Kinetic Study on Surface Dissolution of Nitrogen on Liquid Steel by Isotope Exchange Technique

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The kinetic study of the nitrogen dissolution into the molten steel was investigated by an isotope exchange technique. The effects of O, S, C, B, and Mn addition on surface reaction have been considered at 1873 K. Experimental results show that the rate determining step of nitrogen dissolution into molten Fe–O–S alloys would be dissociation reaction and the rate constant on bare surface of the liquid steel (k^0) is 3.84×10^{-5} (mol/cm²·s·atm). The adsorption coefficients for oxygen, sulfur, and boron which were applied the dissociation determining model were calculated to be $K_O=120$, $K_S=65$, and $K_B=0.9$, respectively. In case of manganese addition, the rate constant can be increased with increasing the content of manganese. It seems that rate constant of bare surface of Fe–Mn alloy should be affected by addition of manganese.

KEY WORDS: kinetics; molten steel; nitrogen; isotope exchange reaction; surface dissolution; adsorption coefficient.

1. Introduction

Novel alloy design concepts such as a lean alloying with light elements (boron, nitrogen, and the like) have recently been proposed to satisfy the increasing demands for the critical properties of steel products. Nitrogen particularly plays a pronounced role in enhancing the mechanical properties of steel, such as nitrogen steel. For example, boron additions produce superior ductility and toughness to that in conventional low-carbon steels partly due to the formation of BN precipitates.^{1–4)} Among the interstitial elements in steels, nitrogen has widely been known as one of the most difficult elements to control because it is easily absorbed into molten steel from the atmosphere during steel refining processes.⁵⁾ Thus, great attention has been paid to preventing nitrogen dissolution from air for producing hyper-clean steels.

A surface reaction of nitrogen on liquid steel and the effect of alloying elements on the reaction kinetics have been investigated by numerous researchers.^{6–12)} The dissolution of nitrogen obeys the Sieverts' law with thermodynamic equilibrium. Therefore, many researchers used the Sieverts' technique for measuring the rate of absorption or desorption of nitrogen in liquid iron and its alloys. They also determined the effects of surfactive and alloying elements on these rates. However, these results of absorption or desorption rate might include a rate of surface reaction which can be divided as adsorption, dissociation, dissolution and desorption between nitrogen molecules and iron melts. In order to elucidate the mechanism of nitrogen dis-

solution and the maximum rate of nitrogen removal, the rate constant of this chemical reaction should be known.

Recently, the method of isotope exchange in studies on the nitrogen dissolution rates has been used to measure only the rate of chemical reaction on the surface of molten steel.^{13,14)} Previous experimental results from the isotope exchange technique indicated that nitrogen dissolution was a first order reaction¹⁵⁾ in terms of nitrogen partial pressure and that its rates strongly depended on surface active elements such as oxygen and sulfur.^{11,13,16)} Glaws and Fruehan^{17–19)} reported the effects of S, Cr and Ni on the rate of nitrogen dissolution reaction on the surface of liquid iron alloys, and Tsukihashi and Fruehan,²⁰⁾ using a carbon-saturated liquid iron specimen, found the effect of some alloying elements (P, Pb, Bi, Te, and S) on the rate of the nitrogen dissolution reaction.

Although extensive research has been carried out, the effects of alloying elements on the nitrogen dissolution rate into liquid steel are inconsistent. In the present study the effects of alloying elements such as oxygen, sulfur, carbon, boron, and manganese on the dissolution rate of nitrogen in the molten steel have been investigated in order to clarify the adsorption and dissolution behavior of nitrogen into liquid steel.

2. Experimental Method

2.1. Rate Constant of Nitrogen Dissolution

Fruehan and Antolin²¹⁾ reported that the nitrogen dissolution rate constant, k_c can be determined with apparent rate

constant (k_a) and gas phase mass transfer coefficient of nitrogen (k_m) as follows:

$$\frac{1}{k_a} = \frac{1}{k_c} + \frac{RT}{k_m} \quad \text{.....(1)}$$

where R (82.1 atm·cm³/mol·K) is the gas constant, T (K) is the gas temperature. In present study, k_a had been measured, k_m could be calculated by Saito equation²²⁾ and then k_c can be calculated.

