

# Effects of Ti, Zr, V, and Cr on the Rate of Nitrogen Dissolution into Molten Iron

HIDEKI ONO, KAZUKI MORITA, and NOBUO SANO

The rate of nitrogen dissolution into molten iron-M (M: Ti, Zr, V, and Cr) alloys at temperatures from 1873 to 2023 K has been measured using an isotope exchange reaction. 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. Of these, Ti increased the reaction rate most and the rate constant for an Fe-0.08 mass pct Ti alloy was 1.5 times larger as that for pure iron at 1873 K. The correlation of rate constant with thermodynamic interaction parameter with nitrogen was observed. This effect is discussed in terms of the change in the activity of the vacant site on the surface of the molten alloy.

## I. INTRODUCTION

THE knowledge 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. To know the maximum rate of nitrogen removal, it is important to know 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. Although this kind of measurement has been made extensively by Belton,<sup>[1]</sup> no studies have been done on the effect of non-surface alloying elements, except for C<sup>[2,3,4]</sup> and Cr.<sup>[5]</sup> Accordingly, in the present study, the effects of Ti, Zr, V, and Cr (which have stronger affinities for nitrogen than Fe) on the reaction rate have been measured using an isotope exchange technique at temperatures from 1873 to 2023 K, and the mechanism of the enhancement of reaction rate and correlations with thermodynamic properties are discussed.

## II. EXPERIMENTAL

Details of the experimental principle, apparatus, and procedure have been given elsewhere.<sup>[6]</sup> Accordingly, only the subjects particular to the present study are briefly described here.

The equation for calculating a rate constant in this work is not the same as that used by Byrne and Belton<sup>[2]</sup> or that in the previous article.<sup>[6]</sup> It was derived as follows. Considering a mass balance of <sup>30</sup>N<sub>2</sub>, Eq. [1] holds on the assumption that the composition of absorbed gas is not affected by desorbed gas, and the fraction of <sup>30</sup>N<sub>2</sub> in the total absorbed nitrogen equals that in the ingoing nitrogen.

$$\frac{P_{N_2} \bar{V}}{RT} ({}^{30}F_i - {}^{30}F_f) = Av({}^{30}F_i - {}^{30}F_{eq}) \quad [1]$$

where  $P_{N_2}$  (atm) is the partial pressure of nitrogen,  $A$  (cm<sup>2</sup>)

is the surface area of molten metal,  $\bar{V}$  (cm<sup>3</sup>/s) is the volume flow rate,  $T$  (K) is the temperature of gas,  $R$  [82.1 (cm<sup>3</sup> · atm/K · mol)] is the gas constant,  ${}^{30}F_{eq}$  is the equilibrium fraction of <sup>30</sup>N<sub>2</sub>, and  ${}^{30}F_i$  and  ${}^{30}F_f$  are the fractions of <sup>30</sup>N<sub>2</sub> in the ingoing and outgoing gases, respectively. Since nitrogen dissolves into molten metal according to Reaction [2], the rate of total nitrogen dissolution,  $v$  (mol/cm<sup>2</sup> · s), which is a first order with respect to the partial pressure of nitrogen,<sup>[6]</sup> is expressed by the following:

$$N_2 \text{ (gas)} = 2\bar{N} \text{ (in metal)} \quad [2]$$

$$v = kP_{N_2} \quad [3]$$

where  $k$  (mol/cm<sup>2</sup> · s · atm) is the rate constant of nitrogen dissolution. Incorporating Eq. [3] into Eq. [1], the rate constant is represented by Eq. [4]:

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

On the other hand, the rate constant equation introduced by Byrne and Belton<sup>[2]</sup> was derived by assuming the complete mixing of gas at a metal surface and is represented by Eq. [5]:

$$k = -\frac{\bar{V}}{ART} \ln \frac{{}^{30}F_f - {}^{30}F_{eq}}{{}^{30}F_i - {}^{30}F_{eq}} \quad [5]$$

Equation [4] gives a smaller value for the rate constant than Eq. [5], and its difference can be ignored when the difference between  ${}^{30}F_i$  and  ${}^{30}F_f$  is small.

