Reaction of Magnesia Refractory on Molten Iron and Refractory Transmutation during Deoxidation*

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Synopsis

This report presents the elucidation on the reaction of magnesia refractory on molten iron and the refractory transmutation during the deoxidation of iron, based on the investigation of the oxygen concentration in iron melted in magnesia crucibles under argon atmosphere and reduced pressures, and the examination of the refractory. The results obtained are the various time-dependent behaviors of dissolved oxygen according to differences in crucibles and environmental conditions, together with the growth of the refractory grains, and the particular transmutations of crucibles as to the deoxidation. The successful explanation of these results can be also discussed on the reasonable assumptions.

I. Introduction

Reactions of refractories on molten steels or slags closely relate, not only to the primary consumption cost, but also to the produced steel qualities. There, therefore, have been many researches about the reactions, most of which attempt the restricted solutions of the particular problems encountered in practices, so only a few basic approaches have been tried.¹⁻⁷⁾

Since refractories for steelmaking are mainly of oxides, the reactions on molten steel can be traced out by changes in the concentration of dissolved oxygen. In the present work, hence, the exploration of the fundamental reactions was carried out by investigating the time-dependent oxygen concentration in molten iron melted in magnesia crucibles under argon or reduced atmosphere. Moreover, the examination was done on refractory transmutation during the deoxidation of molten iron by silicon or manganese.

II. Experimental Method

1. Apparatus and Specimens

The experimental apparatus consists of a furnace, an argon purifier and a rotary oil pump for vacuum. The power for heating the furnace was supplied with a mercury gap spark type high frequency generator (15 kVA, 10 kHz). The temperature of molten iron was measured at the surface with an optical or a two-color pyrometer calibrated with a thermocouple. A Pirani gauge read the reduced pressure.

The crucibles used are mainly of porous magnesia with the apparent porosity of 20 % (MG-1; 98 % MgO, 1 % CaO, and others; 50 O.D. $\times$ 40 I.D. $\times$ 100 mm), and partly of dense one with little porosity (MG-12; 97 % MgO, 1 % CaO, and others; 36 O.D.

$\times$ 26 I.D. $\times$ 100 mm) for comparison. Magnesia bar specimens were also prepared for the observation of the refractory transmutation during the deoxidation of molten iron with silicon or manganese. A prism piece of 5 $\times$ 5 $\times$ 10 mm was sawed out of the identical crucible and fixed into a silica tube with magnesia cement. The bar specimens were thoroughly dried before use.

2. Experimental Procedures

1. Under Argon Atmosphere

300 g of electrolytic iron was melted in a porous magnesia crucible under a refined argon stream by means of high frequency induction heating (150 g of iron in a dense crucible). The dissolved oxygen concentration was adjusted through the oxidation with ferrous oxide addition or steam, or the reduction with hydrogen. The measurement began ($t=0$) when the argon stream rate was rapidly controlled to be 1 500 ml/min and the melt temperature was set at $1\,600 \pm 10^\circ\text{C}$. At suitable intervals, 5~10 g of the molten iron was sucked into a silica tube of 3 mm inner diameter, and quenched into water for the determination of the oxygen concentration. The oxygen analysis was performed by the vacuum fusion isometric pressure or argon fusion coulometric titration method.

Test pieces of the cooled crucibles were sawed out of the parts being about 10 mm below the molten iron surfaces. The pieces were reinforced with resin and polished with boron carbide powder, and γ -alumina and diamond pastes. They were used for microscopic observation, and X-ray diffraction and EPMA analyses (line- and point-analyses, and/or electron absorption and K_α scopes) after the treatment of copper vapor deposition on the surfaces.

2. In Reduced Pressure

The experimental procedures were just similar to the above-mentioned ones for the experiment in porous magnesia crucibles under argon atmosphere until the initial sampling. Then, the reaction chamber was evacuated with the vacuum pump. Whenever the molten iron was sampled, the refined argon was introduced into the chamber, so the evacuation procedure was again repeated soon after the sampling for the continuation of experiment.