2.2. Isotope Exchange Reaction^{15,23)}

Nitrogen dissolution reaction on the surface of liquid steel can be expressed by Eq. (2) and its reaction rate can be defined by Eq. (3) as follows:

$$R = k \cdot p_{\text{N}_2}^m \quad \text{.....(3)}$$

where k is the rate constant of nitrogen dissolution reaction into the liquid steel and m is the reaction order in terms of the nitrogen partial pressure, p_{N_2} . Kobayashi *et al.*¹⁵⁾ reported the nitrogen dissolution in the liquid steel is a first order reaction, therefore m can be assumed to be unity. Since there are three kinds of nitrogen gas isotopes, namely, ²⁸N₂, ²⁹N₂ and ³⁰N₂, the following reactions can be considered as nitrogen dissolution reactions:

The reaction rate constant of nitrogen dissolution on the surface of liquid steel was calculated by mass balance of ²⁹N₂ as follows:

$$-\ln \frac{^{29}F_{eq} - ^{29}F_f}{^{29}F_{eq} - ^{29}F_i} = k \frac{ART}{V/t} \quad \text{.....(7)}$$

where ²⁹F_{eq} is the equilibrium fraction of ²⁹N₂ species, and ²⁹F_i and ²⁹F_f are the fractions of ²⁹N₂ in the ingoing and outgoing gases, respectively. A (cm²) is the area of liquid steel-gas interface, V (cm³) is the gas volume, and t (s) is the reaction time. If complete mixing of the gas is assumed, V/t can be replaced by $\bar{V}$ which is the volumetric flow rate and the rate constant can be expressed as shown in Eq. (8).

$$k = -\frac{\bar{V}}{ART} \ln \left(\frac{^{29}F_{eq} - ^{29}F_f}{^{29}F_{eq} - ^{29}F_i} \right) \quad \text{.....(8)}$$

2.3. Experimental Procedure

A high frequency induction furnace with a quartz tube (OD 50 mm, ID 40 mm, and length 500 mm) was used for the experiments (Fig. 1). A Pt-Pt/13%Rh thermocouple mounted below the pedestal was employed for the temperature measurements. A proportional integral differential (PID) instrument was used to control the temperature within the range of ±3 K. An Al₂O₃ crucible (OD 14.5 mm, ID 12.5 mm, height 40 mm) was used as a melt container which was

Fig. 1. Schematic diagram of experimental apparatus.

located in the graphite heater.

Several LECO[®] standard steel samples (Part No. 502-348, O<20 ppm, S<10 ppm, C<8 ppm, and N<3 ppm) were used to guarantee the uniform initial oxygen and sulfur contents in molten steel. The specimen containing carbon was prepared by mixing the carbon-saturated iron (pre-melted standard sample in carbon crucible at 1 873 K) and the standard samples. In case of the samples containing manganese or boron, an appropriate mixture of standard samples and either manganese (powder, 99%) or boron (grinded crystalline pieces, 99.7%) was pre-melted for target compositions in an Al₂O₃ crucible at 1 873 K. A nitrogen isotope mixture (99.999% ²⁸N₂ : 98% ³⁰N₂ (Cambridge Isotope Laboratories, Inc., MA, USA) in the ratio 97 : 3) was used to measure the dissolution rate constant. The nitrogen partial pressure was fixed in ratios from 0.4 to 0.8 by mixing nitrogen with argon (99.9999%) gas, which was passed through magnesium chips at 723 K. A purified argon and hydrogen (99.9999%) gas mixture was used to remove oxygen on the surface of liquid steel for 2 min before introducing nitrogen gas mixture except for the effect of oxygen on the surface reaction rate.

An Al₂O₃ crucible containing a metal sample of about 9 g was put into the furnace and a dual-alumina lance for gas inlet and outlet (inner lance OD 6 mm, ID 2 mm, outer lance OD 12 mm, ID 8 mm) was inserted into the crucible 5 mm above the surface of liquid steel. The assembly was fixed immovably by alumina cement. Gas was blown at a flow rate of 500 cm³STP/min through the lance. A preliminary experiment indicated those 7 min was required for equilibration. A quadrupole type mass spectrometer (model QUARDSTAR 422, ESS GeneSys, Cheshire, UK) was used to analyze the fraction of each gas component.