An alumina crucible containing metal samples was inserted into a transparent quartz reaction chamber and inductively heated. The experimental temperature was changed from 1823 to 2023 K. The sample temperature was monitored by a dual wavelength infrared pyrometer, sighted onto the metal surface and adjusted manually to within  $\pm 3$  K of the desired temperature. The total gas flow rate was mainly 900 mL/min STP and changed from 700 to 900 mL/min STP.

To prepare Fe-Ti and Fe-Zr alloys, Ti or Zr was added after high-purity electrolytic iron with 2 ppm S was melted at the experimental temperature. In the case of Cr or V, it was initially mixed with electrolytic iron in the alumina crucible before melting. The sample metals were analyzed after each experiment for the relevant elements. Oxygen,

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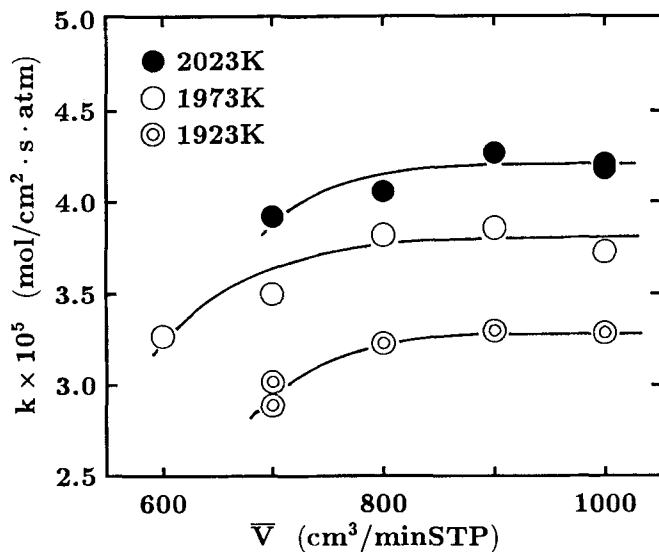


Fig. 1—Dependence of the rate constant for pure iron on flow rate at 1923, 1973, and 2023 K.

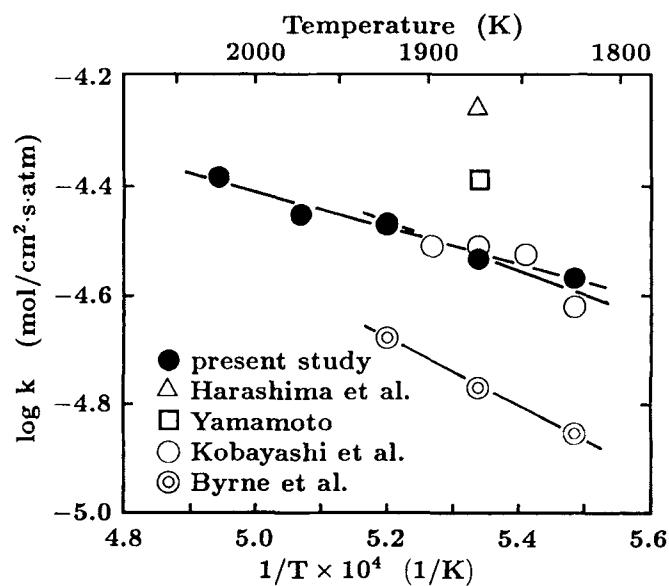


Fig. 2—Dependence of the rate constant of nitrogen dissolution into pure iron on temperature.

nitrogen, carbon, and sulfur contents were also analyzed by LECO\* analyzer.

\*LECO is a trademark of the Leco Corporation, St. Joseph, MI.