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3. With the Addition of Deoxidizers

As soon as the premelted iron containing oxygen was remelted in a magnesia crucible under argon atmosphere, two pieces of the magnesia bar specimens were dipped and held in the melt, out of touch with the crucible wall. The molten iron rapidly stabilized at 1 600 °C was maintained over 1 hr under a refined argon stream of 1 500 ml/min to penetrate iron oxide in the refractory. The experiment was initiated ($t=0$) with the addition of the deoxidizer, 0.5 or 1 % amount of silicon or 1 % of manganese. When the molten iron was sampled, the bar specimen was also lifted out of the melt.

III. Experimental Results

1. Under Argon Atmosphere

When molten iron is kept at 1 600 °C over a long period in the porous magnesia crucible, the oxygen concentration behaves as shown in Fig. 1. The behavior is dependent upon the concentration, namely the higher concentration decreases with the lapse of time, while the lower increases. About 125 ppm is the boundary concentration of both the directional behaviors.

Figure 2 shows the similar time-dependence of the oxygen concentration in the molten iron in the dense magnesia crucible. For comparison with the results obtained in the porous crucible, the dependencies figured are adjusted with the ratios of the molten iron-crucible interface areas, which have been estimated from the differences in the used crucible dimensions and the melted amounts of iron. No difference is perceived between both the dependencies.

Photographs 1 and 2 show the microstructures of the crucibles before and after use, respectively. The grain growth can be observed in the vicinity of the interface to the molten iron.

The concentration profiles in Fig. 3 are the EPMA results on the cross sections of large periclase grains in the crucible after the experiment, an end of which seems to form the interface to the molten iron (the

location 1 in Fig. 3) and another end of which to touch to the pore in the crucible inside (2 in Fig. 3). The intensity indicating the iron concentration has the minimum at a little inner site from the grain center, and shows the higher concentration in the further inside. This knowledge suggests that the infiltration mechanism through the pores or the grain boundaries mainly governs the intrusion of FeO into porous magnesia crucible.

2. In Reduced Pressure

Figure 4 presents the time-dependent oxygen concentration in molten iron in the porous magnesia crucible under reduced pressure. The pressure in the chamber was reduced to be less than 1 mmHg within 1 min, to be about 0.4 mmHg at 5 min and finally reached 0.1~0.3 mmHg, being less and faster in the later period of the experiment. Although no exactly rational results in reduced pressure can be expected by repeating the introduction of argon every sampling time, it should be noted that the time-dependent behavior of the oxygen concentration is similar during the early period to the results obtained under argon atmosphere, then the concentration

Fig. 2. Equivalent time-dependency of the oxygen concentration in molten iron in the dense magnesia crucible under a refined argon stream of 1 500 ml/min; the broken curve obtained in the porous crucible.

Fig. 1. Change in the oxygen concentration in molten iron in the porous magnesia crucible under a refined argon stream of 1 500 ml/min.

Fig. 3. Distributions of iron in magnesia grains (two examples), where the points 1 and 2 indicate the locations of the interfaces to the liquid iron and the inner pore, respectively.

monotonously increases with the elapsing time, and that the increment ratio is a little larger in the later period.

3. With the Addition of Deoxidizers

The concentration profiles of iron and silicon were investigated with an EPMA on the cross section of the porous magnesia crucible in which molten iron had been maintained at 1 600 °C for 1 hr and further for 1 hr after 1 % addition of silicon. An example of the results is shown in Fig. 5. Photograph 3 also shows the electron absorption, Fe-K_α and Si-K_α scanning images on the crucible near the interface. The wide flat peaks of the silicon intensity recognized in Fig. 5 indicate Mg-Fe olivine, forsterite

(Mg₂SiO₄) with a little amount of fayalite (Fe₂SiO₄), which is also confirmed by the X-ray diffraction analysis.

In order to examine the transition of the crucible material with progress in the deoxidation reaction, the bar specimens were used for the experiment of half an hour with 0.5 % addition of silicon. The EPMA results are shown in Figs. 6 and 7, where (a) and (b) are the results on the bar specimens just before the deoxidation treatment and at 5 min since the treatment, respectively, and (c) on the crucible after the experiment. With progress in the reaction, the intensity of iron in the refractory decreases in the vicinity of the interface to the molten iron.