After equilibration, a crucible was quickly withdrawn from the furnace and rapidly quenched in an argon gas. The compositions of each specimen after experiment are listed in Tables 1 and 2. The contents of nitrogen and oxygen were measured by a LECO[®] TC-300 analyzer and those of carbon and sulfur were quantified by a LECO[®] CS-200 analyzer. It was confirmed that the nitrogen and sulfur contents were less than about 10 ppm, and that of oxygen was about 30 ppm. Furthermore, the manganese and boron contents in a specimen were analyzed by an atomic absorption spec-

Table 1. Experimental results of Fe–O–S system.

No.	mass% O	mass% S	k_a (mol/cm ² · s · atm)	k_m/RT (mol/cm ² · s · atm)	k_c (mol/cm ² · s · atm)
1	0.0134	0.0120	4.70E-06	1.55E-04	4.84E-06
2	0.0066	0.0080	5.70E-06	1.88E-04	5.88E-06
3	0.0066	0.0080	6.56E-06	1.88 E-04	6.80E-06
4	0.0008	0.0008	2.44E-05	1.93 E-04	2.79E-05
5	0.0008	0.0006	2.74E-05	1.93 E-04	3.19E-05
6	0.0065	0.0110	6.42E-06	1.94 E-04	6.64E-06
7	0.0424	0.0160	6.26E-07	1.98 E-04	6.28E-07

Table 2. The composition of alloying content of specimen after experiment.

Adding elements (%)	O (%)	N (%)	C (%)	S (%)	X(=Mn, B) (%)
C	0.0008	0.0032	0.0008	0.0008	0.0010
	0.23	0.0034	0.0007	0.229	0.0009
	0.8	0.0031	0.0006	0.801	0.0010
	2	0.0033	0.0006	1.997	0.0009
B	0.003	0.0030	0.0006	0.0008	0.0011
	0.5	0.0030	0.0006	0.0008	0.0011
	1	0.0033	0.0005	0.0007	0.0009
	2	0.0031	0.0004	0.0007	0.0010
Mn	0.1	0.0033	0.0007	0.0009	0.0009
	0.5	0.0032	0.0007	0.0007	0.0010
	3	0.0034	0.0008	0.0008	0.0010
	6	0.0032	0.0009	0.0009	0.0009
	10	0.0034	0.0010	0.0007	0.0010
	15	0.0033	0.0013	0.0008	0.0011

trometer (model 6601-F/G, Shimadzu, Kyoto, Japan).

3. Results and Discussion

3.1. Rate Determining Step for Fe–O–S System

Nitrogen dissolution into liquid steel can be described as follows:

where $\square$ refers to a vacant site on the surface of liquid steel and the superscript ‘ad’ denotes an adsorbed nitrogen atom or molecule on the vacant site. Generally, nitrogen gas adsorption or dissociation steps on a surface of liquid steel are known as the rate determining step of the reaction of nitrogen dissolution. Ono *et al.*²⁴⁾ reported that Fe–O system containing over the 150 ppm of oxygen would be obedient to dissociation rate determining model and the same to the Fe–S system reported by Lee *et al.*¹⁵⁾ This can be originated from the surface active property of oxygen and sulfur and

be explained by the site-blockage model.^{6,10,11,13,17,24–26)}

If the rate determining step is considered to be the dissociation of nitrogen molecules (Eq. (9-b)), then the adsorption step (Eq. (9-a)) can be assumed in equilibrium. In this case, Eq. (3) can be expressed by Eq. (10) and satisfy Eq. (11).