### III. RESULTS

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  $\bar{V}_{N_2+H_2}$  at 1923, 1973, and 2023 K, which were investigated by changing nitrogen flow rate at a constant hydrogen flow rate, 500 cm<sup>3</sup>/min STP. At

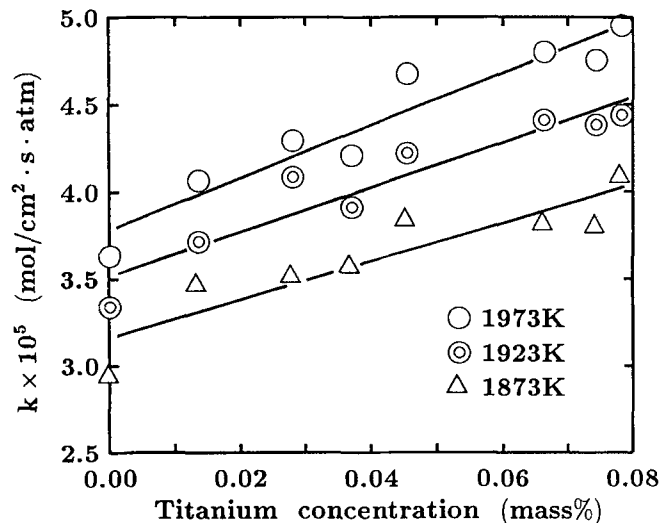


Fig. 3—Dependence of the rate constant of nitrogen dissolution on titanium concentration.

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 Figure 1, the total flow rate of 900 cm<sup>3</sup>/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,<sup>[6]</sup> subsequent measurements were made at total flow rate of 900 cm<sup>3</sup>/min STP ( $\bar{V}_{N_2} = 200$  cm<sup>3</sup>/min STP,  $\bar{V}_{H_2} = 700$  cm<sup>3</sup>/min STP).

The dependence of the rate constant for pure iron on temperature is shown in Figure 2 with the values in the literature<sup>[2,6]</sup> obtained by the same technique. As described in the Section II, the rate constant equation is different in the present study. The values reported by Kobayashi *et al.*<sup>[6]</sup> were recalculated using Eq. [4] and are shown in Figure 2. If Eq. [5] is applied to the present work, the rate constant is about 1.1 times larger than the values shown in Figure 2. From the results of the rate of nitrogen desorption under reduced pressures by Harashima *et al.*<sup>[7]</sup> and Yamamoto,<sup>[8]</sup> the rate constants of nitrogen dissolution were calculated using the equilibrium constant of Eq. [2]<sup>[9]</sup> and are also shown in Figure 2. The rate constant obtained by the present work is in excellent agreement with Kobayashi *et al.*,<sup>[6]</sup> who used an electric resistance furnace. A linear relationship obtained by the present work is described by Eq. [6]:

$$\log k \text{ (mol/cm}^2 \cdot \text{s} \cdot \text{atm)} = -\frac{3300}{T} - 2.76 \text{ (1823 to 2023 K)} \quad [6]$$

Dependences of the rate constant on Ti, Zr, V, and Cr concentrations are shown in Figures 3, 4, 5, and 6, respectively. In Figure 6, the values in the literature<sup>[5]</sup> are also plotted. Formation of nitride restricted the concentration of added elements except Cr, whose nitride is not stable over the whole composition. The critical values for formation of nitride in the present condition were calculated<sup>[9]</sup> and are listed in Table I. Although the present zirconium content at 1923 K in Figure 4 is beyond the critical limit in Table I, the formation of ZrN was not observed. Clearly, it is found

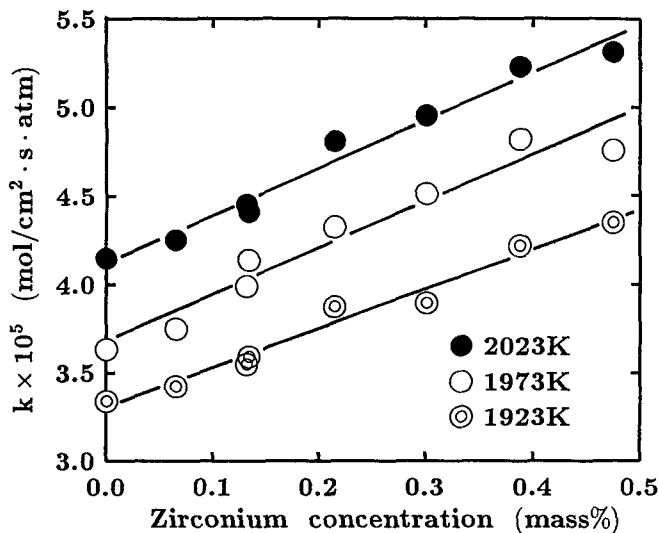


Fig. 4—Dependence of the rate constant of nitrogen dissolution on zirconium concentration.

