Mechanism of Resulfurization in Magnesium Desulfurization Process of Molten Iron

Jian YANG, Mamoru KUWABARA, Takayuki TESHIGAWARA and Masamichi SANO

Department of Materials, Physics and Energy Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya, Aichi-Ken, 464-8603 Japan. 1) Formerly University Student, Nagoya University; now in Ironmaking Department, Kakokawa Works, Iron and Steel Sector, Kobe Steel Corporation, 1, Kanazawa-cho, Kakogawa, Hyougo-Ken, 675-0137 Japan.

(Received on April 28, 2005; accepted on July 20, 2005)

During magnesium desulfurization of molten iron, the desulfurization product of MgS floats up to the melt surface. After magnesium supply terminates, resulfurization tends to take place because of the transfer of sulfur from MgS into the melt. In the present study, a simplified experiment was designed to clarify this resulfurization mechanism. With MgS powders added onto the melt surface, the transfer rate of sulfur from MgS into the melt was measured.

Two kinds of mechanisms are revealed to be responsible for the resulfurization in the magnesium desulfurization process. One is decomposition of MgS under the inert atmosphere; the other is oxidation of MgS under the oxidative atmosphere.

It is also found that increasing temperature and oxygen partial pressure in the atmosphere increased the transfer rate of sulfur into the melt and the resulfurization ratio. But the increase in the added amount of MgS did not change the resulfurization ratio largely under the present experimental conditions. The resulfurization rate was smaller by using MgO crucible than that by using Al2O3 crucible. Addition of CaO and the activated charcoal powders onto the melt surface could significantly prevent sulfur of MgS on the melt surface from transferring into the melt.

With a simplified first-order rate equation, the calculated capacity coefficient for transfer of sulfur from MgS to melt is increased with increasing the temperature and the oxygen partial pressure in the atmosphere, but does not change with adding different amounts of MgS onto the melt surface.

KEY WORDS: desulfurization; resulfurization; magnesium; MgS; ultra-low sulfur steel; molten iron.

1. Introduction

Many attempts have been made to use magnesium as a desulfurization reagent for molten iron. However, magnesium has the normal boiling point of 1380 K, which is much lower than the temperature of hot metal pretreatment. When magnesium metal is plunged into the hot metal, violent vaporization of magnesium is liable to result in a decrease in desulfurization efficiency and lack of safety in operation. This makes magnesium less attractive than the most commonly used CaO-containing flux. To reduce the violent magnesium vaporization and to make use of magnesium more safely and conveniently, several methods were developed in the past thirty years, such as Mag-Coke, Salt-coated magnesium, Mag-lime, and Mg-containing wire methods. By use of these methods, magnesium could be added into the hot metal in a more controlled manner. However, from an economical viewpoint, it is beneficial to use magnesium from the cheap secondary sources, for example, MgO or dolomite.

We have proposed a new method of desulfurization of molten iron with magnesium vapor produced in situ by carbothermic and aluminothermic reduction of magnesium oxide. Mg-C or MgO-Al pellets were charged into a tube, which was immersed into the molten iron. Heated by heat conduction from the molten iron, magnesium oxide in the pellets was reduced by carbon or aluminium to produce magnesium vapor, which was injected directly into the molten iron together with argon carrier gas to react with sulfur dissolved in it.

The desulfurization process with the MgO-Al pellets was characterized by easy and safe operation and low cost, and the sulfur concentration in the molten iron could be quickly decreased to below 10 ppm. On the basis of the mixed-control model of gas- and liquid-phase mass transfer, this desulfurization process was analyzed to elucidate the desulfurization mechanism.

Another important problem of the magnesium desulfurization of molten iron is how to improve the desulfurization efficiency of magnesium ($\eta_{\text{Mg}}$). A typical result obtained by Yonezawa et al. showed that with the mixture of CaO containing flux and 10–25% Mg powder, the $\eta_{\text{Mg}}$ value was only 10% when the sulfur concentration was reduced from 0.012 to 0.002%. In our previous article, a novel method for improving $\eta_{\text{Mg}}$ by adjusting the initial magnesium molar ratio in the bubble through changing the Ar car-
rier gas flow rate was proposed. When the initial magnesium molar ratio in the bubble was adjusted to the optimum value, the desulfurization proceeded most rapidly and the $n_{S,Mg}$ value was the highest.

The sulfur concentration tends to increase to some extent after the magnesium supply terminates. This resulfurization phenomena were reported by Nakanishi et al.\textsuperscript{17}) and by Nakamura et al.\textsuperscript{18}) In our previous experiments,\textsuperscript{12,13,16} the resulfurization also took place at the later period of desulfurization, when the production rate of magnesium vapor significantly decreased and the magnesium concentration in the melt dropped to a very low level. In order to make the magnesium desulfurization process more applicable to a practical industrial operation, resulfurization problem in this process needs to be studied as well.

