Nitrogen Dissociation Rate at Solid Surface of Ferrous Alloys

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The nitrogen dissociation rates at the surface of solid iron–M (M: Si, Al, Mn, Cr, and Ti) alloys have been measured by an isotope exchange technique at temperatures ranging from 1 473 to 1 798 K. From the present results, the rate constant of nitrogen dissociation at the surface of pure solid iron is derived as 1.97×10^{-5} [mol/(cm²·s·atm)] at 1 773 K and the apparent activation energies for the nitrogen dissociation at the surfaces of δ -Fe and γ -Fe ([mass ppm O]=10.3, [mass ppm S]=7) at $P_{N_2}=0.05$ (atm) are calculated as 127 and 162 (kJ/mol), respectively. The effects of the alloying elements on the nitrogen dissociation rate at the surface of solid iron have the same tendency as those at the surface of liquid iron investigated previously by a similar method to the present study; the nitrogen dissociation rate is increased by the addition of Mn, Cr, or Ti and is decreased by the addition of Si or Al. The degree of the effects of increasing or decreasing the rate by the alloying elements for the solid iron is found to be smaller than that for the liquid iron.

KEY WORDS: nitrogen dissociation; isotope exchange; activation energy; solid iron; rate constant; chemical reaction; alloying element.

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} Byrne and Belton³) firstly measured the nitrogen dissolution rate by an isotope exchange technique and showed the effect of carbon is negligibly small up to the addition of 4.3 mass %. Glaws and Fruehan⁴) measured the nitrogen dissolution rate by both sieverts and isotope exchange techniques and compared those results. The dissociation of nitrogen molecule at the surface of molten iron was proven to be a rate-limiting step. Ban-ya *et al.*⁶) measured the nitrogen removal rate from molten iron, the effects of C and Cr upon which were investigated. Kobayashi *et al.*⁷) measured the nitrogen dissolution rate by the isotope exchange technique and showed the reaction is a first order with respect to the nitrogen partial pressure and the activation energy is calculated 95 kJ/mol. By one of the present authors and others,⁸) the effects of Ti, Zr, V, and Cr on the rate were previously investigated by the same technique. It is shown that the elements which have stronger affinity with nitrogen than iron increase the rate and the reason is explained by an increase of the activity of the vacant site at the metal surface. A correlation between the effects of increasing the rate and the interaction parameters of the additive elements with nitrogen is also shown. Subsequently, Morita *et al.*¹¹) investigated the effects of Al, Si, and B on the rate. It was shown that these elements de-

crease the rate because of the weaker affinity with nitrogen than iron.

As described above and reviewed by Belton,¹²) a large number of researches of nitrogen reaction rate with molten iron have been conducted. On the other hand, the reaction rate of nitrogen at the surface of solid iron has been investigated over 1960 to 1970's. Turkdogan and Grieveson¹³) measured the nitrogen transfer rate for γ -Fe in N_2 – H_2O – H_2 mixtures at 1 273 K and showed the rate is proportional to the square root of the nitrogen partial pressure and is inversely proportional to the oxygen activity. Grabke^{14,15}) measured the nitrogen dissociation rate at iron foils at 973 to 1 273 K by the measurements of the electrical resistance of the iron foils in the flow apparatus in N_2 – H_2 –(H_2O) mixtures and also showed the retarding effect of oxygen on the rate. These studies for solid iron are conducted at comparatively lower temperatures and it cannot be necessarily said that these results agree with each other, since the metal phase mass transfer may limit the rate in the measurements. Moreover, when the nitrogen activity decreases by the solutes, which have the stronger affinity with nitrogen, such as Cr and Ti, it is considered important to understand the chemical reaction rates at the surface of solid iron alloys for the difficulty of decreasing the nitrogen contents. In the present study, the nitrogen dissociation rates at the surface of solid iron–M (M: Si, Al, Mn, Cr, and Ti) alloys have been measured by the isotope exchange technique, in which the measured values are not affected by the metal phase mass transfer in principle. The present results are compared with the results for the previous studies for solid iron at lower temperatures^{13–15}) and for molten iron based alloys^{8,11}) car-

ried out by a similar method to the present work.