In the manner illustrated for the silicon deoxida-

Photo. 1.
Cross-sectional microphotographs of
(a) porous and (b) dense magnesia
crucibles.

Photo. 2.
Grain growth at the interfaces of
(a) porous and (b) dense magnesia
crucibles.

tion, Photo. 4 and Figs. 8 to 10 show the results found during the deoxidation with 1 % addition of manganese. The characteristics recognized are that (i) the concentration profile of manganese in the crucible is the most similar to the type of thin film diffusion, the one of a substance initially confined in a region, (ii) sticking occurs between the crucible and the metal, and (iii) many metal particles precipitate in the crucible interior (till about 0.3 mm inner from the interface).

IV. Discussion

1. Time-dependent Oxygen Concentration in Molten Iron under Argon Atmosphere

For the molten iron kept in the porous magnesia crucible under the argon stream, it is found that the time-dependent oxygen concentration can be expressed by a modified exponential function with the constants α , β and γ ,

$$[O] = \alpha + \beta \cdot \exp(\gamma \cdot t) \dots\dots\dots(1)$$

Fig. 4. Time-dependent oxygen concentration in molten iron in the porous magnesia crucible under a reduced pressure of $(2 \pm 1) \times 10^{-1}$ mmHg; the broken curves obtained under a refined argon stream of 1 500 ml/min.

where, $[O]$: the oxygen concentration (wt%) in molten iron
 t : the elapsing time (sec).

The curves shown in Fig. 1 are based on Eq. (1) with the constants summarized in Table 1 which have been estimated by the least square method. It comes into notice that the γ -values are almost same throughout the experiments of Nos. 4 to 8, which are substantially significant in consideration of the errors. Therefore, the relation

$$\left(\frac{d[O]}{dt}\right)_{t-1} - \left(\frac{d[O]}{dt}\right)_{t-2} \doteq \gamma([O]_{t-1} - [O]_{t-2}) \dots\dots\dots(2)$$

may exist between the time-dependent oxygen con-

Fig. 5. Radial distributions of iron and silicon near the interface of the porous magnesia crucible after 1 hr 1 % Si deoxidation.

(a) Si- K_{α} (b) Fe- K_{α} (c) Electron absorption

Photo. 3. Electron beam scanning images near the interface of the crucible shown in Fig. 5.

Fig. 6. Radial distributions of iron and silicon in the porous magnesia crucible.

Fig. 7. Radial distributions of iron and silicon in the dense magnesia crucibles.

Photo. 4. Electron beam scanning images near the interface of the crucible shown in Fig. 8.

centration at any times of $t-1$ and $t-2$. This relation is of use for the discussion on the reaction mechanism described in next section.

2. Reaction Mechanism and Rate

When molten iron is maintained in magnesia crucibles under argon stream or reduced atmosphere, the observed facts are the time-dependent oxygen concentrations (Figs. 1 to 3), the grain growth on the

Fig. 8. Radial distributions of iron and manganese near the interface to the porous magnesia crucible after 30 min of 1 % Mn deoxidation.

crucible surface (Photos. 1 and 2) and the diffusion of iron into the refractory grains (Fig. 3). The reactions to be considered, which result in these observations, are,

- 1) on the interface (with the area of A_{g-l}) between molten iron and atmosphere
 - ① $\text{Mg} \rightarrow \text{Mg} (g)$ (evaporation reaction)
 - ② $1/2 \text{O}_2 (g) \rightarrow \text{O}$ (oxidation reaction)
- 2) on the interface (with the area of A_{l-s}) between molten iron and crucibles

Table 1. Constants for the analysis of the time-dependent oxygen concentration in molten iron.