This study focuses on clarification of the mechanisms that are responsible for the resulfurization in the magnesium desulfurization process. Effects of temperature, oxygen partial pressure in the atmosphere, initial sulfur concentration and materials of crucible on the resulfurization are investigated experimentally. New methods of prevention of resulfurization are developed and the rates of resulfurization are kinetically explained.

2. Resulfurization Phenomena in Magnesium Desulfurization of Molten Iron

The reduction of magnesium oxide by aluminum takes place in two stages.\textsuperscript{19}) At the first stage, the magnesium oxide is reduced to produce magnesium vapor and MgO · Al₂O₃ spinel; at the second stage, the spinel is further reduced by aluminum.

When the magnesium vapor produced by the above reductions is injected directly into the molten iron, the desulfurization proceeds as follows:

$$\text{Mg} (g) + S = \text{MgS} (s) \quad \text{......................... (1)}$$

$$\Delta G^\circ = -404.07 + 0.16 921T \text{ (kJ/mol)} \quad \text{......................... (2)}$$

This desulfurization experiments were carried out using the apparatus that was described in our previous articles.\textsuperscript{12,13,16} Pellets containing magnesium oxide and aluminum were charged into a graphite tube, which was immersed into the molten iron. Owing to the aluminothermic reduction of magnesium oxide, the magnesium vapor was produced and injected into the molten iron to react with the sulfur dissolved in it.

Figure 1 shows the typical experimental results of changes in reduction efficiency of magnesium oxide ($n_{R,MgO}$), sulfur and magnesium concentrations in the molten iron with time. Under the conditions of a temperature of 1 673 K, pellet mass of 1.0 g (specific pellet consumption of 2.7 kg/t), a carrier gas flow rate of $5.0 \times 10^{-7}$ m$^3$/s and the inert atmosphere, the reduction efficiency of magnesium oxide rose rapidly, and magnesium vapor and spinel were produced at the first stage before 20 min, and then the spinel was reduced slowly at the second stage after 20 min. The sulfur concentration decreased from the initial concentration of 494 to 33 ppm in 15 min. Subsequently, the resulfurization took place, and the sulfur concentration increased to 56 ppm at 60 min, and to 110 ppm at 120 min.

The magnesium concentration in the melt rose rapidly at first. After reaching the maximum of 58 ppm at 10 min, it dropped gradually to 23 ppm at 60 min, and to 10 ppm at 120 min.

The reduction rate of magnesium oxide was fast at first, but after 20 min it became very slow, and very little magnesium vapor was produced and injected into the molten iron. Thus the magnesium concentration in the melt dropped to a very low level after 20 min. This was the reason why the resulfurization took place at the later period of the experiment.

3. Experimental Apparatus and Procedure

Figure 2 is a schematic diagram of the experimental apparatus for studying the resulfurization. A high frequency induction furnace (15 kW, 100 kHz) was used to melt electrolytic iron of 350 g in an alumina or magnesia crucible of 40 mm i.d. and 100 mm in height. The mixture of argon and oxygen gases with the adjusted flow rates was blown onto the melt surface to control the oxygen partial pressure in the atmosphere.

In order to study the resulfurization mechanism in the
magnesium desulfurization process of molten iron, a simplified experiment was conducted instead of the actual desulfurization process with magnesium vapor produced in situ by aluminothermic reduction of magnesium oxide. MgS powders were added onto the metal surface after melting the iron to study the transfer rate of sulfur from MgS on the melt surface into the melt. This is because in the actual desulfurization process, the desulfurization product, MgS, floats up to the melt surface, and then the resulfurization takes place due to the transfer of sulfur from MgS on the melt surface into the melt.

After the MgS powders were added onto the melt surface, they were lightly stirred to cover the melt surface evenly, and then the resulfurization experiment was started. In some experiments, CaO or C powders were added onto the melt surface together with the MgS powders to study their effects on prevention of resulfurization. In another experiment, only CaS powders were added onto the melt surface to make a comparison of the resulfurization rates by MgS and CaS, which are the desulfurization products by Mg and Ca, respectively. All of the experimental conditions are listed in Table 1. To study the resulfurization process, the transfer rate of sulfur from the melt surface into the melt was examined by taking samples from the melt at appropriate time intervals to analyze sulfur content. The sulfur content was determined by non-scattered infrared ray detector after the sample was burned in a pure oxygen gas. The results of the sulfur analyses were calibrated by two kinds of standard samples (15/1000 ppm and 300/1000 ppm).

