Interfacial Resistance to Nitrogen Desorption from Molten Iron*

By Masamitsu TAKAHASHI,** Ye-Tao HAN,** Masamichi SANO,**
Kazumi MORI*** and Masahiro HIRASAWA****

Synopsis

A study on the rate of nitrogen desorption from molten iron by Ar injection together with blowing onto the melt has been made by the use of Al_2O_3 and MgO crucibles, and with deoxidations by Al and C addition. The flow rates of gas injected into and blown onto the melt were about 80 and 1 100 Ncm^3/min , respectively. The immersion depth of the nozzle was 3.3–4.5 cm. During the experiment, the bubble formation time was measured by means of a pressure pulse technique.

The rate data are compared with those calculated on the basis of a mixed control model. By comparison of the calculated results with the experimental ones, the interfacial resistance to nitrogen desorption is quantitatively estimated. The interfacial resistance exists on the free surface while not on the bubble–metal interface. Under the same deoxidation condition, the rate of nitrogen desorption determined by the use of Al_2O_3 crucible is lower than that obtained by the use of MgO crucible. This comes from the fact that the interfacial resistance exists on the free surface of the melt contained in an Al_2O_3 crucible although the free surface looks clean. In the deoxidation with Al, the Al_2O_3 layer on the surface greatly retards the rate of desorption.

Key words: steelmaking; nitrogen desorption; interfacial resistance; Al_2O_3 crucible; oxide film.

I. Introduction

It is well-known that the existence of a very small amount of impurities (insoluble surface active elements) in aqueous solutions at room temperature drastically reduces the rate of mass transfer through gas–liquid and liquid–liquid interfaces.¹⁾ Such a resistance to mass transfer is called the interfacial resistance. In metallurgical reactions at elevated temperatures, for example Fe– N_2 reaction, it is found that the rate of chemical reaction is depressed by the adsorption of surface active elements on the interface.²⁾ However, when an oxide film exists on the interface, it may give an interfacial resistance.[†] Glen and Richardson³⁾ found that the oxidation of levitated droplet of liquid copper is impeded by the presence of SiO_2 film even when the amount of Si existing in the metal is as little as 2 ppm. No study has been made on the interfacial resistance for gas–molten iron reactions.

Previously, studies on the rate of nitrogen desorption without interfacial resistance by Ar injection⁴⁾ and by Ar injection together with Ar blowing onto the melt⁵⁾ were made by the authors. It was found that Ar blowing onto the melt markedly enhances the

nitrogen desorption, and that the nitrogen–molten iron reaction is controlled by liquid- and gas-phase mass transfers and chemical reaction on the gas–metal interface.

In the present study, experiments similar to the previous ones have been done by the use of Al_2O_3 and MgO crucibles, and with deoxidations by Al or C addition. The experimental data are compared with those calculated on the basis of a reaction model which can estimate the nitrogen desorption both through the bubble interface and through the free surface. By comparison of these results, the interfacial resistance due to the alumina layer formed on the melt by Al added or the oxide layer formed by impurities from the atmosphere is estimated and the effect of the crucible material on the interfacial resistance is examined.

II. Experimental

The experimental apparatus is the same as that used in the previous studies.^{4,5)} A Tammann furnace was used to melt electrolytic iron in a crucible which was set in a mullite reaction tube. Crucibles used in the experiments were MgO (38 mm in I.D., 100 mm in height) and Al_2O_3 (39 mm in I.D., 100 mm in height). The experimental temperature was 1 853 K. After the iron being melted, the oxygen concentration of the melt was controlled so as to be about 100 ppm under an Ar– H_2 atmosphere. In the experiment with deoxidation by C addition (named as C deoxidation), 0.4 g of C was added and then nitrogen was absorbed to the saturated concentration at $P_{\text{N}_2}=1$ atm. In the experiment with deoxidation by Al addition (named as Al deoxidation), 0.4 g of Al is added after the absorption of nitrogen. Then the desorption of nitrogen by Ar injection together with Ar blowing onto the melt was started. The change in the nitrogen concentration of the melt with time was determined by chemical analyses of the samples taken out at suitable time intervals. Chemical analyses were made also for oxygen and aluminum. The concentration of dissolved oxygen [%O] of the melt deoxidized with Al was determined on the assumption that the dissolved oxygen is in equilibrium with dissolved aluminum.⁶⁾

