Behavior of Magnesium in the Desulfurization Process of Molten Iron with Magnesium Vapor Produced In-situ by Aluminothermic Reduction of Magnesium Oxide

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The behavior of magnesium in the desulfurization process of molten iron with magnesium vapor produced in-situ by the aluminothermic reduction of magnesium oxide has been investigated.

The magnesium concentration first increased rapidly, reaching the maximum, and then decreased gradually to a very low level. The magnesium concentration of the molten iron was mainly that of the dissolved magnesium and the following decrease in the magnesium concentration was due to the evaporation from the melt surface and the mass transfer of the dissolved magnesium to the bubble surface. Under the present experimental conditions, the magnesium concentration increased with increasing temperature, pellet mass, carrier gas flow rate and decreasing initial sulfur concentration.

Decreasing the pellet mass and increasing initial sulfur concentration made the desulfurization efficiency higher and decreased the amounts of magnesium dissolving into the melt and leaving the melt. The equilibrium relation between [ppmMg] and [ppmS] did not conflict with the present experimental results at temperatures from 1 553 to 1 673 K.

A mathematical model for analyzing the behavior of magnesium in the present desulfurization process has been developed. The calculated magnesium and sulfur concentrations are well consistent with the experimental results. The calculated results demonstrate that the existence of the peak of magnesium concentration is reasonable. The present mathematical model can also explain the effects of pellet mass and initial sulfur concentration on the behavior of magnesium injected into the melt.

KEY WORDS: desulfurization; kinetics; magnesium vapor; magnesium dissolution; magnesium oxide; aluminothermic reduction; ultra-low sulfur steel; immersion tube; pellet; molten iron.

1. Introduction

Magnesium is the only metal commonly used for the desulfurization of molten iron. To make use of magnesium more efficiently and safely, many methods have been developed, for example, magnesium wire,1) Mag-Coke,2,3) Salt-coated magnesium4), Mag-Lime5–8) and magnesium vapor 9) methods.

Speer and Parlee10) studied the solubility of magnesium in molten iron and found that magnesium concentration was proportional to its partial pressure in the atmosphere. They also obtained an equilibrium constant at various temperatures from their experimental data for the solution of magnesium into carbon-saturated iron. Engh et al.11) developed the relation between the dissolved magnesium concentration in the molten iron and the magnesium vapor pressure: \([\text{ppmMg}] / P_{\text{Mg}} \text{(atm)} = 5600 \text{ at } 1533 \text{ K}\). Furthermore, combining with the thermodynamic data of the desulfurization by magnesium vapor, they deduced the solubility product of magnesium and sulfur in the molten iron as \([\text{ppmMg}] \cdot [\text{ppmS}] = 180\). Zhang et al.12) investigated the dissolution equilibrium of magnesium vapor in liquid iron in a two-temperature zone furnace using the vapor pressure method. At 1 873 K, they concluded that the dissolution equilibrium constant of magnesium vapor in liquid iron is \(K = a_{\text{Mg}} / P_{\text{Mg}} \text{(atm)} = 0.023\) and the solubility of magnesium is 590 ppm when \(P_{\text{Mg}} = 1 \text{ atm}\). In addition, Han et al.13) obtained that the solubility product for the Mg–S equilibrium in liquid iron at 1 873 K is \(K_{\text{MgS}} = [\text{ppmMg}] \cdot [\text{ppmS}] = 2.0 \times 10^4\) under MgS(s) saturation.

The kinetic study of dissolution of magnesium vapor into pig iron was made by Iron and Guthrie.9,14,15) They concluded that the efficiency of magnesium dissolution ranged between 20 and 80%. By considering the dissolution of magnesium during the bubbling and the evaporation of magnesium during the holding after terminating the magnesium injection, they predicted the magnesium behavior during the bubbling and the holding separately.

In our previous papers, a new desulfurization method of
argon gas at a flow rate of 1.3 mol. A high frequency induction furnace (15 kW, 100 kHz) was used to melt electrolytic iron of 0.4 mm O.D. had 5 holes of 1.0 mm diameter at its lower part, through which the magnesium vapor and argon carrier gas to react with sulfur. This desulfurization process is characterized by high desulfurization efficiency of magnesium, easy and safe operation and lower cost, and can easily decrease sulfur concentration in molten iron to below 10 ppm. A mathematical model of this desulfurization process was also developed based on a mixed-control model of gas- and liquid-phase mass transfer.

The purpose of the present study is to clarify the magnesium behavior in the desulfurization process. The change in magnesium concentration with time is measured during the desulfurization. The experimental conditions, such as temperature, pellet mass, initial sulfur concentration and carrier gas flow rate, are varied. The behavior of magnesium injected into the melt and the relation between sulfur and magnesium contents in the melt are investigated. Furthermore, a mathematical model is developed to examine the behavior of magnesium during the desulfurization process.