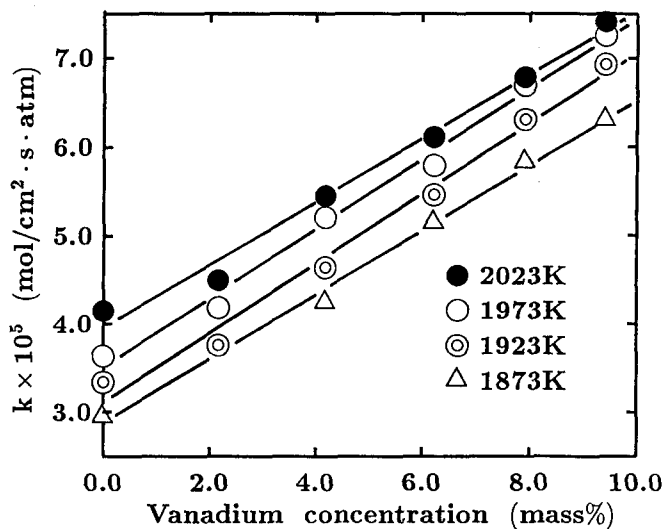


Fig. 5—Dependence of the rate constant of nitrogen dissolution on vanadium concentration.

that the rate constant of nitrogen dissolution increases linearly by the addition of Ti, Zr, V, and Cr. Titanium is the most effective of these elements for increasing the rate of dissolution 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.

#### IV. DISCUSSION

The rate constants for purified molten iron by other investigators are shown in Figure 2. The rate constant measured by Harashima *et al.*<sup>[7]</sup> at a pressure of about  $10^{-2}$  atm seems to be somewhat larger than the present values. However, for plotting their results, their equation was extrapolated to give the interfacial chemical reaction rate constant as functions of oxygen and sulfur contents for estimation of the value for the purer iron used in the present work ( $[\text{pct O}] = 0.0010$ ,  $[\text{pct S}] < 0.0005$ ). Considering the fact that their measured value was about  $2 \times 10^{-5}$  (mol/cm<sup>2</sup> · s

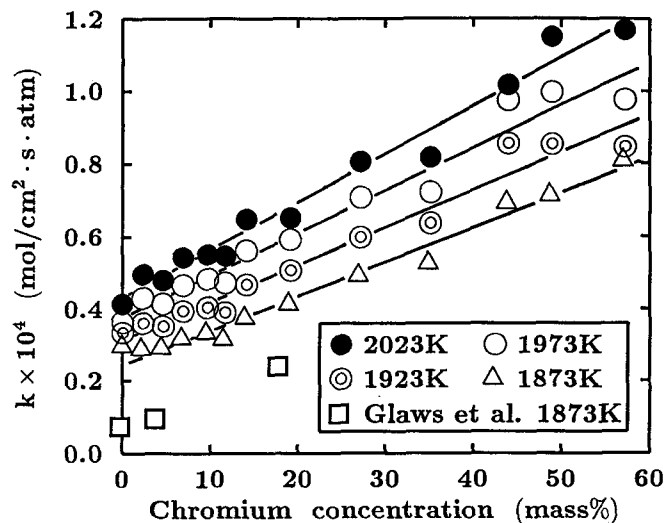


Fig. 6—Dependence of the rate constant of nitrogen dissolution on chromium concentration.

Table I. Critical Concentrations of Added Elements in Molten Iron for Nitride Formation at  $P_{N_2} = 0.22$  Atm

Temperature (K)	(Mass Percent)		
	TiN	ZrN	VN
1873	0.0774	0.229	24.6
1923	0.145	0.348	32.3
1973	0.263	0.518	41.8
2023	0.462	0.757	53.5

· atm) at its maximum, which is smaller than the value of the present work, this extrapolation would not be applicable to these lower oxygen and sulfur contents. The value by Yamamoto<sup>[8]</sup> 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.