* Based on the paper presented to the 112th ISIJ Meeting, October 1986, S949, at Nagoya University in Nagoya. Manuscript received on April 15, 1987; accepted in the final form on July 3, 1987. © 1987 ISIJ

** Graduate School, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464.

*** Department of Metallurgy, Beijing University of Iron and Steel Technology, 30 Xue Yuan Road, Beijing, China.

**** Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464.

† Here, the interfacial resistance is defined as the additional resistance which results from the existence of the film of oxides at the interface.

In the case of Al deoxidation the surface is covered with alumina and in the other cases the surface looks clean. In the present study, the extent of the influence of the surface oxides on the nitrogen desorption rate is investigated.

In each experiment, the frequency of the bubble formation was measured to obtain the bubble formation time and the bubble-metal interfacial area which were needed for theoretical analysis.

The mass of the melt was 330~380 g and the immersion depth of the nozzle was 3.3~4.5 cm. The gas flow rate through the nozzle (V_g) was fixed at about 80 Ncm³/min. The rate of Ar flow through the lance was 1 100 Ncm³/min. The lance of 6 mm in I.D. was kept at the position 10 mm above the melt surface.

In some experiments with Al deoxidation, nitrogen desorption by Ar injection was only done. In these cases, a MgO ring (or a Al₂O₃ ring) was placed on the surface⁴⁾ and Ar-N₂ mixture in equilibrium with nitrogen in the melt was blown onto the free surface to obtain such an experimental condition that the reaction through the free surface can be neglected. The flow rate of Ar-N₂ gaseous mixture was 380 Ncm³/min.

III. Experimental Results and Discussion

1. Nitrogen Desorption only by Ar Injection

In order to elucidate the presence of interfacial resistance to nitrogen desorption on the free surface and the bubble interface, it is needed to distinguish between the reaction rates at the two boundaries. Nitrogen desorption through the bubble interface without the interfacial resistance was studied previously by the authors.⁴⁾ Here, the experiment similar to the previous one was done for the melt deoxidized with Al and the existence of the interfacial resistance on the bubble interface was examined.

1. Change in Nitrogen Concentration with Time

Figure 1 shows typical examples of the change in nitrogen concentration with time obtained from the experiment with Al addition. In the figure, the con-

Fig. 1. Change in nitrogen concentration with time obtained from the experiment on nitrogen desorption through the bubble interface.

centration change obtained in the previous experiment without Al addition is also shown for comparison. The figure shows that [%N] tends to decrease faster with the decrease in [%O] as reported previously.

2. Reaction Model of Nitrogen Desorption through the Bubble Interface

The reaction model is based on the mixed control of liquid- and gas-phase mass transfer and chemical reaction on the bubble interface. This model was proposed in the previous study.⁴⁾

The change in the amount of nitrogen in a bubble with time is given by the following equation:

$$\begin{aligned} \frac{dn_{N_2}}{dt} &= k_L \cdot A \cdot \frac{\rho_L}{100M_{N_2}} ([\%N] - [\%N]_i) \\ &= k_C \cdot A \cdot \frac{\rho_L}{100M_{N_2}} ([\%N]_i - K^2 P_{N_2,i}) \\ &= k_G \cdot A \cdot \frac{1}{RT} (P_{N_2,i} - P_{N_2}) \quad \dots\dots\dots (1) \end{aligned}$$