| Effects of | $T$ (K) | $P_{O_2}$ (atm) | $W_{MgS}$ (g) | $W_{Cr}$ (g) | Crucible materials | Added mass of CaO (g) | Added mass of C (g) |
|-----------|---------|----------------|----------------|-------------|-------------------|----------------------|-------------------|
| Temperature | 1773     | 0.05           | 0.19           | 0           | MgO                | 0                    | 0                 |
|           | 1673     | 0.05           | 0.19           | 0           | MgO                | 0                    | 0                 |
|           | 1573     | 0.05           | 0.19           | 0           | MgO                | 0                    | 0                 |
| Oxygen Partial Pressure in Atmosphere | 1673     | 0.10           | 0.19           | 0           | MgO                | 0                    | 0                 |
|           | 1673     | 0.05           | 0.19           | 0           | MgO                | 0                    | 0                 |
| MgS Mass | 1673     | 0.05           | 0.065          | 0           | MgO                | 0                    | 0                 |
|           | 1673     | 0.05           | 0.190          | 0           | MgO                | 0                    | 0                 |
|           | 1673     | 0.05           | 0.320          | 0           | MgO                | 0                    | 0                 |
| Crucible Materials | 1673     | 0.05           | 0.19           | 0           | MgO                | 0                    | 0                 |
|           | 1673     | 0.05           | 0.19           | 0           | MgO                | 0                    | 0                 |
| Added Mass of CaO | 1673     | 0.05           | 0.19           | 0           | MgO                | 0                    | 0                 |
|           | 1673     | 0.05           | 0.19           | 0           | MgO                | 1.84                 | 0                 |
| Addition of MgS or CaS | 1673     | 0.05           | 0.19           | 0           | MgO                | 0                    | 0                 |
| Added Mass of C | 1673     | 0.05           | 0.19           | 0           | MgO                | 0                    | 0                 |

4. Resulfurization Principle in Magnesium Desulfurization of Molten Iron

There are two kinds of resulfurization mechanisms which are divided according to the oxygen partial pressure in the atmosphere. One is decomposition of the desulfurization product of MgS under the inert atmosphere. The other is oxidation of MgS under the oxidative atmosphere.

4.1. Resulfurization by Decomposition of MgS

Desulfurization with magnesium vapor and the associated free energy change are described in Eqs. (1) and (2). Since no desulfurization slag is added in the present experiment, the activity of MgS is uniform. Because the carbon concentration is much higher than the concentrations of the other elements in the melt, the Henrian activity coefficient of sulfur is given by $\log f_S^H = -0.11 \times [\%C]^{20}$. From Reaction (1), one can obtain $a_Mg = a_Mg \cdot exp(\Delta G^\circ / RT)$, where $a_Mg = P_{Mg,S}$ and $a_S = f_S [ppmS]$. The equilibrium relation between the magnesium partial pressure ($P_{Mg,S}$ (atm)) and the sulfur concentration ([ppmS]) at the interface of slag and melt is given as

$$P_{Mg,S} \cdot [ppmS] = 10^{4 \times -0.11 \times [\%C]} \exp \left( \frac{-404070 + 169.21T}{8.314T} \right)$$

............................................................(3)

On the other hand, the apparent equilibrium constant for the solution of magnesium vapor into the carbon-saturated iron can be derived from Speer and Parlee’s results$^{22}$:

$$\log K' = \log \frac{[ppmMg]}{10^4 \cdot P_{Mg,S}} = -7.82 + \frac{11839}{T} \quad ....(5)$$

Combining Eqs. (3) and (5), one can obtain the solubility product of Mg and S at the slag–melt interface for the carbon-saturated iron.

$$Mg + S = MgS(s) \quad ..............(6)$$
This equilibrium relation is plotted in Fig. 3. The figure clearly shows that the equilibrium sulfur concentration increases with decreasing the magnesium concentration and increasing the temperature. Namely, an increase in the temperature and a decrease in the dissolved magnesium concentration will accelerate the decomposition of MgS and promote the resulfurization.