2. Experimental Apparatus and Procedure

Figure 1 shows the experimental apparatus. The present experimental apparatus and procedure are the same as those described previously. A high frequency induction furnace (15 kW, 100 kHz) was used to melt electrolytic iron of 350 g in a graphite crucible of 40 mm I.D. and 100 mm height. An inert atmosphere was maintained by blowing argon gas at a flow rate of $1.3 \times 10^{-3} \text{ m}^3/\text{s}$ onto the melt surface. The graphite immersion tube of 10 mm I.D. and 15 mm O.D. had 5 holes of 1.0 mm diameter at its lower part, through which the magnesium vapor and argon carrier gas were injected into the melt.

The pellet contained magnesia powder (average diameter 0.4 $\mu$m and purity higher than 99.9%) and aluminum powder (75–150 $\mu$m in size and purity higher than 99.5%). After mixing the magnesium oxide and aluminum powders at a molar ratio of 3:2, the pellets were formed by using a cold isostatic press under a pressure of 150 MPa for one hour. The initial sulfur concentration was adjusted by adding FeS to molten iron, and then the tube charged with the pellets was immersed into the melt until its tip reached 2 mm from the crucible bottom. The magnesium behavior together with the desulfurization process was investigated by analyzing the samples taken from the melt at appropriate time intervals to obtain magnesium and sulfur contents.

The magnesium content in the sample was determined by Induction Coupled Plasma Emission Spectroscopy (ICP) within the relative scattering of 5%. The sulfur content was determined by non-scattered infrared rays detector after the samples were burned in pure oxygen gas. The results of sulfur analyses were calibrated by two kinds of standard samples (15±5 ppm and 150±10 ppm).

3. Experimental Results

3.1. Change in [ppmMg], [ppmS] and $\eta_R$ with Time

The reduction of magnesium oxide by aluminum takes place in two stages. At the first stage, magnesium vapor and MgO·Al₂O₃ spinel are formed by the following reaction:

$$4\text{MgO}(s) + 2\text{Al}(l) = 3\text{Mg}(g) + \text{MgO} \cdot \text{Al}_2\text{O}_3(s) \quad \text{...........................................(1)}$$

$$\Delta G^\circ = 465.6 - 0.287T \text{ (kJ/mol)}} \quad \text{...........................................(2)}$$

At the second stage, the reduction of the spinel by the excess aluminum proceeds as

$$3(\text{MgO} \cdot \text{Al}_2\text{O}_3)(s) + 2\text{Al}(l) = 3\text{Mg}(g) + 4\text{Al}_2\text{O}_3(s) \quad \text{...........................................(3)}$$

$$\Delta G^\circ = 607.7 - 0.279T \text{ (kJ/mol)}} \quad \text{...........................................(4)}$$

The reduction efficiency of the pellet, $\eta_R$, is defined as the ratio of the mass of MgO reduced during the experiment, $W_R$, to the initial mass of MgO in the pellet, $W_0$:

$$\eta_R = (W_R/W_0) \times 100 \% \quad \text{...........................................(5)}$$

Desulfurization with magnesium vapor is assumed to take place on the bubble surface, and can be written as

$$\text{Mg(g)} + \text{S} = \text{MgS(s)} \quad \text{...........................................(6)}$$

$$\Delta G^\circ = -404.07 + 0.16921T \text{ (kJ/mol)}} \quad \text{...........................................(7)}$$

Since no desulfurization slag was used in the present experiment, the Raoultian activity of the reaction product, MgS, was $a_{\text{MgS}} = 1$. And since the carbon concentration was much higher than the concentrations of the other elements in the melt, such as sulfur, silicon and manganese, the Henrian activity coefficient of sulfur was given by $\log f_S = 0.11[\%C]$. The equilibrium relation between the magnesium partial pressure, $P_{\text{Mg}}$ (atm), and the sulfur concentration, [ppmS], is given as

$$P_{\text{Mg}} \cdot \text{[ppmS]} = 10^{4-0.11[\%C]} \exp \left( \frac{-404.070 + 169.217T}{8.3147} \right) \quad \text{...........................................(8)}$$

From the above equation, one can deduce that the equilibrium sulfur concentration in the melt decreases with decreasing temperature and increasing magnesium partial pressure.

As shown in Fig. 2, in the first 20 min, the reduction of pellet proceeded fast according to Reaction (1). After 20 min, the pellet reduction, corresponding to Reaction (3),

![Fig. 1. Experimental apparatus.](Image)
slowed down. Under the conditions of temperature 1 673 K, pellet mass 1.5 g and carrier gas flow rate $5.0 \times 10^{-7} \text{ m}^3/\text{s}$, the sulfur concentration decreased from 200 ppm to below 5 ppm in 15 min. In the first 10 min, the magnesium concentration in the melt rose rapidly. This is because excess amount of the pellet of 1.5 g was used to desulfurize the molten iron of $[\text{ppmS}]_0=200$ and the reduction rate of magnesium oxide was fast during the period. Therefore, some of the produced magnesium dissolved into the melt and the maximum magnesium concentration reached 230 ppm at around 10 min. After that, the magnesium concentration dropped gradually to 14 ppm at 120 min.