2. Experimental

An alumina crucible (26 mm O.D., 20 mm I.D.) containing high-purity electrolytic iron([mass ppm S]=7, [mass ppm P]=3) weighing 100 g was inserted into a transparent quartz furnace tube and inductively heated up to 1873 K in an Ar-H₂ mixture and the iron sample was sufficiently deoxidized with H₂. After it was held for 1 h at 1873 K, the iron sample was cooled rapidly and was perpendicularly cut off at the height of 5 mm. The surface of the iron sample was ground on a polishing board of No. 600. Using the iron sample preliminary prepared above, the measurements were conducted as follows. The sample was put in the alumina crucible, the size of which was equal to that used for the preparation and the clearance between the crucible and the sample was filled with alumina powder. The alumina crucible was inserted into the transparent quartz reaction chamber and inductively heated in a hydrogen to the experimental temperature, which was changed from 1473 to 1798 K. The temperature of the sample was monitored by a dual wavelength infrared pyrometer, sighted onto the metal surface and adjusted manually to the desired temperature within an error of ± 3 K. After reaching the experimental temperature, the ingoing gas was changed to an Ar-H₂-N₂ mixture, and the measurements of the nitrogen dissociation rate on the metal sample were started. The nitrogen in the ingoing gas contains about 1 at% nitrogen isotope, ³⁰N₂. The total gas flow rate was 1 000 cm³/min (s.t.p.) ($\bar{V}_{\text{Ar}}=750$, $\bar{V}_{\text{H}_2}=200$, $\bar{V}_{\text{N}_2}=50$ cm³/min (s.t.p.)). The tip of the gas inlet tube (14.9 mm O.D., 10.8 mm I.D.) was located 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 fraction of isotope nitrogen in the ingoing and outgoing gases, ³⁰F_i and ³⁰F_f, through a quartz capillary tube (0.375 mm O.D., 0.075 mm I.D.). The measurements were finished when the fraction of ³⁰N₂ for total nitrogen (²⁸N₂+²⁹N₂+³⁰N₂) in the outgoing gas became unchanged and showed a constant value for 10 min, 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. Each oxygen content of the samples used in the present work is shown in **Table 1**. To prepare the alloying samples, the additive elements were initially mixed with the electrolytic iron in the alumina crucible before being inserted in the furnace.

As well as the case of the dissolution in the molten iron, when nitrogen dissolves into the solid iron, it is accompanied by the adsorption and dissociation of nitrogen at the metal surface. Accordingly, the same equation for the molten iron can be applied for the solid iron. The derivation of the equation for calculating a rate constant has been given elsewhere^{3,7,8,11)} and the summary is briefly described here. By considering a mass balance of ³⁰N₂, the following equation holds on the assumption that the fraction of ³⁰N₂ in the total absorbed nitrogen is equal to that in the ingoing nitrogen:

$$\frac{P_{\text{N}_2} \bar{V}}{RT} (^{30}F_i - ^{30}F_f) = Av(^{30}F_i - ^{30}F_{\text{eq}}) \quad \text{.....(1)}$$

Table 1. The oxygen contents of the iron based alloy samples used in the present work.

Sample	mass ppm O
Fe (Flow rate)	11.9
Fe (Temperature)	10.3
Fe - 3 mass%Ti	11.5
Fe - 10 mass%Cr	23.2
Fe - 20 mass%Cr	25.9
Fe - 3 mass%Mn	10.2
Fe - 3 mass%Al	11.8
Fe - 1 mass%Si	12.8
Fe - 3 mass%Si	14.7