4.2. Resulfurization by Oxidation of MgS

Under the oxidative atmosphere, the resulfurization in the magnesium desulfurization process of molten iron is determined by oxidation of MgS. The oxidation of MgS can be expressed as

\[
\text{MgS (s) + } \frac{1}{2} \text{O}_2 \rightarrow \text{MgO (s) + S} \quad \text{........................................................................(8)}
\]

\[
\Delta G^0 = - 326.48 + 0.03594T \text{ (kJ/mol)} \quad \text{........................................................................(9)}
\]

Since no desulfurization slag is used in the present experiment, and since MgS and MgO are in solid state, both of the activities of MgS and MgO are uniform. Thus the equilibrium relation between the sulfur concentration ([ppmS]_S) and the oxygen partial pressure (P_{O_2,S}) at the interface of slag and melt, which will be explained at the later parts of this paper, is given by

\[
[\text{ppmS}]_S = 10^{0.18 - 0.11[\%C]_S + 11 \times 3.9/T} \times \exp \left( \frac{-404.070 + 169.21T}{8.314T} \right) \quad \text{...........................................(7)}
\]

The equilibrium relation of the sulfur concentration ([ppmS]_S) versus root of the oxygen partial pressure in the atmosphere (P_{O_2,S}^{1/2}) is shown in Fig. 4. It is seen that the equilibrium sulfur concentration increases with increasing the oxygen partial pressure in the atmosphere, but decreases with increasing temperature. One noteworthy point is that the influence of temperature on resulfurization is different between the two kinds of resulfurization mechanisms. Namely, a higher temperature accelerates the resulfurization by the mechanism of the decomposition of MgS when the magnesium concentration in the melt is constant, but represses the resulfurization by the mechanism of the oxidation of MgS when the oxygen partial pressure in the atmosphere is not changed.

5. Experimental Results and Discussion

5.1. Effect of Temperature on Resulfurization

Figure 5 shows the experimental results of resulfurization and the lines show the calculated ones at the temperatures of 1 573, 1 673 and 1 773 K. The calculated results will be explained in the later part of this paper.

At all of the temperatures, the increasing rates of sulfur concentration were fast at first, and then became slow. It is clear that with increasing temperature, the sulfur concentration increased more rapidly, and the final sulfur concentration at 60 min reached a higher value.

If the sulfur of MgS of 0.19 g transfers into the melt completely, the final sulfur concentration is 300 ppm. In fact, not all of the sulfur transfers into the melt. In order to express the degree of resulfurization, a resulfurization ratio (\(\xi_S\)) is introduced, which is defined as the ratio of the mass of sulfur transferred into the melt (W_s) to the initial mass of sulfur of the added MgS (W_{S,0}).

\[
\xi_S = \left( \frac{W_s}{W_{S,0}} \right) \times 100 \% \quad \text{...........................................(11)}
\]

At the temperatures of 1 573, 1 673 and 1 773 K, the final sulfur concentrations are 127, 140, 213 ppm, and the \(\xi_S\) values are calculated to be 42, 47 and 71%, respectively. The \(\xi_S\) values are increased with increasing temperature.
These experimental results can be explained from the mechanism of resulfurization by the decomposition of MgS. This mechanism shows that the equilibrium value of sulfur concentration increases with increasing temperature, if the magnesium concentration in the melt is constant, as illustrated in Fig. 3. In the present case, at a higher temperature, the magnesium concentration on the melt surface should increase owing to the acceleration of decomposition of MgS. On the other hand, the magnesium concentration on the melt surface tends to decrease because of the enhancement of evaporation of magnesium from the melt surface. As a result, it is reasonable to deduce that the magnesium concentration on the melt surface does not change a lot when temperature is raised. Therefore, the mechanism of resulfurization by the decomposition of MgS suggests that increasing temperature accelerates the sulfur transfer into the melt.

On the other hand, according to the mechanism of resulfurization by the oxidation of MgS, when the oxygen partial pressure on the melt surface is constant, an increase in the temperature will prevent sulfur from transferring into the melt as shown in Fig. 4, which seems to be inconsistent with the present experimental results. However, an in-depth argument is needed to illustrate this problem.

In fact, the oxygen partial pressure on the melt surface is determined by the following reaction in the present case:

$$\Delta G^\circ_{298} = -235.60 - 0.16837T (\text{kJ/mol})$$

When the activity of carbon is referred to pure graphite, it is uniform ($a_C=1$) in the carbon-saturated iron. The oxygen partial pressure on the melt surface ($P_{O_2,S}$) is deduced to be

$$P_{O_2,S} = P_{CO_2} \times \exp \left( - \frac{2 \times (235.600 + 168.377T)}{8.314T} \right)$$

If the partial pressure of CO on the melt surface ($P_{CO_2}$) is nearly constant, the correlation of $P_{O_2,S}$ at the temperatures of 1573, 1673 and 1773 K is

$$P_{O_2,S}(\text{at} \ 1573 \ K) = P_{O_2,S}(\text{at} \ 1673 \ K)/8.5 = P_{O_2,S}(\text{at} \ 1773 \ K)/58.2 \ (\text{atm})$$

Namely, with increasing the temperature, the $P_{O_2,S}$ value increases significantly. This leads to a higher equilibrium sulfur concentration as shown in Fig. 4. This is one of the reasons why increasing temperature enhances the sulfur transfer into the melt even if it is considered from the mechanism of resulfurization by the oxidation of MgS. In addition, increasing temperature enhances the transfer rate of sulfur from MgS to the melt and also results in a higher final sulfur concentration.