The sulfur concentration in equilibrium with the magnesium concentration of 230 ppm is 3.9 ppm, which is calculated from the solubility product of $\text{MgS}$. This solubility product will be discussed in the later part of this paper.

When the magnesium concentration was 230 ppm, however, the sulfur concentration was measured to be 13 ppm. At present, it is not clear whether the sulfur is the dissolved one or that of the inclusion (MgS). On the other hand, the magnesium in the melt is mainly the dissolved one and not MgS, and the following decrease in magnesium concentration is attributed to the vaporization from the melt surface and the mass transfer of the dissolved magnesium to the bubble surface rather than the reaction with sulfur in the melt.

### 3.2. Effect of Temperature on Magnesium Concentration in Molten Iron

Figure 3 shows the change in magnesium concentration with time during the desulfurization at 1 553, 1 613 and 1 673 K. The initial sulfur concentration was 230 ppm, however, the sulfur concentration was measured to be 13 ppm. At present, it is not clear whether the sulfur is the dissolved one or that of the inclusion (MgS). On the other hand, the magnesium in the melt is mainly the dissolved one and not MgS, and the following decrease in magnesium concentration is attributed to the vaporization from the melt surface and the mass transfer of the dissolved magnesium to the bubble surface rather than the reaction with sulfur in the melt.

### 3.3. Effect of Pellet Mass on Magnesium Concentration in Molten Iron

The effect of pellet mass on magnesium concentration is presented in Fig. 4. The lines are the calculated results that will be explained later. The maximum magnesium concentrations are about 25, 60 and 160 ppm for the pellet masses of 0.50, 1.0 and 1.5 g, respectively. In the present case, a pellet mass of 0.317 g is theoretically required to completely desulfurize the 350 g molten iron with an initial sulfur concentration of 500 ppm. Therefore, with increasing the pellet mass, the surplus magnesium produced by the reduction of magnesium oxide increases, and this leads to more magnesium dissolving into the melt.

### 3.4. Effect of Initial Sulfur Concentration on Magnesium Concentration in Molten Iron

The results given in Fig. 5 show the changes in magnesium concentration with time for the initial sulfur concentrations $[\text{ppmS}]_0=1 \, 380, 900$ and 490. The lines are the calculated results. The changes in sulfur concentration with time are also presented in the same figure. The temperature was 1 673 K, the pellet mass 1.5 g and the carrier gas flow rate $5.0 \times 10^{-7} \text{ m}^3/\text{s}$. Although the maximum magnesium concentration was keeping low level during the whole desulfurization process due to the fact that the reduction rate of magnesium oxide was slow. At 1 613 and 1 673 K, the maximum magnesium concentrations reached 70 ppm at 20 min and 160 ppm at 5 min, respectively. This is because at a higher temperature, a faster reduction rate of magnesium oxide results in more magnesium dissolving into the melt.

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Fig. 2. Change in $\eta R$, $[\text{ppmS}]$, and $[\text{ppmMg}]$ with time.

Fig. 3. Effect of temperature on magnesium concentration.

Fig. 4. Effect of pellet mass on magnesium concentration.

Fig. 5. Effect of initial sulfur concentration on magnesium concentration.
concentration reached 160 ppm at the initial sulfur concentration of 490 ppm, it decreased markedly with increasing initial sulfur concentration and dropped to 80 and 24 ppm for the initial sulfur concentrations of 900 and 1380 ppm, respectively. The initial sulfur concentration had a pronounced influence on the dissolution of magnesium into molten iron.

Let us consider the mass transfer of magnesium in the bubble and sulfur in the melt to the bubble-melt interface. Since the mass transfer rate of magnesium in the bubble is usually greater than that of sulfur in the melt, the rate-controlling step is the mass transfer of sulfur in the melt. Therefore, the present experimental results can be explained by the fact that increasing the initial sulfur concentration results in more magnesium reacting with sulfur on the bubble surface and less magnesium dissolving into the melt. In addition, the effect of initial sulfur concentration on the magnesium concentration again demonstrates that the desulfurization with magnesium vapor takes place mainly on the bubble surface as described in our previous paper.

3.5. Effect of Carrier Gas Flow Rate on Magnesium Concentration in Molten Iron

The effect of carrier gas flow rate on the magnesium concentration in the melt is given in Fig. 6. When the carrier gas flow rate was 0 m$^3$/s, the magnesium partial pressure in the immersion tube was about 1.0 atm, and the reduction of magnesium oxide was suppressed. As a result, the magnesium concentration was low during the whole desulfurization process. An increase in carrier gas flow rate promoted reduction of magnesium oxide. Thus, the magnesium concentration reached the higher maximum value more quickly.