where P_{N_2} denotes the partial pressure of nitrogen (atm), A the surface area of solid metal (cm²), $\bar{V}$ the volume flow rate (cm³/s), T the temperature of gas (K), R the gas constant [$=82.1$ (cm³·atm/K·mol)], $^{30}F_{\text{eq}}$ the equilibrium fraction of ³⁰N₂, and $^{30}F_i$ and $^{30}F_f$ the fractions of ³⁰N₂ in the ingoing and outgoing gases, respectively. Since nitrogen dissociates at the metal surface according to Eq. (2), the rate of nitrogen dissociation v [mol/(cm²·s)], which is a first order with respect to the partial pressure of nitrogen, is expressed by Eq. (3),

$$\text{N}_2(\text{g}) = 2\text{N}(\text{at the metal surface}) \quad \text{.....(2)}$$

$$v = kP_{\text{N}_2} \quad \text{.....(3)}$$

where k is the rate constant of nitrogen dissociation [mol/(cm²·s·atm)]. Substitution of Eq. (3) into Eq. (1) gives the rate constant as follows:

$$k = \frac{\bar{V}}{ART} \cdot \frac{^{30}F_i - ^{30}F_f}{^{30}F_i - ^{30}F_{\text{eq}}} \quad \text{.....(4)}$$

3. Results and Discussion

3.1. Nitrogen Dissociation Rate at the Surface of Pure Solid Iron

Prior to the investigation of the effects of alloying elements, the rate of nitrogen dissociation at the surface of pure solid iron was measured at temperatures ranging from 1473 to 1773 K, and the subsequent experimental conditions, such as the gas flow rate, were determined from those results. Figure 1 shows the dependence of the rate constant for high-purity iron on total flow rate, $\bar{V}_{\text{N}_2+\text{H}_2+\text{Ar}}$, at 1773 K, which is investigated by changing argon flow rate at constant hydrogen and nitrogen flow rates ($\bar{V}_{\text{H}_2}=200$, $\bar{V}_{\text{N}_2}=50$ cm³/min (s.t.p.)). At lower flow rates, smaller rate constants are observed because of insufficient supply of the gases onto the metal surface. Accordingly, we need to measure at higher flow rates, which give a constant value for the rate constant. From **Fig. 1**, the total flow rate of 1 000 cm³/min (s.t.p.) is shown to be necessary to eliminate the effect of gaseous mass transfer as much as possible. Based on these results, the subsequent measurements were carried out at a total flow rate of 1 000 cm³/min (s.t.p.) ($\bar{V}_{\text{H}_2}=200$, $\bar{V}_{\text{N}_2}=50$, $\bar{V}_{\text{Ar}}=750$ cm³/min (s.t.p.)). The dependence of the rate constant for pure solid iron on temperature is shown in **Fig. 2** with the values for pure liquid iron^{3,8,11)} obtained by the same technique. The cause of the discrepancy among the values for pure liquid iron, in particular, between the data by Byrne *et al.*³⁾ and the others,^{8,11)} has not been clarified; it

Fig. 1. Dependence of the rate constant for pure iron on total flow rate, $\bar{V}_{N_2+H_2+Ar}$ at 1773 K.

Fig. 2. Dependence of the rate constant of nitrogen dissociation at the surface of pure iron on temperature.

is considered that the difference may be explained by the oxygen content of metal,^{7,11)} which is not mentioned in the article of Byrne *et al.* From this point of view, the present results should be compared with the values by Morita *et al.*¹¹⁾ or one of the present authors and others,⁸⁾ because the oxygen content of the present work, 10.3 mass ppm, is between that of the former,¹¹⁾ 7 to 8 mass ppm, and that of the latter,⁸⁾ 16 mass ppm. It is found from Fig. 2 that the rate constants obtained by the present work are a little smaller than the values expected by extrapolating the values for the molten iron to lower temperatures and the logarithms of the rate constants show a linear relationship against the reciprocal of temperature. The linear relationships obtained by the regression analysis of the present results for δ -Fe and γ -Fe are described respectively as follows:

$$\log k_{\delta\text{-Fe}} = -\frac{6640}{T} - 0.954 \quad (1673 \text{ to } 1773 \text{ K}) \dots (5)$$

Table 2. The activation energies for the reaction of nitrogen dissociation at the iron surfaces.