5.2. Effect of Oxygen Partial Pressure in Atmosphere on Resulfurization

The oxygen partial pressure can be adjusted by changing the gas flow rates of argon and oxygen that are blown onto the melt surface. The changes in the experimental and the calculated sulfur concentrations with time under the oxygen partial pressures of 0, 0.05 and 0.10 atm are shown in Fig. 6. The oxygen partial pressure in the atmosphere had a significant influence on the transfer rate of sulfur from MgS on the melt surface into the melt. A higher oxygen partial pressure in the atmosphere gave a faster transfer rate of oxygen from the atmosphere to the surface of melt, and thus enhanced transfer of sulfur from the surface to the melt. At the end of the experiments, the resulfurization ratios ($\xi_S$) are calculated to be 37, 47, 74% under the oxygen partial pressures of 0, 0.05 and 0.10 atm, respectively. They are higher under a higher oxygen partial pressure in the atmosphere. Referring to Fig. 4, one can find that these results are in accord with the calculated equilibrium sulfur concentrations at the different oxygen partial pressures in the atmosphere when the temperature is constant. This also suggests that the mechanism of resulfurization by the oxidation of MgS plays an important role under the oxidative atmosphere.

5.3. Effect of MgS Mass on Resulfurization

In the desulfurization process, a higher initial sulfur concentration results in more MgS produced and floated up to the melt surface. Therefore, it is necessary to study the effect of added mass of MgS on resulfurization rate. With the assumption of desulfurization ratio of 100%, the MgS masses of 0.065, 0.19 and 0.32 g correspond to the initial sulfur concentrations of 100, 300 and 500 ppm, respectively. Figure 7 presents that the sulfur concentration increased faster with adding more MgS onto the melt surface.
sulfur concentrations at 60 min were 57, 140 and 307 ppm in the cases of MgS masses of 0.065, 0.19 and 0.32 g, respectively. The resulfurization ratios (ξ) are, therefore, calculated to be 57, 47 and 61 %, respectively. It is noted that the ξ values do not decrease with increasing added mass of MgS, which suggests that it is far from reaching the equilibrium value of sulfur under the present conditions.

Although a part of sulfur of MgS on the melt surface transferred into the melt according to Eq. (6) or Eq. (8), a part of MgS is oxidized to produce MgO and SO2 according to the following equation:

\[
\text{Mg}_2\text{S} (s) + \frac{3}{2} \text{O}_2 (g) = 2\text{MgO} (s) + 3\text{SO}_2 (g)
\] (16)

\[
\Delta G_{\text{16}}^0 = -1103.74 + 0.16936T (\text{kJ/mol})^{20} \ldots \ldots (17)
\]

The change in the Gibbs free energy is \(\Delta G_{\text{16}}\) = -820.40 kJ/mol at 1 673 K, which indicates that the above reaction is liable to take place under the present experimental conditions. From the calculated ξ values, one can come to the conclusion that 47–61 % sulfur of MgS on the melt surface transfers into the melt, while the remaining MgS is oxidized to form MgO and SO2, and then this part of sulfur is released into the atmosphere.

5.4. Effect of Crucible Materials on Resulfurization

Effect of crucible materials on resulfurization is shown in Fig. 8. The sulfur transfer rate into the melt using Al2O3 crucible was distinctly greater than that using MgO crucible and the final sulfur concentration reached a higher value. At the end of the experiments, the resulfurization ratios (ξ) are calculated to be 47 and 56 % for MgO and Al2O3 crucible, respectively. These results can be explained from both of the mechanisms of resulfurization by the decomposition and by the oxidation of MgS.