4. Discussion

4.1. Behavior of Magnesium Injected into the Melt

During the desulfurization process, a part of magnesium reacted with sulfur in the melt, while the other parts dissolved into the melt and also left the melt with bubbles. A part of magnesia in the pellet remained unreduced. The relative amounts of magnesium of these four parts change with the progress of desulfurization and are expressed as following:

The ratio of unreduced MgO, $\eta_{UR}$, is defined by

$$\eta_{UR} = \frac{W_{Mg}}{W_{Mg,0}} \times 100 \% \quad (9)$$

The desulfurization efficiency of the pellet, $\eta_{S,P}$, is defined as the ratio of the mass of Mg actually used for desulfurization, $W_{Mg,S}$, to the initial mass of Mg in the pellet, $W_{Mg,0}$. Here, $W_{Mg,S}$ is calculated from the initial and the minimum sulfur concentrations.

$$\eta_{S,P} = \left( \frac{W_{Mg,S}}{W_{Mg,0}} \right) \times 100 \% \quad (10)$$

Finally, the ratio of Mg leaving the melt, $\eta_{L,Mg}$, which is defined as the ratio of the mass of Mg leaving from the melt surface without reacting with sulfur in the melt and dissolving into the melt to the initial mass of Mg in the pellet, is written as follows:

$$\eta_{L,Mg} = \frac{W_{Mg,L}}{W_{Mg,0}} \times 100 \% \quad (11)$$

The relative values of $\eta_{UR}$, $\eta_{S,P}$, $\eta_{Mg,S}$, and $\eta_{L,Mg}$ are significantly affected by the pellet mass as shown in Fig. 7. It is obvious that the more pellet mass is used, the lower is $\eta_{S,P}$, the higher are $\eta_{Mg,S}$ and $\eta_{L,Mg}$. When the pellet mass increased from 0.5 to 1.5 g, $\eta_{S,P}$ decreased from 46 to 20%, $\eta_{Mg,S}$ increased from 4 to 9%, and $\eta_{L,Mg}$ increased from 27 to 56%. Namely, most of the produced magnesium left the melt surface without combining with sulfur or dissolving into the melt.

Figure 8 represents the influence of initial sulfur concentration on the behavior of magnesium vapor injected into the melt. The increase in the initial sulfur concentration not only increases the mass transfer rate of sulfur in the melt, but also decreases the amount of the surplus pellet. Therefore, as the initial sulfur concentration was increased...
from 200 to 1380 ppm, \( \eta_{S,P} \) rose from 11 to 46%, \( \eta_{m,Mg} \) dropped from 12 to 1% and \( \eta_{l,Mg} \) from 64 to 40%.

4.2. Relation between [ppmMg] and [ppmS]

The solubility product of Mg and S in the carbon-saturated iron at various temperatures can be derived from Speer and Parlee's results. They determined the equilibrium constant for the solution of magnesium vapor into the carbon-saturated iron as follows:

\[
\text{Mg(g)} = \text{Mg} \quad \text{..................................(12)}
\]

Combining Eqs. (8) and (13), the solubility product of Mg and S at various temperatures in the carbon-saturated iron can be represented by

\[
\text{Mg} + \text{S} = \text{MgS(s)} \quad \text{.................................(14)}
\]

\[
\log K'_{11} = \log \frac{[\text{ppmMg}]}{10^7 \cdot P_{Mg}'} = -7.82 + \frac{11839}{T} \quad \text{...........(13)}
\]

\[
[\text{ppmMg}] = 10^{0.18 - 0.11(\%C) + 11839/T} \cdot \exp \left(-\frac{404070 + 169.217}{8.3144T} \right) \quad \text{...........(15)}
\]

At 1533 K, the saturated carbon concentration is 4.5%, and the calculated solubility product is [ppmMg] · [ppmS] = 299. This value is a little different from that obtained by Engh et al. [ppmMg] · [ppmS] = 180.

It should be mentioned that Eq. (13) is a regression equation using the experimental data ranging from 1530 to 1645 K. Here, we try to compare the results calculated from Eq. (15) with our experimental results at the temperatures of 1553, 1613 and 1673 K. The experimental and calculated relations between [ppmMg] and [ppmS] are given in Fig. 9. The data of sulfur concentrations are cited from our previous paper. The calculated solubility products are [ppmMg] · [ppmS] = 360, 570 and 890 for the saturated carbon concentrations of 4.5, 4.7 and 4.8% at 1553, 1613 and 1673 K, respectively. It can be seen that all of the experimental data are above the calculated equilibrium line of [ppmMg] · [ppmS] at the stage of sulfur concentration decreasing. The calculated equilibrium line is the lowest level that the relation between [ppmMg] and [ppmS] can reach during the desulfurization period. This implies that the calculated results of [ppmMg] · [ppmS] do not conflict with the present experimental results.