In Figure 6, the rate constant obtained by Glaws and Fruehan<sup>[5]</sup> is smaller than that of the present work. One of the reasons for this discrepancy would be a retarding effect of sulfur; the authors 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.*,<sup>[10]</sup> the rate constant for an iron including 50 ppm sulfur at 1873 K gives the value of  $1.8 \times 10^{-5}$  (mol/cm<sup>2</sup> · 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. [2]. Equation [2] can be divided into the two steps represented by Equations [7] and [8], where  $\square$  and

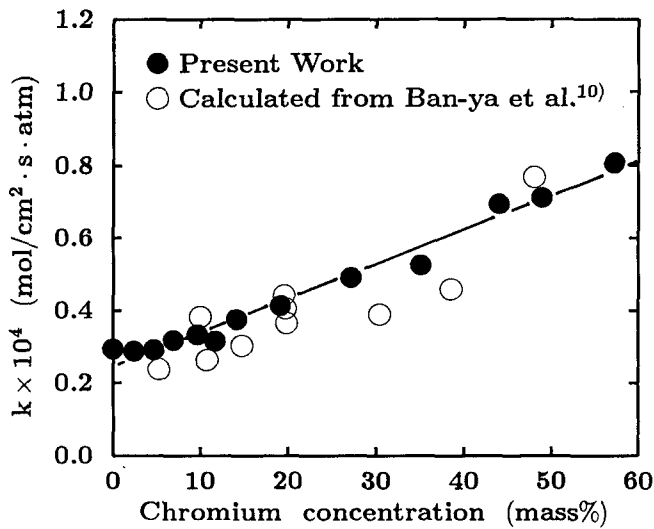


Fig. 7—Comparison of the rate constant for Fe-Cr alloy with the desorption rate data at 1873 K.

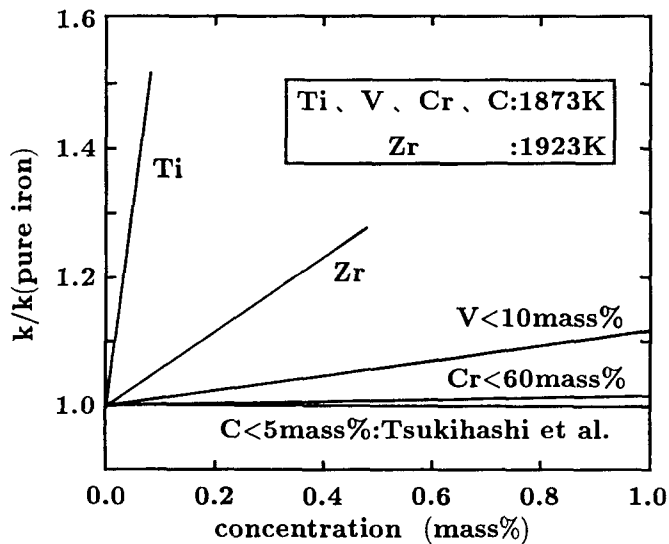
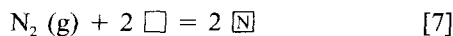


Fig. 8—The effect of added elements on the rate constant of nitrogen dissolution.

$\square$  denote vacant site on the metal surface and site occupied by nitrogen, respectively.



Assuming that the reaction represented by Eq. [7] is a rate-determining step with the step given by Eq. [8] at virtual equilibrium, the rate equation for Eq. [7] can be described by Eq. [9] or [10].