The reaction of the dissolved magnesium in the melt with the alumina crucible is given by

\[
\text{Al}_2\text{O}_3 (s) + 3\text{Mg} = 3\text{MgO} (s) + 2\text{Al}
\] \ldots \ldots (18)

\[
\Delta G_{\text{18}}^0 = 44.94 - 0.2140T (\text{kJ/mol})^{20,22} \ldots \ldots (19)
\]

Equation (19) gives that \(\Delta G_{\text{18}}^0 = -313.08\) kJ/mol at 1 673 K. It is also possible to form spinel according to

\[
4\text{Al}_2\text{O}_3 (s) + 3\text{Mg} = 3(\text{MgO} \cdot \text{Al}_2\text{O}_3 ) (s) + 2\text{Al}
\] \ldots \ldots (20)

\[
\Delta G_{\text{20}}^0 = -17.43 - 0.2611T (\text{kJ/mol})^{20,22,23} \ldots \ldots (21)
\]

where \(\Delta G_{\text{20}}^0 = -454.25\) kJ/mol at 1 673 K. So, the dissolved magnesium produced by the decomposition of MgS (by Eq. (6)) is consumed by the reaction with Al2O3 crucible. The decomposition of MgS is, therefore, promoted and the transfer rate of sulfur into the melt becomes fast in the case of Al2O3 crucible.

On the other hand, considering the reaction between MgO and Al2O3, and using the free energy data obtained by K. Fujii et al., we obtain

\[
\text{Al}_2\text{O}_3 (s) + \text{MgO} (s) = 3\text{MgO} \cdot \text{Al}_2\text{O}_3 (s)
\] \ldots \ldots (22)

\[
\Delta G_{\text{22}}^0 = -20.790 - 0.0157T (\text{kJ/mol})^{23} \ldots \ldots (23)
\]

By combination of Eqs. (8) and (22), the resulfurization reaction together with the associated Gibbs free energy change, in the case of Al2O3 crucible, can be written as

\[
\text{Mg}_2\text{S} (s) + \frac{1}{2} \text{O}_2 + \text{Al}_2\text{O}_3 = \text{MgO} \cdot \text{Al}_2\text{O}_3 + \text{S}
\] \ldots \ldots (24)

\[
\Delta G_{\text{24}}^0 = -347.27 + 0.02024T (\text{kJ/mol}) \ldots \ldots (25)
\]

where \(\Delta G_{\text{24}}^0 = -313.41\) kJ/mol, which is lower than \(\Delta G_{\text{16}}^0\) of -266.35 kJ/mol at 1 673 K. So, the oxidation of MgS will be promoted and the sulfur transfer rate into the melt will become fast.

5.5. Prevention of Resulfurization by Addition of CaO

Addition of CaO onto the melt surface was tried to prevent resulfurization. The experimental results are shown in Fig. 9. Before the experiments, the powders of CaO and MgS were mixed and then were added onto the melt surface. When no CaO was added onto the melt surface, the sulfur concentration increased rapidly to 140 ppm at 60 min. Addition of 0.19 g CaO significantly decreased the sulfur transfer rate into the melt and the sulfur concentration dropped to 64 ppm at 60 min. Addition of 0.19 g CaO significantly decreased the sulfur transfer rate into the melt and the sulfur concentration dropped to 64 ppm at 60 min. It is considered that MgS reacts with CaO to form CaS and MgO, while CaS has higher stability than MgS. The reaction can be written as

\[
\text{Mg}_2\text{S} + \text{CaO} (s) = \text{CaS} (s) + \text{MgO} (s)
\] \ldots \ldots (26)

\[
\Delta G_{\text{26}}^0 = -97.82 + 0.0063T (\text{kJ/mol}) \ldots \ldots (27)
\]

The free energy change of -87.28 kJ/mol at 1 673 K means that this reaction is liable to take place under the present ex-
experimental conditions. Equation (26) shows that 0.19 g CaO is just the quantity to react with 0.19 g MgS theoretically. When up to 1.84 g of CaO, which corresponded to the specific consumption of reagent of 5 kg/ton, was added, the transfer of sulfur into the melt was almost completely repressed and the final sulfur concentration was down to 22 ppm. It is clearly shown that the addition of CaO onto the melt surface is an effective method for preventing sulfur from transferring into the melt.

Furthermore, the stabilities of MgS and CaS were examined experimentally by adding only MgS or CaS onto the melt surface to study the sulfur transfer rates into the melt. Figure 10 presents the experimental results. It is clear that CaS has much higher stability than MgS even under the oxidative atmosphere.

5.6. Prevention of Resulfurization by Addition of C

Further effort has been made to prevent resulfurization by adding activated charcoal powders onto the melt surface. In this case, 0.19 g MgS was first added onto the melt surface and then the activated charcoal powders of 3.68 g, which corresponded to the specific consumption of reagent of 10 kg/ton, was added onto the melt surface. In contrast to the result without addition of activated charcoal powders, Fig. 11 shows that addition of 3.68 g activated charcoal powders markedly decreased the sulfur transfer rate into the melt and the resulfurization ratios ($\alpha_{S}$) at the end of experiments decreased from 47 to 20%. The reason why the resulfurization was markedly prevented is due to the fact that the layer of the activated charcoal powders was formed on the melt surface by addition of the activated charcoal powders and the transfer of oxygen in the atmosphere to the melt surface was greatly inhibited.