No.	α	β	γ	I
1	0.0073	-0.0036	-1.24×10^{-4}	-4.96
2	0.0125	-0.0031	-1.64×10^{-4}	-4.78
3	—	—	—	—
4	0.0295	0.0164	-6.11×10^{-5}	-3.61
5	0.0278	0.0229	-5.53×10^{-5}	-3.61
6	0.0340	0.0229	-5.97×10^{-5}	-3.31
7	0.0410	0.0232	-4.45×10^{-5}	-3.05
8	0.0851	0.0494	-6.78×10^{-5}	-2.25

a) $t=0$ min, 0.10 % O b) $t=5$ min, 0.041% O c) $t=30$ min, 0.034 % O
(where the points show the interfaces to the liquid iron)

Fig. 9. Radial distributions of iron and manganese in the porous magnesia crucible.

a) $t=0$ min, 0.063 % O b) $t=5$ min, 0.024 % O c) $t=30$ min, 0.019 % O
(where the points show the interfaces to the liquid iron)

Fig. 10. Radial distributions of iron and manganese in the dense magnesia crucible.

- ③ $\text{Fe (l)} + \text{MgO (s)} \rightarrow \text{Mg} + \text{FeO (in MgO)}$
 (exchange reaction)
 ④ $\text{MgO (s)} \rightarrow \text{Mg} + \text{O}$ (dissolution reaction)
 ⑤ $\text{Fe (l)} + \text{O} \rightarrow \text{FeO (in MgO)}$
 (grain growth reaction).

The reason why the reaction ② is to be considered is that the partial pressure of the residual oxygen in the refined argon guaranteed with the used purifier (the volume ratio less than 0.1 ppm) is higher than the one of oxygen dissolved in the molten iron under the present conditions (about 5×10^{-9} atm estimated at maximum).

According to the study investigated on the evaporation of manganese out of molten iron by Ito and Sano,⁹⁾ it is estimated that the rate of the evaporation reaction ① can be expressed by the first order equation of the evaporating element concentration (magnesium in the present case) under both the conditions of argon stream and reduced pressure, and that the over-all transfer coefficient is much larger under the reduced pressure.

In the oxidation reaction ②, the kinetic equation is anticipated to be of the second order under argon atmosphere and of the first order under reduced pressure from the analogical estimation based on the study about the dissolution of nitrogen into molten iron.⁹⁾

There is no direct information, nor even the estimation method, concerning to the exchange reaction ③. Although many kinetic equations are generally introduced for the dissolution reaction, such as the Nernst's equation based on the rate-controlling mechanism of mass transfer in melt and the various ones based on the rate-controlling of chemical reactions,¹⁰⁾ no knowledge about the dissolution reaction ④ makes even the analogy impossible.

The reaction ⑤ is of the grain growth of magnesia at the surface, resulting in the solid solution of FeO. There are three different models proposed for the growth mechanism of crystal grains in dilute solutions¹¹⁾ like the present case. These are of ⑧ the usual random growth with the formation of atomically rough surface, ⑨ the directional growth with the fairly smooth surface on the edge of spiral dislocation and ⑩ the directional nucleation-growth with atomically perfect flat surface. When the driving force of the growth (the super-saturation, *etc.*) is not so much, the model ⑩ can be excluded and the rate is also in proportional to the driving force based on the model ⑧ or the square in the case of the model ⑨.

Next, the material transfer rate is balanced about oxygen and magnesium in molten iron on the assumption of perfect mixing in the bulk of the molten iron.

On the time-dependent oxygen,

$$\begin{aligned} d[\text{O}]/dt &= (\text{the increasing rate due to the reaction ④}) \\ &\quad - (\text{the decreasing rate due to the reaction ⑤}) \\ &\quad + (\text{the increasing rate due to the reaction ②}) \\ &\quad \dots\dots\dots(3) \end{aligned}$$

On the magnesium,

$$\begin{aligned} d[\text{Mg}]/dt &= (\text{the increasing rate due to the reaction ③}) \\ &\quad + (\text{the increasing rate due to the reaction ④}) \\ &\quad - (\text{the decreasing rate due to the reaction ①}) \\ &\quad \dots\dots\dots(4) \end{aligned}$$