- where, n_{N_2} : amount of nitrogen in a bubble (mol)
 t : time (s)
 A : bubble-metal interfacial area (cm²)
 M_{N_2} : molecular mass of nitrogen (g/mol)
 ρ_L : density of the melt (g/cm³)
 $[\%N]_i$: nitrogen concentration at the bubble-metal interface (mass%)
 $P_{N_2,i}$: nitrogen partial pressure at the bubble-metal interface (atm)
 K : equilibrium constant of molten iron-nitrogen reaction (mass%/atm^{1/2})
 P_{N_2} : nitrogen partial pressure in the bubble (atm)
 k_L : liquid-phase mass transfer coefficient ($= 2\sqrt{D_N v_B / (\pi d_B)}$) (cm/s)
 k_C : chemical reaction rate constant (cm/(%·s))
 k_G : gas-phase mass transfer coefficient ($= 2\sqrt{D_G v_B / (\pi d_B)}$) (cm/s)
 R : gas constant (atm·cm³/(mol·K))
 T : temperature of the melt (K)
 D_N : diffusivity of nitrogen in molten iron (cm²/s)
 D_G : diffusivity of nitrogen in Ar-N₂ mixture (cm²/s)
 v_B : bubble rising velocity ($= \sqrt{0.5 d_B g}$) (cm/s)
 d_B : bubble diameter (cm)
 g : acceleration of gravity (cm/s²).

The bubble formation time is equal to the reciprocal of the frequency of the bubble formation which was measured during the experiment. On the assumption that the bubble shows spherical in shape, the bubble-metal interfacial area is calculated from the bubble formation time, the gas flow rate through the nozzle and the amount of nitrogen entered the bubble. Both liquid- and gas-phase mass transfer coefficients are estimated according to Higbie's model. In the calculation of the desorption rate, the chemical reaction rate constant k_C is taken as a parameter to be determined by the trial and error

method. The existence of the interfacial resistance is investigated by comparison of k_c obtained from the present experiment with that obtained under the condition of no interfacial resistance in the previous work.

3. Examination of the Interfacial Resistance on the Bubble Interface

In Fig. 2 the chemical reaction rate constant k_c obtained in the present experiment is shown, compared with that obtained in the previous studies on nitrogen absorption⁷⁾ and desorption.⁴⁾ The symbols of ● and ○ in the figure indicate k_c with Al deoxidation. The symbols of ⊙ and ○ show k_c without Al addition. The figure shows that all the k_c are well correlated as the same function of $[\%O] + [\%S]/2$ as that found in the previous studies, irrespective of the crucible materials and the deoxidation methods. It reveals that the interfacial resistance does not exist on the bubble interface. This may be due to the fact that the oxide film is not formed on the bubble interface because the bubble diameter is relatively large (≈ 1 cm) and the renewal time of bubble interface is short.

2. Nitrogen Desorption by Ar Injection together with Blowing onto the Melt

As reported previously,⁵⁾ in the experiment used a MgO crucible and without Al or C addition, the rate of nitrogen desorption from molten iron by Ar injection together with blowing onto the melt is very high. In this case, the contribution of nitrogen desorption through the free surface to the overall reaction rate is very large and the average effective free surface area is 2.1 times as large as the cross sectional area of the crucible. The present experimental data are discussed, compared with those of the previous work.

1. Change in Nitrogen Concentration with Time

Typical examples of the change in nitrogen concentration $[\%N]$ with time determined by the use of MgO crucible are shown in Fig. 3. The symbol of ○ indicates the experimental data without Al or C addition. In this case, $[\%N]$ decreases to below 0.001 in 30 min in spite of the relatively high oxygen concentration. On the result for C deoxidation (●), the oxygen concentration $[\%O]$ is 0.003, but the rate of nitrogen desorption is about the same as that without deoxidation (○). In the experiment with Al addition (●) the oxygen concentration is the lowest among those of the three experiments, but the desorption rate is the smallest. It is considered that the alumina layer on the free surface gives the interfacial resistance and lowers the rate of nitrogen desorption.