$$v = k_0 P_{\text{N}_2} a_{\square}^2 \quad [9]$$

$$= k_0 P_{\text{N}_2} \frac{K_8 a_{\square_{\text{N}}}^2}{a_{\text{N}}^2} \quad [10]$$

where  $k_0$  is the forward rate constant for Eq. [7] and  $K_8$  is the equilibrium constant for Eq. [8]. Combining Eqs. [9] and [10] with Eq. [3],  $k$  is expressed by Eq. [11] or [12] as follows:

$$k = k_0 a_{\square}^2 \quad [11]$$

$$= k_0 \frac{K_8 a_{\square_{\text{N}}}^2}{a_{\text{N}}^2} \quad [12]$$

According to Eq. [11], alloying elements may affect the dissolution rate of nitrogen through affecting the activity of vacancy site relative to that of pure iron ( $a_{\square}$ ) 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. [8] being at equilibrium, the desorption rate  $v'$  is expressed by Eq. [14], being proportional to the square of nitrogen concentration, as seen in Eq. [15], where  $k'$  is the rate constant for the reverse reaction of Eq. [7] and  $f_{\text{N}}$  is the activity coefficient of nitrogen in molten iron. Hence, the rate constant  $k_d$  is represented by Eq. [16]:

$$v' = k' a_{\text{N}}^2 \quad [13]$$

$$= \frac{k' a_{\square_{\text{N}}}^2 f_{\text{N}}^2 [\text{pct N}]^2}{K_8} \quad [14]$$

$$= k_d [\text{pct N}]^2 \quad [15]$$

$$k_d = \frac{k' f_{\text{N}}^2 a_{\square}^2}{K_8} \quad [16]$$

Using the relationships of Eqs. [17] and [18], Eq. [16] may be rewritten as Eq. [19]:

$$\frac{k_0}{k'} = K_7 \quad [17]$$

$$K_2 = K_7 K_8 \quad [18]$$

$$k_d = \frac{k_0 f_{\text{N}}^2 a_{\square}^2}{K_2} \quad [19]$$

$$= \frac{k f_{\text{N}}^2}{K_2} \quad [20]$$

According to Eq. [19], alloying elements should affect not only  $f_{\text{N}}$  but also  $a_{\square}$  in the desorption rate studies. For this confirmation, the dissolution rate constant for Fe-Cr alloys  $k_d$ , measured by Ban-ya *et al.*,<sup>[10]</sup> who employed the conventional method using Eq. [20] with known  $K_2$ <sup>[9]</sup> and  $f_{\text{N}}$ <sup>[11]</sup> values. The calculated  $k$  values are also shown in Figure 7 with the present data at 1873 K. The consistence of the results obtained by two entirely different experimental techniques indicates that the proposed mechanism of the dissociation and adsorption of nitrogen is valid and they are rate determined by Eq. [7]. The effect of carbon on the desorption rate was explained by its effect only on the activity of nitrogen in the metal.<sup>[10]</sup> This is because carbon happens to have no effect on the activity of the vacant site in Eq. [19].

According to the previous discussions, the effect of added elements was put in order using the concept of the activity of vacant site. In Figure 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 concentrations. The effect of carbon by Tsukihashi and Fruehan<sup>[4]</sup> is also shown in Figure 8. The slopes of the straight lines in Figure 8 correspond to  $a_{\square}^2/(\text{mass pct M})$  according to Eq. [11]. These values are compared in Table II with the interaction parameters for the elements with nitrogen. As shown in Table II, the effect

**Table II. Interaction Parameters of Added Elements with Nitrogen and Slopes of Straight Lines (Described in Figure 8)**

Added Elements	$e_N^i$ (1873 K)	$a_N^2$ /[Percent 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

of Ti addition is much larger than that of Zr in spite of the fact that their interaction parameters are nearly equal. Although the quantitative correlation cannot be observed and the data for interaction parameter are not very accurate, an element that has stronger affinity for nitrogen generally tends to increase the nitrogen dissolution rate more effectively by increasing the activity of vacant site.

### V. CONCLUSIONS

The rate of nitrogen dissolution into molten iron-M (M: Ti, Zr, V, and Cr) 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.
2. Titanium significantly increases the reaction rate, and the rate constant for an Fe-0.08 pct Ti alloy is 1.5 times larger than that for pure iron at 1873 K.
3. The alloying elements have been shown to enhance the

dissolution rate by increasing the activity of vacant site at the metal surface. The consistence of the present results with those of desorption studies is shown.

4. A correlation between the degree of the rate increase by added elements and their interaction parameters with nitrogen is observed.

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