$$R = k_{9-b} \cdot a_{\text{N}_2^{\text{ad}}} \cdot a_{\square} = k_{9-b} \cdot K_{9-a} \cdot a_{\square}^2 \cdot p_{\text{N}_2} \dots \dots \dots (10)$$

$$k = k_{9-b} \cdot K_{9-a} \cdot a_{\square}^2 \dots \dots \dots (11)$$

where K_{9-a} is the equilibrium constant of Eq. (9-a), $a_{\text{N}_2^{\text{ad}}}$ and $a_{\square}$ are the activities of adsorption site and vacant site, respectively. In an ideal case, the activity of vacant site can be denoted as $1 - \sum \theta_i$, where θ_i is the fraction of adsorption sites devoted to be additive element i . In addition, if element i exhibits Langmuir ideal adsorption behavior, then $\square + i = i^{\text{ad}}$. Accordingly, the relationship between the coverage due to adsorption of i onto the surface and the activity of i can be expressed by Eq. (12).

$$\frac{\sum \theta_i}{1 - \sum \theta_i} = K_i \cdot a_i \dots \dots \dots (12)$$

where K_i is the adsorption coefficient of additive element i . Therefore, the effect of additive adsorption onto the surface of liquid steel on the rate constant of nitrogen dissolution reaction can be explained by Eq. (13).

$$k = k_{9-b} \cdot K_{9-a} \cdot (1 - \sum \theta_i)^2 = \frac{k_{9-b} \cdot K_{9-a}}{\left(1 + \sum K_i \cdot f_i [\text{mass\% of } i]\right)^2} \dots \dots \dots (13)$$

where f_i is the Henrian activity coefficient of element i . In case of pure liquid iron, denominator is unity then $k (= k_{10-b} \cdot K_{10-a} = k^0)$ can be understood the rate of nitrogen dissolution on bare surface of liquid iron. Equation (13) indicates that the effect of additive element, i , on the rate of nitrogen dissolution reaction can be evaluated by its adsorption coefficient. Consequently, the adsorption coefficient will be defined by the graphical relationship between the measured rate constant and the activity of the additive element.

Figure 2 and Table 1 show the experimental results of present study in Fe–O–S system based on Eq. (13). Where,

Fig. 2. Relation between $\sqrt{k_c}$ and $1/(1+120a_O+65a_S)$ at 1873 K.

the adsorption coefficient of oxygen (K_O) and sulfur (K_S) could be evaluated by multiple regression analysis as 120 and 65, respectively. Figure 2 indicates that the rate constant of nitrogen dissolution in square root has a linear relationship with $1/(1+120a_O+65a_S)$. It means that Fe–O–S system is obedient to dissociation rate determining model. Here, the slope of straight line means the rate constant of nitrogen dissolution on bare surface of liquid steel in square root, $\sqrt{k^0}$ and its value was estimated as 0.0062. Therefore, k^0 is the 3.84×10^{-5} (mol/cm²·s·atm). In order to inspect this result, the rate constant on bare surface of liquid steel was shown in Fig. 3 with the temperature dependence of rate constant of nitrogen dissolution which was estimated by several authors.^{13–15, 24)} As shown in Fig. 3, the dependence of temperature on the rate constant is different from each group according to the rate determining model. The present result is in good agreement with the Kobayashi *et al.*'s and Ono *et al.*'s data based on dissociation determining model. The other is based on adsorption determining model, which were obtained by Belton *et al.*^{13,14)} The difference of the rate constant from each other is about twice, and the activation energies also differ from 95.0 kJ/mol (Kobayashi *et al.*) and 121 kJ/mol (Byrne and Belton). According to discussion of Kobayashi *et al.*, these discrepancies would be affected by purity of blowing gas. One of assumption, if the oxygen should be included in blowing gas, there would be possible that the nitrogen compete with oxygen for dissolution into liquid steel. However, since the competition effect of oxygen and nitrogen on the nitrogen dissolution into liquid steel has not been experimentally proved yet, further studies will be required.