Figure 4 shows examples of the change in nitrogen concentration with time determined by the use of Al_2O_3 crucible. In the experiments without deoxidation (Δ) and with C deoxidation ($\blacktriangle$), the oxides can not be detected on the free surface and the surface looks clean. But the rates of nitrogen desorption in these experiments (Δ , $\blacktriangle$) are about the same as the rate of nitrogen desorption with alumina layer on the surface ($\blacktriangle$). It should be noted that the desorption rate obtained by the use of Al_2O_3 crucible is lower than that obtained by the use of MgO crucible shown

Fig. 2. Chemical reaction rate constant plotted against $[\%O] + [\%S]/2$.

Fig. 3. Change in nitrogen concentration with time determined by the use of MgO crucible.

Fig. 4. Change in nitrogen concentration with time determined by the use of Al_2O_3 crucible.

in Fig. 3.

Figures 5 to 7 show the changes in nitrogen concentration with time determined by the use of MgO crucible, compared with those obtained by the use of Al_2O_3 crucible, to investigate the difference in the desorption rate due to the materials of crucible.

Figure 5 represents the results obtained from the experiment without Al or C deoxidation. The free surface looks clean in both experiments with MgO and Al_2O_3 crucibles. In the case of MgO crucible, the rate of nitrogen desorption is high and $[\%N]$ decreases from 0.012 to 0.001 in about 50 min. In the case of Al_2O_3 crucible, $[\%N]$ decreases at most to 0.002 in the same period of 50 min.

The change in nitrogen concentration with time for C deoxidation is shown in Fig. 6. The free surface of the melt looks clean regardless of Al_2O_3 and

Fig. 5. Comparison of changes in nitrogen concentration with time determined by the use of MgO and Al₂O₃ crucibles.

Fig. 6. Comparison of changes in nitrogen concentration with time determined by the use of MgO and Al₂O₃ crucibles, with C deoxidation.

Fig. 7. Comparison of changes in nitrogen concentration with time determined by the use of MgO and Al₂O₃ crucibles, with Al deoxidation.

MgO crucibles. However, nitrogen desorption by the use of MgO crucible progresses faster than that by the use of Al₂O₃ crucible, although the difference between the two is not so large as that shown in Fig. 5. Figure 7 represents the experimental results obtained under the condition of Al deoxidation. The rate of nitrogen desorption determined by the use of MgO crucible is a little higher than that determined by the use of Al₂O₃ crucible. The difference between the two is smaller than that shown in Fig. 6. When the melt is deoxidized with Al, alumina formed by

deoxidation exists on the melt surface. The free surface of the melt in the Al₂O₃ crucible is fully covered with alumina and it is difficult to observe the event of bubble collapsing at the melt surface. In the case of MgO crucible, alumina is brought near to the wall of the crucible and the free surface of the molten iron can frequently be observed. It is confirmed that the different conditions of the free surfaces are connected with the difference in the desorption rate in Fig. 7. Figures 3 to 7 show that the rate of nitrogen desorption depends on the crucible material and/or the method of deoxidation. Although [%O] is decreased to a very low value in the case of deoxidation with Al, alumina formed by deoxidation gives the interfacial resistance and the desorption rate is reduced in spite of low oxygen concentration. Under the same deoxidation condition, the rate of nitrogen desorption by the use of MgO crucible is higher than that by the use of Al₂O₃ crucible. Since the rates of desorption by the use of Al₂O₃ crucible both with C deoxidation and without Al or C deoxidation are lower than those by the use of MgO crucible, it is clear that in the case of Al₂O₃ crucible the interfacial resistance is present although the free surface looks clean. As can be seen from the results in Sec. III. 1. 3, the interfacial resistance is not present on the bubble interface. Hence, it is evident that the depression of the rate of nitrogen desorption by Ar injection together with blowing onto the melt is brought about by the interfacial resistance on the free surface. The interfacial resistances observed in Figs. 3 to 7 are estimated quantitatively by comparison of the experimental results with those calculated on the basis of the reaction model. 2. Reaction Model for the Bubble Interface and the Free Surface The reaction model and the method of calculation adopted are the same as those in the previous study⁵⁾ and the detailed description of the model is omitted. According to the reaction model, the nitrogen desorption through the bubble interface and that through the free surface are calculated separately. The reaction model for the bubble interface is the same as that shown in Sec. III. 1. 2. Because the interfacial resistance does not exist on the bubble interface, the amount of nitrogen removed through the bubble interface can be calculated by using k_c shown in Fig. 2. As far as the nitrogen desorption through the free surface is concerned, the reaction proceeds under such a condition that the resistance to the gas-phase mass transfer can be neglected. Hence, the desorption rate can be calculated on the basis of the mixed control of liquid-phase mass transfer and the chemical reaction. The rate of nitrogen desorption through the free surface is expressed as follows:

$$\begin{aligned} \frac{dn_{N_2,s}}{dt} &= k_{L,s} \cdot A_s \cdot \frac{\rho_L}{100M_{N_2}} ([\%N] - [\%N]_{i,s}) \\ &= k_c \cdot A_s \cdot \frac{\rho_L}{100M_{N_2}} ([\%N]_{i,s}^2 - K^2 P_{N_2,s}) \end{aligned} \quad \dots\dots\dots (2)$$

where, $n_{N_2,s}$: amount of nitrogen removed through the free surface (mol)
 A_s : effective free surface area (cm²)
 $[\%N]_{i,s}$: nitrogen concentration at the free surface (mass%)
 $k_{L,s}$: liquid-phase mass transfer coefficient for the melt surface (cm/s)
 $P_{N_2,s}$: nitrogen pressure in the gas phase (=0 atm).

The chemical reaction rate constant k_c shown in Fig. 2* and the liquid-phase mass transfer coefficient determined in the previous study,⁵⁾ 0.03 cm/s, are used in the calculation. Since the effective free surface area is unknown, it is taken as a parameter. If the interfacial resistance exists on the free surface, the effective free surface area is considered to become smaller. Thus, the interfacial resistance on the free surface is estimated from the effective free surface area.

On the basis of the reaction model, the amount of nitrogen desorbed through the bubble interface and that through the free surface can be calculated, respectively. The change in nitrogen concentration with time is calculated from the sum of the amounts of nitrogen desorbed through the bubble interface and through the free surface.

3. Determination of the Effective Free Surface Area

In the previous study,⁵⁾ the effective free surface area was determined in the nitrogen concentration region where the nitrogen desorption through the free surface was almost controlled by the chemical reaction. However, $[\%O]$ in the melt is very low and the region of the chemical reaction control hardly exists in the present study. In the range of high nitrogen concentration, the liquid-phase mass transfer plays an important role in the nitrogen desorption. Hence, the calculated result is largely dependent on the mass transfer coefficient $k_{L,s}$. As described in the previous paper, $k_{L,s}$ is a parameter to be determined by the trial and error method. It is not appropriate to compare the calculated results with the experimental ones in the range of high nitrogen concentration.

Therefore, in the present study, the effective free surface area is determined in the range of $[\%N] < 0.01$ where the resistance to the liquid-phase mass transfer is relatively small. A typical example of determination of the effective free surface area is shown in Fig. 8. In the figure, the symbol of $\circ$ represents the change in nitrogen concentration with time determined from the experimental result and the thin lines indicate those calculated by the use of various values of β ($\beta \equiv A_s/A_c$, A_s : effective free surface area, A_c : cross sectional area of the crucible). The nitrogen concentration $[\%N] = 0.01$ on the thick line is taken as the initial value of nitrogen concentration $[\%N]_0$ in the calculation. By comparison of the experimental result with the calculated one, β is estimated. Under the conditions shown in Fig. 8, β is determined to be 0.35 ± 0.15 .