On the other hand, the experimental data tend to be lower than the calculated equilibrium line after the sulfur concentration becomes the minimum. In the period, the desulfurization ceases and the resulfurization takes place. Since the magnesium in the melt evaporates from the melt surface and transfers to the bubble surface, the magnesium concentration decreases. The sulfur concentration should increase to satisfy the solubility product of [ppmMg] · [ppmS] constant. But the resulfurization rate or the dissociation rate of MgS is slow. As a result, the experimental data become below the calculated equilibrium line in the resulfurization period.

5. Kinetics of Magnesium Behavior during the Desulfurization of Molten Iron

The behavior of magnesium in the present desulfurization process is analyzed with the mixed control model of gas- and liquid-phase mass transfer. The kinetics equations and the method of analysis are similar to those in our previous papers.

To simplify the present kinetic study, the desulfurization by dissolved magnesium reacting with sulfur in the melt is neglected. Consequently, the main desulfurization site is assigned.
sumed to be on the bubble surface. In addition, although the product of desulfurization, MgS, exists on the bubble surface and floats up with the bubble to the melt surface, the change in effective surface area of the bubble is neglected. The resulfurization reaction on the metal surface is also neglected.

It is assumed that the mass transfer of magnesium and sulfur to the bubble–melt interface simultaneously controls the overall desulfurization rate. In addition, since the experimental temperature is high, the chemical reaction between magnesium and sulfur at the interface is assumed not to be a rate-controlling step. With respect to the evaporation of magnesium from the melt surface, the rate-controlling step is assumed to be the mass transfer of dissolved magnesium to the melt surface because the magnesium partial pressure in the atmosphere is quite low due to argon gas blowing onto the melt surface.

The other assumptions are as follows: The sulfur concentration and the temperature in the melt are uniform. The bubble is of spherical shape and there is no disintegration or coalescence during the bubble ascent.

5.1. Model of Gas- and Liquid-phase Mass Transfer

On the basis of the above assumptions, one can write the following equations for a single bubble:

$$\frac{dn_s}{dt} = -k_{1,S} A \frac{\rho_m}{10^6 M_s} (\text{ppmS}) - \text{[ppmS]}$$ .............................(16)

$$\frac{dn_{Mg,M}}{dt} = -k_{1,Mg} A \frac{\rho_m}{10^6 M_{Mg}} (\text{ppmMg}) - \text{[ppmMg]}$$ .............................(17)

$$\frac{dn_{T,Mg,M}}{dt} = -k_{g,Mg} \frac{\rho_m}{RT} A (P_{Mg} - P_{Mg,g})$$ .............................(18)

On the bubble surface, the equilibrium relation between magnesium vapor and dissolved magnesium is given by:

$$\text{[ppmMg]} = H \rho_{Mg,g}$$ .............................(19)

where $H$ is the Henry’s constant, which is calculated from Eq. (13) to be 1 800 ppm/atm at 1 673 K.

Between magnesium vapor pressure and dissolved sulfur concentration, the following equilibrium relationship holds on the bubble surface:

$$K_{MgS} = \frac{10^4}{P_{Mg,g} \cdot j_s \cdot \text{[ppmS]}}$$ .............................(20)

From the mass balance among magnesium in the bubble, magnesium and sulfur in the melt, we have

$$\frac{dn_{Mg,M}}{dt} = \frac{dn_{Mg,M}}{dt} - \frac{dn_{Mg,F}}{dt}$$ .............................(21)

Combining Eqs. (16)–(21), the interfacial sulfur concentration can be derived,

$$\text{[ppmS]} = \frac{1}{2} \left\{ \text{[ppmS]} - B \text{[ppmMg]} - EP_{Mg} \right\}$$ .............................(22)

where $E$ and $B$ are

$$E = \frac{k_{g,Mg} \cdot M_s}{\rho_m \cdot RT}$$ .............................(23)

$$B = \frac{k_{1,Mg} \cdot M_s}{k_{1,S} \cdot M_{Mg}}$$ .............................(24)

Combining Eqs. (19), (20) and (22), one can also obtain the interfacial partial pressure of magnesium and magnesium concentration.