3.2. Effects of Oxygen and Sulfur in Liquid Steel on Rate Constant of Nitrogen Dissolution

The effect of oxygen content coexisted with sulfur in the liquid steel on the rate constant of nitrogen dissolution at 1873 K is shown in Fig. 4 with Ono *et al.*'s results for Fe–O system ($k^0 = 5.76 \times 10^{-5}$ (mol/cm²·s·atm), $K_O = 144$ at 1973 K)²⁴⁾ and Nagasaka's results for Fe–S system ($k^0 = 5.3 \times 10^{-5}$ (mol/cm²·s·atm), $K_S = 65$ at 1873 K).²⁷⁾ The effect of oxygen and sulfur content on the rate constant in the present experimental result can be represented by the dissociation rate determining model at 1873 K as follows:

Fig. 3. The rate constant of nitrogen dissolution into liquid steel as a function of reciprocal temperature.

Fig. 4. Dependence of the rate constant of nitrogen dissolution on oxygen or sulfur content in liquid steel.

$$k_c = \frac{3.84 \times 10^{-5}}{(1 + 120a_O + 65a_S)^2} \text{ (mol/cm}^2 \cdot \text{s} \cdot \text{atm)} \quad \dots(14)$$

As shown in Fig. 4 and Eq. (14), the rate constant of nitrogen dissolution into liquid steel dramatically decreases with increasing concentration of oxygen and sulfur and this tendency is in good agreement with the results of Fe–O and Fe–S system. Therefore, it is reasonable that the effect of the surfactive elements on the rate constant which was described in Eq. (12) is put together in the denominator term of the equation of rate constant such as Eq. (14).

The effect of oxygen concentration on the rate of nitrogen dissolution in liquid steel would be stronger than that of sulfur. In order to dissolve nitrogen molecule in liquid steel, two vacant sites are needed. As described in Eq. (9), nitrogen dissolution can be explained by the following sequence. First, nitrogen molecule should occupy one of vacant sites (Eq. (9-a), adsorption step). And the nitrogen molecule reacts with the neighboring vacant sites (Eq. (9-b), dissocia-

tion step) then dissociated nitrogen atoms dissolve into the liquid steel. Because the rate of nitrogen dissolution in liquid steel is determined as the dissociation step, which is given in Eq. (13) and Fig. 2, it seems that the oxygen and sulfur atoms occupied the vacant sites required on dissociation step. The oxygen in liquid steel can play as a surface active element stronger than sulfur ($K_O=120>K_S=65$, present study). Therefore, if there are similar concentration of oxygen and sulfur, oxygen would be a dominant factor affecting nitrogen dissolution reaction rather than sulfur atoms.

3.3. Effect of Carbon in Molten Steel on Rate Constant of Nitrogen Dissolution Reaction

In Fig. 5, the rate constant is plotted against the activity of carbon in the liquid steel at 1873 K and is compared to the literature data.^{16,17,20)} It can be seen that the rate constant of nitrogen dissolution reaction is rarely affected by the activity of carbon, which is in good correspondence to the results measured by Fruehan *et al.*^{17,20)} However, there are slight discrepancies among the rate constant values, which could be originated from a difference in the activity of sulfur in each study. Sulfur in liquid steel is a surface active element like oxygen. Thus, sulfur content in liquid steel also has a significant influence on the effect of carbon on the rate constant. In the present study, the activity of sulfur (a_S) was about 0.001–0.003 with respect to 1 mass% standard state at 1873 K, whereas a_S is 0.11 and 0.25 in Fruehan *et al.*'s experiments, which is hundred times greater than that in the present study. Consequently, the nitrogen dissolution reaction can be described as a function of the activity of sulfur only in the Fe–C–S ternary system. It is of an interest that this is very similar to the expression of surface tension of liquid steel as reported by Kozakevitch *et al.*²⁸⁾

3.4. Effect of Boron in Molten Steel on Rate Constant of Nitrogen Dissolution Reaction

The rate constant for nitrogen dissolution is inversely proportional to boron content up to about 1 mass%, and followed by a nearly constant value at 1873 K as shown in Fig. 6. These phenomena can be justified using the positive interaction parameter of boron with nitrogen in liquid steel alloy of 0.094,²⁹⁾ which contributes to the retardation of nitrogen dissolution. The effect of boron content on the rate constant coincides with the result observed by Morita *et al.*³⁰⁾ However, there is a discrepancy between these studies because of difference in initial oxygen content. The result by Morita *et al.* was determined by using molten iron containing 7–8 mass ppm oxygen.