6. Kinetic Discussion

In the case of the inert atmosphere, according to Eq. (6), the resulfurization rate is controlled by the following steps: transfer of MgS from the slag (here, slag means MgS or the mixture of MgS and produced MgO) to the slag–melt interface; decomposition of MgS at the slag–melt interface; and transfer of sulfur and magnesium from the slag–melt interface into the melt.

In the case of the oxidative atmosphere, according to Eq. (8), the resulfurization rate is controlled by the following steps: transfer of MgS from the slag and transfer of oxygen from the atmosphere to the slag–melt interface; oxidation of MgS at the slag–melt interface; from the slag–melt interface, transfer of sulfur into the melt and MgO into the slag.

Consequently, the kinetic study on the resulfurization is quite complex. It depends on the oxygen partial pressure in the atmosphere. Moreover, to obtain the overall transfer rate of sulfur, it is necessary to know the sulfur concentration at the slag–melt interface. As shown in Eq. (7), the sulfur concentration at the slag–melt interface is dependent on the magnesium concentration at the slag–melt interface. However, the magnesium concentration at the slag–melt interface is determined by the decomposition rate of MgS, the evaporation rate of magnesium, and the mass transfer rate of magnesium in the melt and in the atmosphere. Under the oxidative atmosphere, it further depends on the oxidation rate of MgS. With considering the difficulty to determine the sulfur concentration at the interface and the complexity of kinetics of the transfer of sulfur from slag to melt, the sulfur concentration at the slag–melt interface is assumed to be the final sulfur concentration in every experiment, and the following first-order rate equation for the transfer of sulfur from the slag–melt interface to the melt is used to obtain the capacity coefficient instead of the strict kinetic analysis.

$$\frac{dnS}{dt} = -k_{S,M}(C-C_S) \quad \text{(30)}$$

where $n_S$ (mol) is the number of moles of sulfur in the melt, $t$ (min) is the time, $k_{S,M}$ (m/min) is the mass transfer coefficient of sulfur in the melt, $A$ (m$^2$) is the area of the slag–melt interface, $C$ and $C_S$ (mol/m$^3$) are the sulfur molar concentration in the melt and at the interface, respectively. This rate equation can be changed as

$$\frac{d[\text{ppmS}]}{dt} = -\alpha_S([\text{ppmS}] - [\text{ppmS}]_S) \quad \text{(31)}$$

where $[\text{ppmS}]$ and $[\text{ppmS}]_S$ are the sulfur concentration in the melt and at the interface, respectively. $\alpha_S$ ($\alpha_S = k_{S,M}/V_m$) is the capacity coefficient, and $V_m$ (m$^3$) is the volume of melt.
Integrating Eq. (31), one can obtain the following equation:

\[ \ln \frac{[\text{ppmS}]_t - [\text{ppmS}]_f}{[\text{ppmS}]_0 - [\text{ppmS}]_f} = - \alpha_{s,t} t \]  

(32)

Here, the value of \([\text{ppmS}]_f\) is assumed to be equal to the final sulfur concentration in the melt \([\text{ppmS}]_f\) during each experiment.

The plots of \(-\ln(\frac{[\text{ppmS}] - [\text{ppmS}]_0}{[\text{ppmS}]_0 - [\text{ppmS}]_0})\) vs. time at various temperatures are shown in Fig. 12. The relation of \(-\ln(\frac{[\text{ppmS}] - [\text{ppmS}]_0}{[\text{ppmS}]_0 - [\text{ppmS}]_0})\) vs. time does not show good linearity. One of the reasons is that the transfer of sulfur into the melt was accelerated when the melt surface was lightly stirred before the experiment to make the melt surface covered with the added MgS powders evenly.

From the slopes of the lines, the capacity coefficients are calculated to be 0.067, 0.070 and 0.14 min\(^{-1}\) for the temperatures of 1 573, 1 673 and 1 773 K, respectively. They increase with increasing temperature. Assuming the area of the slag–melt interface to be the cross section area of the crucible, one can calculate the mass transfer coefficients to be 0.0047, 0.0049, 0.0099 cm · s\(^{-1}\) for the temperatures of 1 573, 1 673 and 1 773 K, respectively. These values are much smaller than the usual mass transfer coefficients in the molten iron of the order of 10\(^{-2}\) cm · s\(^{-1}\) in the induction furnace\(^{1,2,24,25}\), which indicates that the rate-controlling steps may include the decomposition or the oxidation of MgS at the slag–melt interface and the transfer of oxygen from the atmosphere to the interface.