The mass transfer rates of sulfur and magnesium during the bubble ascent are written as

$$\frac{dn_s}{dx} = -2 \left( \frac{D_{1,s} \cdot \pi}{(0.5 \cdot g)^{1/2}} \right)^{1/2} \frac{\rho_m}{10^6 M_s} \cdot \left[ \text{ppmS} - \text{[ppmS]} \right]$$ .............................(25)

$$\frac{dn_{Mg,F}}{dx} = -2 \left( \frac{D_{1,Mg} \cdot \pi}{(0.5 \cdot g)^{1/2}} \right)^{1/2} \frac{\rho_m}{10^6 M_{Mg}} \cdot \left[ \text{ppmMg} - \text{[ppmMg]} \right]$$ .............................(26)

During the bubble formation, the number of moles of magnesium used for desulfurization, $n_{s,F}$, and dissolving into the melt, $n_{Mg,F}$, can be expressed by

$$n_{s,F} = \frac{\rho_m}{10^6 M_s} \left( \frac{D_{1,s}}{\pi} \right)^{1/2} \int_0^{t_1} \int_0^{t_{1-s}} \left[ \text{ppmS} - \text{[ppmS]} \right] \cdot \frac{dA(t')}{(t_1-t')^{1/2}} \cdot dt_1$$ .............................(27)

$$n_{Mg,F} = \frac{\rho_m}{10^6 M_{Mg}} \left( \frac{D_{1,Mg}}{\pi} \right)^{1/2} \int_0^{t_1} \int_0^{t_{1-s}} \left[ \text{ppmMg} - \text{[ppmMg]} \right] \cdot \frac{dA(t')}{(t_1-t')^{1/2}} \cdot dt_1$$ .............................(28)

5.2. Mass Transfer Model for Magnesium Evaporation from Melt Surface

The magnesium evaporation from the melt surface is expressed as

$$\frac{d[\text{ppmMg}]}{dt} = \frac{k_{1,Mg}}{\sqrt{\pi \cdot \eta_m}} \cdot \sqrt{\text{[ppmMg]} - \text{[ppmMg]}_s}$$ .............................(29)

where the magnesium concentration on the melt surface, $[\text{ppmMg}]_s$, is taken as 0 because the magnesium partial pressure in the atmosphere is very low. The value of $k_{1,Mg}$ was taken as a fitting parameter and was determined by the
trial and error method as

\[ k_{\text{Mg,s}} = [7.0 + 75.0 \times \exp(-t/221)] \times 10^{-5} \text{ (m/s)} \] ...(30)

The value of \( k_{\text{Mg,s}} \) is 82 \times 10^{-5} \text{ m/s at } t = 0 \text{ s}. Along with the decrease in the magnesium production rate with time, the bubbling agitation becomes weak, and the \( k_{\text{Mg,s}} \) decreases. One can see that Eq. (30) for \( k_{\text{Mg,s}} \) is similar to Eq. (31) for \( \eta_k \) in the next section.

5.3. Calculation Method

The initial number of moles of magnesium in a bubble can be obtained from the experimental data of the reduction efficiency of pellet (\( \eta_k \) vs. time.)

\[ \eta_k = 79.0 \times (1 - \exp(-t/221)) \text{ (})t < 200 \text{ s})...) ...(31) \]

\[ \eta_k = 77.1 + 0.0013t \text{ (})t \geq 200 \text{ s}) .......(32) \]

The amounts of magnesium used for desulfurization and dissolving into the melt by one bubble during the bubble ascent are obtained by simultaneously solving Eqs. (25) and (26) by using the Runge–Kutta–Gill method. During the bubble formation, the amounts are obtained by simultaneously solving Eqs. (27) and (28).

The amounts of magnesium used for desulfurization and dissolving into the melt by one bubble during the bubble formation and ascent are multiplied by the number of bubbles generated per second to obtain the rates of desulfurization and dissolution of magnesium into the melt.

The sulfur diffusion coefficient in the molten iron is \( 1.61 \times 10^{-9} \text{ m}^2/\text{s} \) at 1673 K \(^22\) and the magnesium diffusion coefficient in the melt is assumed to be of the same value. The magnesium diffusion coefficient for Ar–Mg binary system in a bubble is calculated to be \( 3.44 \times 10^{-11} \text{ m}^2/\text{s} \) at 1673 K from Chapman and Enskog’s equation. \(^23\) The bubble diameter is calculated using the equation obtained by Tadaki \( et \) al. \(^24\)

5.4. Calculated Results

5.4.1. Change in Magnesium and Sulfur Concentration with Time

The comparison between the calculated and the experimental results for the dissolved magnesium concentration in the melt is illustrated in Figs. 4 and 5. Under the calculated conditions of temperature 1673 K, initial sulfur concentration 500 ppm and pellet mass 1.5 g, the calculated magnesium concentration accords well with the experimental result in the whole period. Moreover, with decreasing the pellet mass and increasing the initial sulfur concentration, the magnesium concentration decreases. These tendencies are also in agreement with the experimental results. Therefore, the assumptions of the present kinetic model are adequate.

Figure 10 presents the comparison of desulfurization rate between the calculated and the experimental results. The solid and broken lines are the calculated results with and without taking the dissolution of magnesium into consideration. These two calculated results are close, and both are well consistent with the experimental results. Since the mass transfer of sulfur in the melt essentially controls the present desulfurization rate, the dissolution of magnesium into the melt has no noticeable influence on its calculated results.