If boron could act as a surface active element, a decrease in the rate constant of nitrogen dissolution can be explained by the adsorption coefficient. In the composition region at less than 1 mass% boron, the adsorption coefficient of boron is determined to be positive value as shown in Eq. (15).

$$k_c = \frac{3.84 \times 10^{-5}}{(1 + 120a_O + 65a_S + 0.9a_B)^2} \quad (\text{mol/cm}^2 \cdot \text{s} \cdot \text{atm}) \quad (15)$$

In this case, it seems that boron can play as the surface

Fig. 5. Effect of activity of carbon and sulfur on the rate constant of nitrogen isotope exchange reaction.

Fig. 6. Dependence of the rate constant of nitrogen isotope exchange reaction on boron content in liquid steel.

active element, even though its impact is significantly smaller than that of oxygen and sulfur.

Furthermore, a decrease in the rate constant with increasing concentration of boron in the alloys might be attributed to its small atomic size. Because the atomic radius³¹⁾ of boron (0.85 Å) is smaller than that of iron (1.4 Å), boron atoms can probably prohibit the dissolution of nitrogen by occupying the sites between iron atoms. However, since the size effect of boron on the dissolution reaction of nitrogen into liquid steel has not been experimentally proved yet, further studies will be required.

3.5. Effect of Manganese in Molten Steel on Rate Constant of Nitrogen Dissolution Reaction

Figure 7 shows the effect of manganese on the rate constant of nitrogen dissolution in molten steel. For the sake of comparison, the effects of other elements^{32,33)} such as vanadium, chromium, and molybdenum on the rate constant are also shown in Fig. 7. The present result of the effect of manganese on the rate constant of nitrogen dissolution is in good agreement with the results of Ono *et al.* Manganese and vanadium in molten steel show the acceleration effect on the nitrogen dissolution, while the effects of chromium

Fig. 7. Dependence of the rate constant of nitrogen isotope exchange reaction on manganese content in liquid steel.

Table 3. Interaction parameter in liquid iron alloys with nitrogen at 1 873 K.^{29,34)}

Elements	Zr	V	Nb	Cr	Mo	Mn	Ti ³¹⁾
ϵ'_N	-0.63	-0.123	-0.068	-0.048	-0.011	-0.02	-0.36
Elements	C	B	Si	Al			O
ϵ'_N	0.13	0.094	0.048	0.01			0.007

and molybdenum are relatively small. These phenomena could be qualitatively understood based on the interaction between alloy elements and nitrogen in liquid steel as Ono *et al.*^{32,33)} discussed (refer to Table 3^{29,34)}).

As shown in Fig. 7, the rate constant is proportional to manganese content up to about 6 mass% in iron, and followed by a nearly constant value through the composition range investigated. It seems that the transition tendency of the rate constant at 6 mass% manganese in molten steel is probably caused by the change in the thermophysical property of Fe–Mn alloy with increasing concentration of manganese. Arita and Pierre³⁵⁾ reported that the kinematic viscosity³⁶⁾ and inter-diffusivity³⁷⁾ in liquid Fe–Mn alloy at 1 873 K are changed by adding 6 mass% manganese. In addition, it can be understood by the change of excess partial molar free energy of Fe–Mn alloy³⁵⁾ due to change of liquid structure of molten Fe–Mn alloy, which should be more developed in future works. Therefore, the rate constant of nitrogen dissolution in molten Fe–Mn alloy could be described as follow:

$$k_{\text{Fe}\pm\text{Mn}} = \frac{k_{\text{Fe}\pm\text{Mn}}^0}{(1 + K_{\text{O}}^{\text{Fe}\pm\text{Mn}} a_{\text{O}} + K_{\text{S}}^{\text{Fe}\pm\text{Mn}} a_{\text{S}})^2} \quad (\text{mol/cm}^2 \cdot \text{s} \cdot \text{atm}) \quad \dots\dots\dots(16)$$

where, $k_{\text{Fe}\pm\text{Mn}}^0$ is the rate constant of nitrogen dissolution on the bare surface of molten Fe–Mn alloy, and $K_{\text{O}}^{\text{Fe}\pm\text{Mn}}$ and $K_{\text{S}}^{\text{Fe}\pm\text{Mn}}$ are adsorption coefficient of oxygen and sulfur in molten Fe–Mn alloy, respectively.