It is presumed here that the magnesium concentration in molten iron fairly soon reaches the steady value ($d[\text{Mg}]/dt=0$) due to both the reactions ③ and ④, and the contribution ratios of both the reactions settle in constants. In other words, this presumption means that the sum of the first and second terms in the right side of Eq. (4) balances in a short time with the third term of the evaporation rate which can be expressed by the first order of the magnesium concentration, and becomes unvaried in the steady state, so that the rate of the reaction ④ in Eq. (3) settles down in a constant value. Then, Eq. (3) is written down under the condition of argon atmosphere in two ways, separately based on the mechanisms of the usual random growth ⑧ and the directional growth on the steps of spiral dislocation ⑨ respectively as follows;

$$\begin{aligned} \frac{d[\text{O}]}{dt} &= k_4 \left(\frac{A_{l-s}}{V} \right) - k_{5-a} \left(\frac{A_{l-s}}{V} \right) \left(\frac{[\text{O}]}{[\text{O}]_e} \right) \\ &\quad + k_2 \left(\frac{A_{g-l}}{V} \right) ([\text{O}]_{\text{Ar}}^2 - [\text{O}]^2) \dots\dots\dots(5) \end{aligned}$$

$$\begin{aligned} \frac{d[\text{O}]}{dt} &= k_4 \left(\frac{A_{l-s}}{V} \right) - k_{5-b} \left(\frac{A_{l-s}}{V} \right) \left(\frac{[\text{O}]}{[\text{O}]_e} \right)^2 \\ &\quad + k_2 \left(\frac{A_{g-l}}{V} \right) ([\text{O}]_{\text{Ar}}^2 - [\text{O}]^2) \dots\dots\dots(6) \end{aligned}$$

where, k_i , k_{i-j} ($i=1, 2, \dots, 5$; $j=a, b$): the over-all mass transfer coefficients based on the model ① of the reaction ①

V : the volume of molten iron

$[\text{O}]_e$: the oxygen concentration in equilibrium with the steady magnesium concentration

$[\text{O}]_{\text{Ar}}$: the concentration expression of the residual oxygen potential in the refined argon.

Equations (5) and (6) are rearranged in the increasing order terms of $[\text{O}]$ to be

$$\begin{aligned} \frac{d[\text{O}]}{dt} &= \left\{ k_4 \left(\frac{A_{l-s}}{V} \right) + k_2 \left(\frac{A_{g-l}}{V} \right) [\text{O}]_{\text{Ar}}^2 \right\} \\ &\quad - \left\{ \frac{k_{5-a}}{[\text{O}]_e} \left(\frac{A_{l-s}}{V} \right) [\text{O}] - k_2 \left(\frac{A_{g-l}}{V} \right) [\text{O}]^2 \right\} \dots\dots(5') \end{aligned}$$

$$\begin{aligned} \frac{d[\text{O}]}{dt} &= \left\{ k_4 \left(\frac{A_{l-s}}{V} \right) + k_2 \left(\frac{A_{g-l}}{V} \right) [\text{O}]_{\text{Ar}}^2 \right\} \\ &\quad - \left\{ \left(\frac{k_{5-b}}{[\text{O}]_e^2} \right) \left(\frac{A_{l-s}}{V} \right) + k_2 \left(\frac{A_{g-l}}{V} \right) \right\} [\text{O}]^2 \dots\dots(6') \end{aligned}$$

From the comparison of both the above equations with Eq. (2) discussed in Section IV. 1, it can be suggested that the refractory grain grows through the usual random mechanism and that the contribution of the oxidation due to the residual oxygen in the refined argon is quite small. The latter small con-

tribution is coincident with no difference in the time-dependent behaviors of the oxygen concentration obtained in the porous and dense crucibles, even the sizes of which are different. Except in the early period, in which the magnesium concentration reaches the steady value, the equation which expresses the behavior of the oxygen concentration in molten iron is after all

$$d[O]/dt = M - N[O], \dots\dots\dots(7)$$

where, $M \equiv (k_4 A_{l-s}/V) + k_2(A_{g-l}/V)[O]_{Ar}^2$
 $N \equiv (k_{5-a}/[O]_e)(A_{l-s}/V).$

From the integration of Eq. (7),

$$\ln |[O] - (M/N)| = -Nt + I, \dots\dots\dots(8)$$

where, I : an integral constant.