5.4.2. Behavior of Magnesium Injected into the Melt

By the use of the present model, the rates of magnesium reacting with sulfur, dissolving into melt, leaving the melt without reacting with sulfur or dissolving into the melt, and evaporating from the melt surface are calculated. The results are plotted in Fig. 11.

Since the sulfur concentration and the magnesium oxide reduction rate decrease with time, the rate of magnesium used for desulfurization decreases with time. The decrease in the dissolution rate of magnesium into the melt is attributed to the decreases in the magnesium partial pressure and the number of bubbles generated per second. The increase in the rate of magnesium leaving the melt at the initial stage is due to the decrease in the sulfur concentration and the subsequent decrease is caused by the decrease in the magnesium production rate. The rate of evaporation of the dissolved magnesium increases with increasing magnesium concentration, reaches the maximum and then decreases with the decrease in both the magnesium concentration and the mass transfer coefficient of magnesium for the melt surface.

The existence of the peak of magnesium concentration can be explained from the results given in Fig. 11. At the initial stage of the experiment, the magnesium concentration increases rapidly since the dissolution rate of magne-
sium is much greater than the evaporation rate. It reaches the maximum at 5 min and turns to decrease with time because the evaporation rate is conversely greater than the dissolution rate.

5.4.3. Effects of Pellet Mass and Initial Sulfur Concentration on Magnesium Concentration in Molten Iron

The changes in magnesium concentration with time for various pellet masses are shown in Fig. 4. The calculation is made under the conditions of initial sulfur concentration 500 ppm, temperature 1673 K and carrier gas flow rate $5.0 \times 10^{-3}$ m$^{-3}$/s. The assumptions are that the reduction rate of magnesium oxide does not change with the pellet mass and therefore Eqs. (31) and (32) can be applied to predict the reduction efficiency of pellet.

The calculated magnesium concentrations are higher than the experimental results for the pellet mass of 1.0 g as shown in the same figure. However, the calculated results show that with decreasing pellet mass, the magnesium concentrations decrease. This tendency is in agreement with the experimental results. The less pellets are used, the lower the magnesium partial pressure is in the bubble and the less bubbles are generated per second. Therefore, the dissolution rate of magnesium into the melt decreases, which leads to the decrease in magnesium concentration.

Figure 5 presents the calculated results for the effect of initial sulfur concentration on magnesium concentration. The calculation conditions are temperature 1673 K, pellet mass 1.5 g and carrier gas flow rate $5.0 \times 10^{-3}$ m$^{-3}$/s. Higher initial sulfur concentration increases the mass transfer rate of sulfur in the melt, and hence decreases the magnesium partial pressure on the bubble surface. This accounts for the decrease in the magnesium concentration. This tendency is also consistent with the experimental results. However, comparing between the experimental and the calculated magnesium concentrations, it is found that when the initial sulfur concentrations are 900 and 1380 ppm, the calculated magnesium concentrations are considerably higher than the experimental ones. The reason may be that with increasing initial sulfur concentration, the more desulfurization product, MgS, exists on the bubble surface, which decreases the surface area. But in the present calculation, this phenomenon is not taken into account.

6. Conclusions

For the purpose of clarifying the behavior of magnesium in the desulfurization process of molten iron with magnesium vapor produced in-situ by the aluminothermic reduction of magnesium oxide, the effects of temperature, pellet mass, initial sulfur concentration and carrier gas flow rate on the magnesium concentration in the melt have been investigated. The behavior of magnesium injected into the melt and the relation between the magnesium and the sulfur concentrations in the melt have been made clear. Furthermore, a mathematical model for analyzing the behavior of magnesium has also been developed. The following conclusions have been drawn:

(1) In the present desulfurization process, the magnesium concentration first increased rapidly, reaching the maximum, and then decreased gradually to a very low level. When the magnesium concentration reached the maximum, the sulfur concentration became very low. Therefore, the magnesium in the melt was mainly the dissolved one and the following decrease in magnesium concentration was due to the evaporation from the melt surface and the mass transfer of the dissolved magnesium to the bubble surface.

(2) Under the present experimental conditions, the magnesium concentration increased with increasing temperature, pellet mass, Ar carrier gas flow rate and decreasing initial sulfur concentration.

(3) Decreasing pellet mass and increasing initial sulfur concentration favored the desulfurization efficiency of pellet, and decreased the amounts of magnesium dissolving into the melt and leaving the melt.

(4) The equilibrium relation between [ppmMg] and [ppmS] did not conflict with the present experimental results at the temperature of 1553, 1613 and 1673 K. During the desulfurization period, the relations between magnesium and sulfur concentrations were above the equilibrium line; but during the resulfurization period, they became below the equilibrium line due to the slow resulfurization rate.