However, the atomic radius³¹⁾ of manganese (1.4 Å) is almost same that of iron (1.4 Å), and it form the near ideal solution in molten steel³⁸⁾ which confirmed by activities behavior in the iron–manganese binary system at 1 863 K.³⁹⁾ Therefore, the mole fraction of iron and manganese on the

Fig. 8. Relationship between concentration of manganese and $k_{\text{Mn}}^0 / (1 + K_{\text{O}}^{\text{Mn}} a_{\text{O}} + K_{\text{S}}^{\text{Mn}} a_{\text{S}})^2$.

surface of molten Fe–Mn alloy would be expected to depend on their concentration. Moreover, the adsorption of nitrogen on molten Fe–Mn alloy could occur independently with different interaction between nitrogen and iron or manganese atoms on surface of Fe–Mn liquid alloy, of which was expected from different solubility of nitrogen in iron and manganese (nitrogen solubility in pure liquid iron: about 0.04 mass%, in pure liquid Mn: about 1.2 mass% at 1 873 K). Tentatively assuming the modified Langmuir adsorption isotherm and considering above mentioned thermodynamic consideration, $k_{\text{Fe}\pm\text{Mn}}^0$ and Eq. (16) would be rearranged to (17) and (18), respectively.

$$k_{\text{Fe}\pm\text{Mn}}^0 = k_{\text{Fe}}^0 X_{\text{Fe}} + k_{\text{Mn}}^0 X_{\text{Mn}} \quad \dots\dots\dots(17)$$

$$k_{\text{Fe}\pm\text{Mn}} = \frac{k_{\text{Fe}}^0 \cdot X_{\text{Fe}}}{(1 + 120a_{\text{O}} + 65a_{\text{S}})^2} + \frac{k_{\text{Mn}}^0 \cdot X_{\text{Mn}}}{(1 + K_{\text{O}}^{\text{Mn}} a_{\text{O}} + K_{\text{S}}^{\text{Mn}} a_{\text{S}})^2} \quad \dots\dots\dots(18)$$

where, X is the mole fraction of iron and manganese, k_{Mn}^0 is the rate constant of nitrogen on the bare surface of molten manganese, K_{O}^{Mn} and K_{S}^{Mn} are adsorption coefficient of oxygen and sulfur in molten manganese, respectively. Because there is no available literature data related to manganese, Eq. (18) could not be completed. However, the value of $k_{\text{Mn}}^0 / (1 + K_{\text{O}}^{\text{Mn}} a_{\text{O}} + K_{\text{S}}^{\text{Mn}} a_{\text{S}})^2$ could be estimated by using present measured data for $k_{\text{Fe}\pm\text{Mn}}$ and k_{Fe}^0 as shown in Fig. 8. The value of $k_{\text{Mn}}^0 / (1 + K_{\text{O}}^{\text{Mn}} a_{\text{O}} + K_{\text{S}}^{\text{Mn}} a_{\text{S}})^2$ is approximately evaluated as 10 times as greater than the value of $k_{\text{Fe}}^0 / (1 + 120a_{\text{O}} + 65a_{\text{S}})^2$. There are two possible explanations for this complex phenomenon as follow; First, the rate constant of nitrogen dissolution on bare surface of liquid manganese, k_{Mn}^0 would be higher than k_{Fe}^0 , because the thermodynamic interaction between nitrogen and manganese is greater than that of iron. Second, the adsorption coefficients of oxygen and sulfur in molten manganese could be smaller than that in molten iron. Because the solubility of oxygen and sulfur in manganese is larger than that in iron which can be inferred from binary phase diagrams of Fe–O,³⁸⁾ Fe–S,³⁸⁾ Mn–O⁴⁰⁾ and Mn–S,⁴⁰⁾ oxygen and sulfur in bulk liquid manganese liquid would be more stable than that of

Fig. 9. Effect of content of alloying elements on the nitrogen isotope exchange reaction.

in bulk liquid iron. However, these explanations are qualitative discussion, further studies will be required.