The value of $[O]_{\infty} \equiv (M/N)$ can be estimated to be 0.0125 in the steady state of Eq. (7) ($d[O]/dt=0$) from the experimental results shown in Fig. 1. The integral constant, however, cannot be determined from the experimental initial condition, since it is the imaginal initial value of $\ln |[O] - [O]_{\infty}|$ when the magnesium concentration reaches a steady constant. Thus, the integral constants I in Table 1 were estimated by plotting the values of the left side terms of Eq. (8) against the time, and extrapolating the straight line relations obtained during the later experimental period to $t=0$. These relations are summarized in Fig. 11. Based on the gradient of the straight line, N is to be $1.82 \times 10^{-5} \text{ sec}^{-1}$ and M is $2.28 \times 10^{-7} \text{ sec}^{-1}$.

The adequacy of the above discussion was further examined for the three selected experiments with the different oxygen concentration levels (Nos. 1, 6 and 8). The results shown in Fig. 12 indicate that the curves calculated by Eq. (8) quite well fit the data over the wide range of the oxygen concentration except in the early period. The figure also discloses together with Fig. 11 that about 1 hr is necessary for the establishment of the steady magnesium concentration.

The same analytical explanation is possible for the experimental results in the dense magnesia crucible. For the behavior of the oxygen concentration under reduced pressure, however, the equation

$$\begin{aligned} \frac{d[O]}{dt} &= k'_4 \left(\frac{A_{l-s}}{V} \right) - k'_{5-a} \left(\frac{A_{l-s}}{V} \right) \left(\frac{[O]}{[O]_e'} \right) \\ &\quad + k'_2 \left(\frac{A_{g-l}}{V} \right) ([O]_v - [O]) \\ &= \left\{ k'_4 \left(\frac{A_{l-s}}{V} \right) - k'_2 \left(\frac{A_{g-l}}{V} \right) [O]_v \right\} \\ &\quad - \left\{ \left(\frac{k'_{5-a}}{[O]_e'} \right) \left(\frac{A_{l-s}}{V} \right) + k'_2 \left(\frac{A_{g-l}}{V} \right) \right\} [O] \\ &= M' - N'[O] \dots\dots\dots(9) \end{aligned}$$

is led instead of Eq. (5), where the upper prime means the different values from the ones in the argon atmosphere, the lower subscript v of $[O]$ the condition of reduced pressure,

$$M' \equiv (k'_4 A_{l-s}/V) - k'_2(A_{g-l}/V)[O]_v$$

and

$$N' \equiv (k'_{5-a}/[O]_e')(A_{l-s}/V) + k'_2(A_{g-l}/V).$$

The behavior shown in Fig. 3 can be well explained on the supposition of $M' \gg N'[O]$, in spite of the different interpretations for the contribution of the oxidation reaction ② in Eq. (9) which is dependent upon the composition of the residual gas in the chamber under the reduced pressure. According to the observed fact of the higher reducibility of the pressure in the later period, it is also qualitatively reasonable that the oxygen concentration have a tendency of a little more increment later under the reduced pressure. However, since the reduction of pressure and the introduction of argon are repeated several times during the experiment as already detailed, the assumption of the steady magnesium concentration is not proper, and the quantitative interpretation is impossible.

3. Diffusion of Iron in Magnesia

The interdiffusion coefficient of iron (II) ion in practically single periclase crystals is calculated to be about $4 \times 10^{-9} \text{ cm}^2/\text{sec}$ from the concentration profiles instanced in Fig. 3. The coefficient in the single crystal has been reported to be $1 \times 10^{-9} \text{ cm}^2/\text{sec}$ in the air at 1 600 °C by Wuensch and Vasilos,¹²⁾ 2×10^{-9}

Fig. 11. Discussion on the mechanism of the time-dependent oxygen concentration in molten iron in the porous magnesia crucible under a refined argon stream of 1 500 ml/min.

Fig. 12. Coincidence between the data and the curves calculated with Eq. (8).

cm^2/sec under the same conditions and $7 \times 10^{-10} \text{cm}^2/\text{sec}$ in $P_{\text{O}_2} = 10^{-6} \text{atm}$ at 1600°C by Tagai *et al.*¹³⁾ Therefore, the present calculation is in a fair coincidence with these values. But, Rigby *et al.*¹⁴⁾ have suggested that the coefficient is dependent upon the concentration of iron (III) ion or positive hole which is ruled by the oxygen potential in atmosphere. Blank and Pask¹⁵⁾ have also reported the concentration-dependency. From the survey of the references concerned, thus, the transfer of iron in periclase is subject to the diffusion of positive hole.