It is confirmed that β is independent of the initial value of the nitrogen concentration ($[\%N]_0 = 0.008 \sim 0.012$), and the calculated change in nitrogen concentration with time agrees well with the experimental result over the wide range of nitrogen concentration including the region influenced markedly by the liquid-phase mass transfer.

3. Interfacial Resistance on the Free Surface

Figure 9 represents the relation between β and $[\%O]$. The differences in the methods of deoxidation and the materials of crucible are indicated by different symbols. The vertical line shows the scattering of β . The dotted line shows the average value of β determined in the previous work by the use of MgO crucible and without Al or C deoxidation.

Under the condition of Al deoxidation, β obtained by the use of MgO crucible ($\bullet$) and that determined by the use of Al_2O_3 crucible ($\blacktriangle$) are below 1.0, that is, the effective free surface area is smaller than the cross sectional area of the crucible. Figure 9 shows that alumina existing on the free surface gives the interfacial resistance and the contribution of the nitrogen desorption through the free surface to the overall reaction rate is reduced appreciably.

In the case of Al deoxidation, β obtained by the use of MgO crucible is a little larger than that obtained by the use of Al_2O_3 crucible. This is due to the fact that alumina is brought near to the wall of

Fig. 8. Determination of effective free surface area.

Fig. 9. Relation between β and $[\%O]$ under various experimental conditions.

* Here, it is assumed that the presence of the oxide layer on the free surface does not affect k_c .

MgO crucible because alumina tends to react with MgO.

In the three cases of MgO crucible with C deoxidation (●), Al₂O₃ crucible both with C deoxidation (▲) and without Al or C addition (Δ), β are smaller than 2.1. In these cases (●, ▲, Δ), the free surface looks clean similarly to the free surface in the previous experiment in which the value of β was 2.1. Especially in the cases of Al₂O₃ crucible without Al deoxidation (Δ, Δ), the values of β are below 0.5 and almost the same as that with Al deoxidation (▲). This means that the interfacial resistance exists on the free surface of the melt without Al deoxidation.

After the experiment, qualitative analyses were made for the surface of some solidified specimens by means of an X-ray microanalyzer and an electron spectroscopy analyzer. Silicon was detected for all the surfaces of the specimens. In order to investigate the influence of Si in more detail, Si dissolved in the bulk metal was also analyzed.

The relation between [%Si] and β is shown in Fig. 10. In the figure, the results of the previous study⁵⁾ denoted by (○) are also shown for comparison. For all the specimens examined, [%Si] is higher than that in the electrolytic iron (≈ 0.005) and β becomes small with increasing [%Si]. It is presumed that Si is originated from SiO₂ of the mullite reaction tube which is reduced to SiO by a reducing atmosphere and to Si by Al or C in the melt. Since oxygen serving as a surface active element is adsorbed on the free surface and [%Si] is high, a film containing SiO₂ may form on the free surface. This film gives the interfacial resistance. Further studies are needed to clarify the mechanism of the formation of oxides on the free surface of the molten iron.

According to the material of crucible, the data shown in Fig. 10 are classified into two groups: group I for MgO crucible and group II for Al₂O₃ crucible. The silicon concentration [%Si] of group I is much lower than that of group II. This comes from the fact that basic oxide MgO reacts with acidic oxide SiO₂ and the activity of SiO₂ is lowered.

According to the methods of deoxidation, in both cases of MgO crucible and Al₂O₃ crucible, [%Si] determined in the experiments with C or Al deoxidation becomes higher than that without C or Al

addition. This is owing to the fact that SiO in the atmosphere is reduced by C or Al and the content of Si in the melt is enriched.

The interfacial resistance to nitrogen desorption can be explained as follows. In the case of MgO crucible, when the melt is deoxidized with Al, alumina gives the interfacial resistance. Under the condition of C deoxidation, the film of SiO₂ gives the interfacial resistance. However, under the condition of C addition the interfacial resistance in MgO crucible is much smaller than that in Al₂O₃ crucible. This is due to the difference in the components of the interfacial film.