	Phase	Temperature (K)	Activation energy (kJ/mol)
Present work (δ -Fe)	Solid	1673 to 1773	127
Present work (γ -Fe)		1473 to 1623	162
Grabke ¹⁴⁾ (γ -Fe)		1185 to 1273	220
Grabke ¹⁴⁾ (α -Fe)		973 to 1185	235
Byrne <i>et al.</i> ³⁾	Liquid	1823 to 1923	121
Tsukihashi <i>et al.</i> ⁵⁾ (Fe-C _{saturated})		1723 to 1873	113
Kobayashi <i>et al.</i> ⁷⁾		1823 to 1923	95
Previous work ⁸⁾		1823 to 2023	63
Morita <i>et al.</i> ¹¹⁾		1873 to 2023	52

$$\log k_{\gamma\text{-Fe}} = -\frac{8460}{T} + 0.230 \quad (1473 \text{ to } 1623 \text{ K}) \dots (6)$$

The reaction rate of nitrogen dissociation at the surface of solid iron is largely affected by the amount of adsorbed solutes, which block the reaction sites at the surface. It is known that the adsorbed oxygen, sulfur, and nitrogen itself have large effects on the reaction rate of nitrogen dissociation at the surface of solid iron, in particular. The oxygen and sulfur contents of the iron used in the present work are 10.3 and 7 mass ppm, respectively, and the measurements were conducted at $P_{N_2} = 0.05$ (atm). From Eqs. (5) and (6), the apparent activation energies for the reaction of nitrogen dissociation at the surface of δ -Fe and γ -Fe ([mass ppm O] = 10.3, [mass ppm S] = 7) at $P_{N_2} = 0.05$ (atm) are calculated to be 127 and 162 kJ/mol, respectively. The activation energies for the molten iron reported by several investigators are shown in Table 2 with the present results. As described above, the amounts of the adsorbed solutes at the surface of the sample have a large effect on the calculated activation energies; it is necessary to know the difference of the solutes contents when those values are discussed. By comparing the apparent activation energies for δ -Fe and γ -Fe derived in the present work with those for the molten iron,^{8,11)} the oxygen contents of which are almost the same as that of the present work, the values for the present work are found to be larger than those for the molten iron from Table 2. One of the reasons of their difference is considered to be caused by the temperature dependence of the amounts of the adsorbed solutes.

Grabke¹⁴⁾ studied the nitrogen dissociation rate at iron foils in a N_2 - H_2 mixture by the measurements of the electrical resistance of the iron foils. The results are shown by the dashed and dotted lines in Fig. 3 with the present results. The equations for α -Fe and γ -Fe by Grabke are represented respectively as follows:

$$\log k'_{\alpha} = -\frac{12280}{T} + 1.643 \quad (973 \text{ to } 1185 \text{ K}) \dots (7)$$

$$\log k'_{\gamma} = -\frac{11470}{T} + 1.079 \quad (1185 \text{ to } 1273 \text{ K}) \dots (8)$$

From these equations, the apparent activation energies for α -Fe and γ -Fe are calculated as 235 and 220 kJ/mol, respectively, which are larger than the values derived in the present study, as shown in Table 2. It can be found from

Fig. 3. Dependence of the rate constant of nitrogen dissociation at the surface of pure solid iron on temperature.