4. Transmutation of Magnesia Crucibles with Deoxidations

1. Deoxidation with Silicon

(1) Phases in FeO–MgO–SiO₂ System

Figure 13 is the schematic isothermal phase diagram of FeO–MgO–SiO₂ system at 1600°C . In the present investigation, there finally remained three condensed phases of liquid iron, (Mg, Fe)O and (Mg, Fe)₂SiO₄. The co-existence range of these phases is figured by the mark of (M+O). On the other hand, the activity of silica a_{SiO_2} was thermodynamically calculated to be $0.11 \sim 0.23$ from the concentrations of silicon and oxygen in the molten iron 1 hr after the deoxidation treatment.¹⁶⁾ Suzuki *et al.*¹⁷⁾ have reported to get $a_{\text{SiO}_2} = 0.07$ 2 hr after. From the activity measurement of the melts in FeO–SiO₂,¹⁸⁾ MgO–SiO₂¹⁹⁾ and CaO–FeO–SiO₂²⁰⁾ systems, about 0.3 can be estimated for the a_{SiO_2} in the (L+M+O) field of Fig. 13, too. Further, $a_{\text{SiO}_2} = 0.02$ can be obtained in the co-existence zone of MgO and Mg₂SiO₄ from the free energy of formation of Mg₂SiO₄.²¹⁾ Hence $a_{\text{SiO}_2} = 0.02 \sim 0.3$ can be concluded for the (M+O) field. This conclusion is in a good agreement with the results of the present work and of Suzuki *et al.*¹⁷⁾

(2) Formation of Forsterite and Removal of FeO in Magnesia Crucibles

According to the concentration profiles shown in Photo. 3, silicon has no gradual distribution in the vicinity of the interface and spreads over the locations formerly occupied with the pores. This locality can

be interpreted as follows. The deoxidation product (SiO₂) reacts on the magnesia crucible containing FeO into a molten slag, which dissolves and thickens MgO finally to form forsterite with the infiltration into the crucible pores.

On the other hand, Figs. 6 and 7 show that the FeO concentration in the magnesia grains decreases with progress in the deoxidation reaction. This can be reasoned by the reduction of FeO at the molten iron–crucible interface due to the reaction,

The figures (b) and (c) in Figs. 6 and 7 also indicate the transfer lag of FeO in the crucible materials by the maximum peak positions of the iron concentration which are shifted to a little inner sites away from the interfaces.

2. Deoxidation with Manganese

(1) Phases in FeO–MgO–MnO System

Supposed of the negligibly small amounts of trivalent ions in this system, the formation of a continuous solid solution is to be considered as shown in Fig. 14, a schematic isothermal phase diagram at 1600°C . The final phases remained in the present experiment are liquid iron and (Mg, Mn, Fe)O. The compositions on the crucible surfaces are also plotted in the same figure by means of the EPMA analysis. On the other hand, a_{MnO} was calculated to be $0.1 \sim 0.2$ from the concentrations of manganese and oxygen in the molten iron 1/2 hr after the addition of the deoxidizer. These values seem reasonable for the a_{MnO} in the solid solution area of Fig. 14.

(2) Reaction between Deoxidation Product and Crucible

As the deoxidation is carried out by 1 % addition of manganese in the present study, the formed product is a solid solution of (Fe, Mn)O except in the early period. Thus, it can be thought that the product precipitates and/or adheres in a thin filmy way on the crucible surface of (Mg, Fe)O solid solution and then both the solid solutions unite to a single phase due to the mutual interdiffusion.

V. Summary

The reaction between magnesia and molten iron was elucidated by investigating the time-dependent

Fig. 13. Schematic phase diagram of FeO–MgO–SiO₂ system at 1600°C .

Fig. 14. Schematic phase diagram of FeO–MgO–MnO system at 1600°C .

oxygen concentration in the iron melt in magnesia crucibles under argon atmosphere and reduced pressure. Moreover, the transmutation of magnesia refractory was examined during the deoxidation of molten iron with silicon or manganese. The results and the discussions are summarized as follows.