3.6. Comparison with the Effect of Various Elements

In order to compare the effects of bulk concentration of carbon, manganese and boron on the nitrogen dissolution rate in the liquid steel, $k^0/k^0_{\text{pure iron}}$ ratios are plotted against their contents as shown in Fig. 9 along with the results measured by Glaws and Fruehan,¹⁸⁾ Tsukihashi and Fruehan,²⁰⁾ Ono *et al.*,³³⁾ and Morita *et al.*³⁰⁾ when the content of each additive elements is less than 1 mass% (Here, Cr³³⁾ and V are exceptions.). The rate constant of nitrogen dissolution on the liquid steel is demonstrated as a relative value, $k^0/k^0_{\text{pure iron}}$ where indicates the one for pure iron. The positive slope of $k^0/k^0_{\text{pure iron}}$ indicates the positive effect of a specific element on the dissolution of nitrogen into the molten steel, whereas the negative slope represents a retardation effect. The slope of each line denotes the term $a_{\text{N}}^2/[\text{mass}\% i]$.³³⁾

In Fig. 9, titanium, zirconium, chromium, vanadium and manganese show positive slope. This means an acceleration of nitrogen dissolution due to an increase in the activity of vacant sites on the surface of liquid steel with the addition of these elements. On the contrary, aluminum, silicon and boron play roles in retarding nitrogen dissolution. Even if these elements do not occupy the vacant sites as do surfactive elements, it seems that they could obstruct nitrogen diving into the liquid steel by decreasing the activity of vacant site. It is observed that carbon does scarcely contribute to the rate constant. These results can be qualitatively supported by considering their interaction parameters with nitrogen.

Figure 10 was constructed to compare the slopes of the lines in Fig. 9 with the interaction parameters between nitrogen and each element in the liquid steel at high temperatures. It appears that the interaction parameter has a linear relationship with the value of $a_{\text{N}}^2/[\text{mass}\% i]$ as given in Eq. (19). Here, Ti is excluded in least square regression.

$$\frac{a_{\text{N}}^2}{[\text{mass}\% i]} = -1.03 \times e_{\text{N}}^i - 0.062 \quad (r^2 = 0.71) \quad \dots (19)$$

Fig. 10. Relationship between the interaction parameters of the alloying elements with nitrogen and slopes of straight lines in Fig. 9.

However, this relationship is a qualitative expression for the alloying element effects on the nitrogen dissolution reaction because the interaction parameter indicates the affinity between alloying elements and nitrogen in bulk phase. Therefore, further study will be required to clarify the interaction between nitrogen and alloying elements on the surface of the liquid steel.

4. Summary

The effect of alloying elements such as oxygen, sulfur, carbon, manganese, and boron on the dissolution rate of nitrogen into molten steel has been investigated in order to clarify the adsorption and dissolution behavior of nitrogen into the steel melts. The following conclusions are drawn:

- (1) The rate determining step of nitrogen dissolution into Fe–O–S system is the dissociation reaction. It means that the role of surface coverage is very important.
- (2) The rate constant of nitrogen isotope exchange reaction on the bare surface of the liquid steel, k^0 , was estimated to be 3.84×10^{-5} (mol/cm² · s · atm).
- (3) The effects of surfactive elements such as oxygen and sulfur on nitrogen dissolution reaction are described by dissociation rate determining model as follow:

$$k_c = \frac{3.84 \times 10^{-5}}{(1 + 120a_{\text{O}} + 65a_{\text{S}})^2} \quad (\text{mol/cm}^2 \cdot \text{s} \cdot \text{atm})$$

($K_{\text{O}} = 120, K_{\text{S}} = 65$)

- (4) Boron can interrupt the nitrogen dissolution into liquid steel. It seems that the boron can be played as a weak surface active element (adsorption coefficient, $K_{\text{B}} = 0.9$) and its small atomic size could also contribute to decrease the rate constant.

- (5) Manganese could accelerate the nitrogen dissolution into the liquid steel due to interaction with nitrogen stronger than iron.

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