Fig. 3 that the present results are about two orders of magnitude higher than the data of Grabke, when the present results are extrapolated to lower temperatures. However, the existence of the adsorbed solutes taken into account, the difference may not be so large; the retarding effect of the adsorbed solutes, such as oxygen, on the rate appears more clearly at lower temperatures, which is confirmed by the measurements in $N_2-H_2O-H_2$ mixtures by Grabke.¹⁵⁾ The kinetics of nitrogenization and denitrogenization of γ -Fe is also studied under controlled oxygen partial pressures by Turkdogan and Grieveson¹³⁾ at 1273 K using iron strips. The measured rates are shown to be proportional to the square root of the nitrogen partial pressure, which suggests that the transfer of nitrogen atoms limits the reaction rate. For example, the rate constant, which is proportional to the first order of the nitrogen concentration in metal, is given to be 1.33×10^{-6} cm/s under the condition of $P_{H_2O}/P_{H_2} = 0.035$. Although the value cannot be converted to the rate constant directly comparable with the present results, the value is estimated much smaller than the present results. The discrepancy is considered to be probably caused by the oxygen contents and the difference of the rate limiting stage of the reaction.

Here, the effect of gaseous phase mass transfer on the rate constant obtained by the present work is estimated. According to Eq. (9), the Sh number is affected by the gas flow rate at the present condition ($Re = 6.87$), and it can be calculated using the parameters shown subsequently.

$$Sh = (k_g d / D) = (0.27 \pm 0.07) (r_s / d)^{-1.5} Re^{0.76} Sc^{0.5} \dots (9)$$

where k_g (cm/s), d (cm), D (cm²/s), r_s (cm) denote the mass transfer coefficient of gas phase, the diameter of the gas blowing tube, the diffusion coefficient of the gas, and the radius of alumina crucible, respectively. In the present work, $d = 1.08$ (cm), $r_s = 1.0$ (cm), and D can be evaluated as 5.55 cm²/s from the Fuller's equation.¹⁷⁾ The Sh number is calculated as 0.100 and k_g / RT becomes 2.00×10^{-4} mol/(cm²·s·atm) at 1773 K, while the rate constant for the pure

Table 3. The effect of the gaseous mass transfer on the rate constant of nitrogen dissociation in each experiment at 1773 K.

Sample	k [mol/(cm ² ·s·atm)]	k' [mol/(cm ² ·s·atm)]	$(k' - k) / k$ (%)
	Measured	Converted	
Fe	1.97×10^{-5}	2.18×10^{-5}	10.9
Fe-3%Ti	2.40×10^{-5}	2.72×10^{-5}	13.6
Fe-10%Cr	2.22×10^{-5}	2.49×10^{-5}	12.5
Fe-20%Cr	2.48×10^{-5}	2.83×10^{-5}	14.1
Fe-3%Mn	2.04×10^{-5}	2.27×10^{-5}	11.3
Fe-3%Al	1.61×10^{-5}	1.75×10^{-5}	8.73
Fe-1%Si	1.49×10^{-5}	1.61×10^{-5}	8.07
Fe-3%Si	1.02×10^{-5}	1.07×10^{-5}	5.36

Fig. 4. Dependence of the rate constant of nitrogen dissociation at the surface of Fe-Si alloy on temperature.

solid iron was observed to be 1.97×10^{-5} mol/(cm²·s·atm) at 1773 K. The derived rate constant would be affected at most about 11% by the mass transfer in gas phase, and the chemical reaction rate constant would be converted as 2.18×10^{-5} mol/(cm²·s·atm). Under the assumption of Eq. (9) applicable to all the present experiments, the effect of the gaseous mass transfer on the rate constants derived from the present experimental results was estimated in the same way. The results are shown in Table 3. The effect of the gaseous mass transfer on the measured rate constants can be estimated to be at most 15% from Table 3.

3.2. Effects of Alloying Elements

The dependence of the rate constants for Fe-Si alloys on temperature is shown in Fig. 4 with the values for pure solid iron. The rate constants for Fe-Si alloys are smaller than those for the pure solid iron at same temperature. It can be considered silicon in iron has the effect of decreasing the rate of nitrogen dissociation. The dependence of the rate constant on silicon concentration is shown in Fig. 5; the effect of silicon addition is appeared more clearly as the temperature increases. It is generally considered that the effect of atomic interaction becomes smaller as the temperature is raised and this seems to contradict the present results. The reason can not be explained at present and it is necessary to clarify the temperature dependence of the interaction for further discussion. The variation of the rate

Fig. 5. Dependence of the rate constant of nitrogen dissociation on silicon content of iron.

