitrogen dissolution was derived from their results, which is also shown by a broken line in Fig. 9.

Seeing that the rate constant at 1973 K is about 1.2 times as large as that 1873 K, the rate constants of the present work seem to be still in reasonable agreement with those of Harashima *et al.* and are larger than those from the equation of Ban-ya *et al.* in a low oxygen concentration range ([mass pct O] < 0.015).

The dependences of the rate constant of nitrogen dissolution on selenium and tellurium concentration are shown in Figs. 10 and 11, respectively. The plot in Fig. 10 is drawn using logarithm of k as the vertical axis for comparison with other data. Analyzed selenium or tellurium contents of the samples after experiments were used for plotting the present data. Mowers

Fig. 9. Dependence of the rate constant of nitrogen dissolution in liquid iron on oxygen concentration.

Fig. 10. Dependence of the rate constant of nitrogen dissolution in liquid iron on selenium concentration.

Fig. 11. Dependence of the rate constant of nitrogen dissolution in liquid iron on tellurium concentration.

and Pehlke¹⁴⁾ measured the effect of selenium and tellurium on the rate by Sieverts method at 1873 K and their results are also shown in Figs. 10 and 11. Tsukihashi and Fruehan⁶⁾ measured the effect of tellurium on the rate constant of nitrogen dissolution into carbon saturated molten iron at 1723 K by the same technique as used in the present work and it is also shown in Fig. 11. It is clearly found that both selenium and tellurium retard the reaction of nitrogen with liquid iron significantly. The solid lines in Figs. 10 and 11 are also drawn on the basis of a model discussed below.

It was confirmed in the present work that the rate was strongly affected by oxygen, selenium, and tellurium in the metal. The effect of these surface active species on the chemical rate of gas-metal reaction can be explained as follows. As discussed in case of the non-surface active elements, the effect of surface active elements can be explained by the change in the activity of $a_{\square}$ with physical reason as follows. The effects of oxygen, selenium, and tellurium on $a_{\square}$ due to their thermodynamic affinities for nitrogen are assumed negligibly small because their contents are very low. Accordingly, the depression of the rates is considered to be caused from the blockage of the surface sites by such surface active solutes, as has been previously proposed in the literatures. This consideration has been fully discussed in the previous paper²⁾ and it is concluded that the rate determining step of the nitrogen dissolution could be the reaction expressed as Eq. (24), a part of reaction (10), by comparing the adsorption coefficients of each element with those reported from surface tension data,^{15), 16)} which is excluded in the present discussion. Hence, the solid lines in Figs. 9, 10, and 11 were drawn based on Eq. (25), where k° and K_i denote the constant value and adsorption coefficient of solute i on iron, respectively.

$$k = k^{\circ} / (1 + K_i [\text{pct } i])^2 \quad (25)$$

The values of K_{O} , K_{Se} , and K_{Te} are calculated to be 144, 1120, and 1640, respectively. This means that selenium and tellurium have much greater influence than oxygen and the degree of retarding effect is large in the order of tellurium, selenium and oxygen.

4. Conclusions

The rate of nitrogen dissolution into molten iron-M

(M: Ti, Zr, V, Cr, O, Se, and Te) alloys at temperatures ranging from 1873 to 2023 K has been measured using an isotope exchange reaction, yielding the following results:

1. The rate of nitrogen dissolution into molten iron increases by adding an element such as Ti, Zr, V, and Cr with stronger affinity for nitrogen than Fe, which is considered to be due to the increase in the activity of vacant site at the metal surface. The consistence of the present results with those of desorption studies is shown.

2. A correlation between the degree of the rate increase by non-surface active elements addition and their interaction parameters with nitrogen is observed.

3. The rate constant of nitrogen dissolution measured at low oxygen concentration (< 0.015 mass pct) is larger than the value which was extrapolated from the one obtained by previous investigators at atmospheric pressure and is in reasonable agreement with a value calculated from desorption rate under reduced pressures, in which gas phase mass transfer effects are minimal.

4. Selenium and tellurium more significantly retard the reaction of nitrogen with liquid iron than oxygen, and the degree of retarding effect is large in the order of tellurium, selenium and oxygen.

References

- 1) H. Ono, K. Morita, and N. Sano, *Metall. Mater. Trans. B*, **26**, 991 (1995).
- 2) H. Ono, H. Fukagawa, K. Morita, and N. Sano, *Metall. Mater. Trans. B*, **27**, 848 (1996).
- 3) G. R. Belton, *Metall. Trans. B*, **24**, 241 (1993).
- 4) M. Byrne and G. R. Belton, *Metall. Trans. B*, **14**, 441 (1983).
- 5) P. C. Glaws and R. J. Fruehan, *Metall. Trans. B*, **16**, 551 (1985).
- 6) F. Tsukihashi and R. J. Fruehan, *Trans. Iron Steel Inst. Jpn.*, **27**, 858 (1987).
- 7) P. C. Glaws and R. J. Fruehan, *Metall. Trans. B*, **17**, 317 (1986).
- 8) A. Kobayashi, F. Tsukihashi, and N. Sano, *Iron Steel Inst. Jpn. Int.*, **33**, 1131 (1993).
- 9) K. Harashima, S. Mizoguchi, H. Kajioka, and K. Sakakura, *Tetsu-to-Hagané*, **73**, 1559 (1987).
- 10) K. Yamamoto, Master of Engineering Thesis, The University of Tokyo (1993).
- 11) S. Ban-ya, F. Ishii, Y. Iguchi, and T. Nagasaka, *Metall. Trans. B*, **19**, 233 (1988).
- 12) The Japan Society for the Promotion of Science, The 19th Committee on Steelmaking: Steelmaking Data Sourcebook, Gordon and Breach Science Publishers, New York, NY (1988), pp. 21–26 and pp. 217–234.
- 13) F. Ishii, Y. Iguchi, and S. Ban-ya, *Trans. Iron Steel Inst. Jpn.*, **26**, 128 (1986).
- 14) R. G. Mowers and R. D. Pehlke, *Metall. Trans. B*, **1**, 51 (1970).
- 15) K. Ogino, S. Hara, T. Miwa, and S. Kimoto, *Tetsu-to-Hagané*, **14**, 2012 (1979).
- 16) K. Ogino, K. Nogi, and O. Yamase, *Tetsu-to-Hagané*, **2**, 179 (1980).

Keywords: Nitrogen, Isotope exchange, Kinetics, Iron, Dissolution rate