In the case of Al₂O₃ crucible with and without deoxidation, alumina is considered to be one of the components of the interfacial film. If the melt is deoxidized with Al, alumina is the main component of the interfacial film. In the other cases, it is presumed that the interfacial resistance is mainly given by the film of Al₂O₃-SiO₂.

The presence of the interfacial resistance due to SiO₂ was observed in the oxidation experiment of levitated droplet of liquid copper under a N₂-O₂ atmosphere by Glen and Richardson⁹⁾ and the experiment on the reaction between the molten silver and oxygen in the sinter-mullite crucible by Sano and Mori.⁸⁾ Since the experimental temperature and the molten metal are different from those of the present study, the mechanism of the interfacial resistance in these experiments may not be the same as that in the molten iron. However, it is noted that the oxidation of liquid copper is retarded significantly by the presence of SiO₂ film when the melt is containing Si as little as 2 ppm.

The interfacial resistance which was observed in the molten iron for the first time by the present study suggests the possibility of the formation of oxide film by impurities of a small amount. From the fact that the interfacial resistance gives strong influence on the reaction rate, the mechanism of the formation of oxide film on the free surface is considered as the problem to be solved in future. It is clear that the interfacial resistance can be reduced by the use of the crucible which reacts with the impurities or deoxidation products and hence the rate of nitrogen desorption can be enhanced.

IV. Conclusion

Experiments on the rate of nitrogen desorption from molten iron by Ar injection only or Ar injection together with blowing onto the melt have been done by the use of crucibles of two materials (Al₂O₃ and MgO) and two methods of deoxidation (Al addition and C addition). The interfacial resistance is examined quantitatively for the first time by comparison of the experimental results with the results calculated on the basis of the mixed control model. The results obtained are summarized as follows:

(1) The interfacial resistance exists on the free surface while not on the bubble-metal interface regardless of materials of crucible and methods of deoxidation.

(2) Under the same deoxidation condition, the

Fig. 10. Relation between β and [%Si] under various experimental conditions.

rate of nitrogen desorption determined by the use of MgO crucible is higher than that obtained by the use of Al_2O_3 crucible.

(3) In the case of deoxidation with Al, alumina gives a large interfacial resistance and hence the rate of nitrogen desorption is lowered.

(4) Although the free surface looks clean, the interfacial resistance exists on the free surface of the melt contained in Al_2O_3 crucible. In this case, the film of Al_2O_3 - SiO_2 gives the interfacial resistance.

REFERENCES

- 1) T. K. Sherwood, R. L. Pigford and C. R. Wilke: *Mass Transfer*, McGraw-Hill Inc., New York, (1975), 190.
- 2) For example, K. Mori and K. Suzuki: *Trans. Iron Steel Inst. Jpn.*, **10** (1970), 232.
- 3) S. Ban-ya, T. Shinohara, H. Tozaki and T. Fuwa: *Tetsu-to-Hagané*, **60** (1974), 1443.
- 4) C. G. Glen and F. D. Richardson: *Heterogeneous Kinetics at Elevated Temperature*, ed. by G. R. Belton and W. L. Worrell, Plenum Press, New York, (1970), 369.
- 5) M. Takahashi, H. Matsuda, M. Sano and K. Mori: *Trans. Iron Steel Inst. Jpn.*, **27** (1987), 626.
- 6) M. Takahashi, M. Sano, K. Mori and M. Hirasawa: *Trans. Iron Steel Inst. Jpn.*, **27** (1987), 633.
- 7) The Recommended Equilibrium Data for Steelmaking, ed. by The 19th Comm. (Steelmaking), the Japan Soc. for the Promotion of Sci. (JSPS), JSPS, Tokyo, (1984), 38.
- 8) M. Sano, K. Kadoguchi and K. Mori: *Trans. Iron Steel Inst. Jpn.*, **24** (1984), 825.
- 9) M. Sano and K. Mori: *Tetsu-to-Hagané*, **60** (1974), 1432.