Fig. 6. Dependence of the rate constant of nitrogen dissociation on the additive element content of iron at 1773 K.

constant with the contents of the alloying elements at 1773 K is shown in Fig. 6. From Fig. 6, the rate constant of nitrogen dissociation is found to be increased by the addition of Ti, Cr, and Mn. On the other hand, the addition of Si and Al causes the decrease of the rate of nitrogen dissociation. These tendencies for the effect of the alloying elements are equal to the results for the molten iron.^{8,11)} The effects of the alloying elements on the reaction rate at 1773 K are compared in Fig. 7, in which the effects are shown at the additive concentration range of less than 0.5 mass%. The rate constant is demonstrated as a relative value to that for pure iron. It is found from Fig. 7 that, among the alloying elements investigated in the present work, the promoting effect of Ti is larger than that of Cr and Mn, which have almost the same effect, and the retarding effect of Si is larger than that of Al. The values for iron-0.5mass%M (M: Si, Al, Mn, Cr, and Ti) alloys are compared with the previous work for the molten iron^{8,11)} in Table 4. From Table 4, in the addition of the elements with the promoting effect on the reaction rate (Ti, Cr, and Mn), the value for the liquid iron alloy is larger than that for the

Fig. 7. Effect of the additive elements on the dissociation rate constant of nitrogen dissociation at the iron surface at 1773 K.

Table 4. The relative values for the rate constant of Fe-0.5 mass%M (M: Ti, Cr, Mn, Al, and Si) to that for pure iron, $k/k_{\text{pure iron}}$.

Phase	Present work	Previous work ⁸⁾ Morita et al. ¹¹⁾	
		1873 K	1973 K
Ti	1.037	4.500	-
Cr	1.006	1.008	-
Mn	1.006	-	-
Al	0.969	-	0.875
Si	0.866	-	0.861

solid. On the other hand, in the addition of the elements with the retarding effect on the reaction rate (Al and Si), the value for the liquid iron alloy is smaller. Therefore, it can be considered the effects of the alloying elements on the reaction rate of nitrogen dissociation are larger at the surface of the liquid iron in comparison with the solid iron. It is found that there is a large difference between the present result and the previous one for the molten iron⁸⁾ at the relative value for Fe-0.5mass%Ti. Although the reason of this difference can not be explained explicitly, it may be caused by the difference of the amount of the added titanium; *i.e.*, the added titanium was less than 0.1 mass% in the experiment for liquid iron⁸⁾ and the extrapolated value is tabulated in Table 4, while the present experiment is carried out by adding titanium up to 3 mass%. Moreover, the oxygen concentration of the sample may be the cause of this difference because it is analyzed 115 mass ppm for Fe-Ti alloy in the present work, while the sample for the liquid alloy was 15 to 20 mass ppm.

4. Conclusions

The nitrogen dissociation rates at the surface of solid iron-M (M: Si, Al, Mn, Cr, and Ti) alloys have been measured by an isotope exchange technique at temperatures ranging from 1473 to 1798 K. The following results have been obtained.

(1) The nitrogen dissociation rate increases by the addition of titanium, chromium, and manganese. Among them,

the promoting effect of titanium is the largest and chromium and manganese have almost the same effect.

(2) The nitrogen dissociation rate decreases by the addition of silicon and aluminum. The retarding effect of silicon is larger than that of aluminum.

(3) The effects of the alloying elements on the nitrogen dissociation rate at the surface of solid iron have the same tendency as those at the surface of liquid iron. The degree of the effects of increasing or decreasing the rate for the solid iron is smaller than that for the liquid iron.

(4) The apparent activation energies for the nitrogen dissociation at the surface of δ -Fe and γ -Fe ([mass ppm O]=10.3, [mass ppm S]=7) at $P_{N_2}=0.05$ (atm) are calculated as 127 and 162 kJ/mol, respectively. The values are larger than that for the molten iron.

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