(5) A mathematical model for analyzing the behavior of magnesium in the present desulfurization process has been developed. The calculated magnesium and sulfur concentrations are reasonably consistent with the experimental results.

(6) The calculated results demonstrate that the rates of magnesium used for the desulfurization and dissolving into the melt decrease with time, while those leaving the melt and evaporating from the melt surface increase at first, reaching their maxima, and then decrease slowly. The existence of the peak of magnesium concentration can be explained from these calculated results. The present mathematical model can also reasonably explain the effects of pellet mass and initial sulfur concentration on the behavior of magnesium injected into the melt.

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Nomenclature

\[ A : \] Surface area of a bubble (m$^2$)
\[ A_s : \] Surface area of the melt (m$^2$)
\[ a_{Mg} : \] Henrian activity of magnesium in the melt based on 1 mass % standard state (mass%).
\[ a_S : \] Henrian activity of sulfur in the melt based on 1 mass % standard state (mass%).
\[ a_{MgS} : \] Raoultian activity of MgS based on pure solid MgS (mass%).
\[ A(t) : \] Surface area of a bubble at $t = t_1$ during the bubble formation (m$^2$)
\[ [%C] : \] Mass percent concentration of carbon in the melt (mass%)
\[ d_B : \] Bubble diameter (m)
\[ D_{i,Mg} : \] Diffusion coefficient of magnesium in the melt (m$^2$/s)
$D_{LS}$: Diffusion coefficient of sulfur in the melt (m$^2$/s)
$f_s$: Activity coefficient of sulfur
$g$: Gravitational acceleration (m/s$^2$)
$\Delta G^0$: Standard free energy change (kJ/mol)
$H$: Henry’s constant of Eq. (19)
$k_{g,Mg}$: Mass transfer coefficient of magnesium in the bubble (m/s)
$k_{S}$: Mass transfer coefficient of sulfur in the melt (m/s)
$k_{L,Mg}$: Mass transfer coefficient of magnesium to the bubble surface (m/s)
$k_{L,Mg,s}$: Mass transfer coefficient of magnesium to the melt surface (m/s)
$K_{Mg,S}^*$: Equilibrium constant of Reaction (6) ($K_{Mg,S}^* = \frac{k_{Mg,S}}{k_{S}}$)
$M_{Mg}$: Molecular mass of magnesium (kg/mol)
$M_S$: Molecular mass of sulfur (kg/mol)
$n_{Mg,B}$: Number of moles of magnesium in a bubble (mol)
$n_{Mg,f}$: Number of moles of magnesium dissolving into the melt by one bubble during its formation (mol)
$n_{Mg,1}$: Number of moles of magnesium in the melt (mol)
$n_S$: Number of moles of sulfur in the melt (mol)
$n_{S,f}$: Number of moles of sulfur removed by one bubble during its formation (mol)
$P_{Mg}$: Magnesium partial pressure in the bubble (atm)
$P_{Mg}^*$: Magnesium partial pressure in the atmosphere (atm)
$P_{Mg,i}$: Magnesium partial pressure on the bubble surface (atm)
$[ppmMg]$: Magnesium concentration in the melt
$[ppmMg]_0$: Magnesium concentration on the bubble surface
$[ppmMg]_f$: Magnesium concentration on the melt surface
$R$: Gas constant (atm$\cdot$m$^3$·mol$^{-1}$·K$^{-1}$)
$[ppmS]$: Sulfur concentration in the melt
$[ppmS]_0$: Initial sulfur concentration in the melt
$[ppmS]_f$: Sulfur concentration on the bubble surface
$Q_{Ar}$: Carrier gas flow rate at 273 K and 1 atm (m$^3$/s)
$t$: Time (s)
$t'$: Time for calculating $n_{S,f}$ (s)
$t_1$: Time for calculating $n_{Mg,1}$ (s)
$T$: Temperature (K)
$t_f$: Bubble formation time (s)
$V_m$: Volume of the melt (m$^3$)
$V_{no}$: Rate of consumption of magnesium (mol/s)
$W_0$: Initial mass of MgO in the pellet (g)
$W_{Mg,0}$: Initial mass of Mg in the pellet (g)
$W_{Mg,m}$: Mass of Mg dissolving into the melt (g)
$W_{Mg,S}$: Mass of Mg actually reacting with sulfur (g)
$W_R$: Mass of MgO consumed during the experiment (g)
$x$: Vertical distance from nozzle exit (m)

Greek symbols
$\eta_{Mg}$: Ratio of Mg dissolving into the melt (%)
$\eta_{Mg}^*$: Ratio of Mg leaving the melt (%)
$\eta_R$: Reduction efficiency of the pellet (%)
$\eta_{UR}$: Ratio of unreduced MgO (%)
$\eta_{SP}$: Desulfurization efficiency of the pellet (%)
$\rho_m$: Melt density (kg/m$^3$)

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