(1) When molten iron is kept at 1600 °C in porous magnesia crucibles, the dissolution amount of oxygen increases or decreases with the concentration under argon atmosphere, but increases monotonously under reduced pressure. The almost same behaviors have been detected in dense magnesia crucibles. These results can be well interpreted by the estimation that the transfer of magnesium through the molten iron soon reaches the steady rate and the concentration settles in a constant in the early period. The oxidation rate due to the residual oxygen in the refined argon is negligibly small.

(2) The crystal grain grows near the interface of the crucible. It can be estimated that the growth is based on the usual random mechanism with the formation of atomic rough surface.

(3) When molten iron is deoxidized with silicon in the magnesia crucible containing FeO, the simultaneous reactions proceed to reduce the FeO on the interface and to form the molten slag, which infiltrates into the pores of the crucible to precipitate forstelite. For manganese deoxidation, the filmy solid solution of (Fe, Mn)O precipitates and/or adheres on the interface and forms the solid solution of (Mg, Mn, Fe)O through the interdiffusion.

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REFERENCES

1) W. A. Fischer and A. H. Hoffmann: *Arch. Eisenhüttenw.*,

- 29 (1958), 339.
- 2) S. Sawa, S. Shibutani and M. Ikeda: *Technical Reports of Nippon Tokushuko Co.*, **4** (1968), 3.
- 3) S. Kienow, R. Knüppel and F. Oeters: *Arch. Eisenhüttenw.*, **46** (1975), 57.
- 4) F. Oeters and Y. Wanibe: *Arch. Eisenhüttenw.*, **50** (1979), 37.
- 5) M. Umakoshi, K. Mori and Y. Kawai: *Tetsu-to-Hagané*, **67** (1981), 1726.
- 6) Y. Wanibe, H. Tsuchida, T. Fujisawa and H. Sakao: *Trans. ISIJ*, **23** (1983), 322.
- 7) Y. Wanibe, H. Tsuchida, T. Fujisawa and H. Sakao: *Trans. ISIJ*, **23** (1983), 331.
- 8) K. Ito and K. Sano: *Tetsu-to-Hagané*, **50** (1964), 1161.
- 9) K. Amano, K. Ito and H. Sakao: *Tetsu-to-Hagané*, **62** (1976), 1179.
- 10) Inorganic Reactions Related with Solid, ed. by Japan Inst. Chem., Tokyo Univ. Press, Tokyo, (1975), 177.
- 11) W. D. Kingery, H. K. Bowen and D. R. Uhlmann: *Introduction to Ceramics*, 2nd ed., John Wiley & Sons, New York, (1976), 336.
- 12) B. J. Wuensch and T. Vasilos: *J. Chem. Phys.*, **36** (1962), 2917.
- 13) H. Tagai, T. Iwai and T. Izeki: *J. Ceram. Soc. Japan*, **74** (1966), 366.
- 14) E. B. Rigby and I. B. Cutler: *J. Amer. Ceram. Soc.*, **48** (1965), 95.
- 15) S. L. Blank and J. A. Pask: *J. Amer. Ceram. Soc.*, **52** (1969), 669.
- 16) Recommended Equilibrium Values of Steelmaking Reactions, ed. by the 19th Comm. (Steelmaking) of Japan Soc. Promotion Sci. (JSPS), Nikkan Kogyo Shinbun-sha, Tokyo, (1968), 39.
- 17) K. Suzuki, S. Ban-ya and T. Fuwa: *Tetsu-to-Hagané*, **56** (1970), 20.
- 18) E. Yokoyama and H. Ooi: *Tetsu-to-Hagané*, **55** (1969), 454.
- 19) T. Kawawa and M. Okubo: *Tetsu-to-Hagané*, **53** (1967), 1569.
- 20) R. Sakagami, H. Kawasaki, I. Suzuki and K. Sato: *Tetsu-to-Hagané*, **55** (1969), 550.
- 21) J. F. Elliott, M. Gleiser and V. Ramakrishna: *Thermochemistry for Steelmaking*, II, Addison-Wesley, Mass., (1963), 305.