Similarly, \(-\ln(\frac{[\text{ppmS}] - [\text{ppmS}]_0}{[\text{ppmS}]_0 - [\text{ppmS}]_0})\) vs. time are plotted for the various oxygen partial pressures in the atmosphere in Fig. 13. The capacity coefficients increase with increasing the oxygen partial pressure in the atmosphere, being 0.046, 0.070 and 0.17 min\(^{-1}\) for the oxygen partial pressures in the atmosphere of 0, 0.05 and 0.10 atm, respectively. Furthermore, for different amounts of MgS, plots of \(-\ln(\frac{[\text{ppmS}] - [\text{ppmS}]_0}{[\text{ppmS}]_0 - [\text{ppmS}]_0})\) vs. time are shown in Fig. 14 and almost the same capacity coefficient of 0.070 min\(^{-1}\) is obtained. In a word, the capacity coefficient of sulfur transferring from MgS on the melt surface to the melt is increased with increasing the temperature and the oxygen partial pressure in the atmosphere, but does not change with adding different amounts of MgS onto the melt surface.

By use of the capacity coefficient and Eq. (32), the changes in the sulfur concentrations with time can be calculated and are plotted in Figs. 5, 6, 7 together with the experimental results. Owing to the above-mentioned reasons, some of the experimental sulfur concentrations are higher than the calculated ones during the initial periods. From the above discussion, the kinetics of transfer of sulfur from slag to melt should be further studied in the future.

7. Conclusions

A simplified experiment was conducted in place of actual magnesium desulfurization process to study its resulfurization mechanism. The magnesium desulfurization products, MgS powders, were added onto the iron melt, and then the transfer rate of sulfur from MgS on the melt surface into the melt was studied. The effects of temperature, oxygen partial pressure in the atmosphere, initial sulfur concentration and materials of crucible on the resulfurization were investigated, the methods of prevention of resulfurization were proposed, and the resulfurization rates were analyzed kinetically. From these studies, the following conclusions are obtained:

(1) There are two kinds of mechanisms that are responsible for the resulfurization in the magnesium desulfuriza-
tion process. Under the inert atmosphere, the resulfurization takes place by decomposition of MgS. Under the oxidative atmosphere, the resulfurization proceeds by oxidation of MgS.

(2) With increasing temperature and oxygen partial pressure in the atmosphere, the transfer of sulfur into the melt was enhanced and the resulfurization ratio \( \xi_S \) was increased. A larger amount of MgS added onto the melt surface did not change the \( \xi_S \) value a lot under the present experimental conditions. Using MgO crucible could decrease the transfer rate of sulfur into the melt in comparison with using Al\(_2\)O\(_3\) crucible.

(3) Addition of CaO onto the melt surface was proved to be an effective method to prevent sulfur from transferring into the melt. This is because MgS was transformed into a more stable sulfide of CaS. Another method of adding the activated charcoal powders onto the melt surface was proposed, and was also demonstrated to be effective for preventing sulfur from transferring into the melt due to the decrease in the transfer rate of oxygen in the atmosphere to the melt surface.

(4) With a simplified first-order rate equation, the calculated capacity coefficient for transfer of sulfur from MgS to melt is increased with increasing the temperature and the oxygen partial pressure in the atmosphere, but does not change with adding different amounts of MgS onto the melt surface.

Acknowledgement

This study was supported in part by Grant-in-Aid for Scientific Research (16360372) from the Ministry of Education, Science, Sports and Culture of Japan.

REFERENCES

1) M. Ozawa, Y. Ohtsuka, R. Hori and R. Mori: Private communication, June (1975).
2) S. Yamaguchi, T. Uemura, H. Nashiwa and H. Sagita: Ironmaking & Steelmaking, 5 (1977), 276.
3) W. H. Duquette, N. R. Griffith and T. W. Miller: Open Hearth Proc., 56 (1973), 79.
4) W. G. Wilson and A. Mclean: Desulfurization of Iron and Steel and Sulfide Shape Control, ISS-AIME, Warrendale, PA, (1980), 77.
5) P. J. Koros, R. G. Petrushka and R. G. Kerin: Iron Steelmaker, 4 (1977), 34.
6) A. Aoyagi, Z. Mukuda, S. Takada and S. Oomiya: CAMP-ISIJ, 7 (1994), 221.
7) T. Fujita, K. Matsui, S. Nakajima, K. Semura and M. Endou: CAMP-ISIJ, 7 (1994), 218.
8) K. Kimura, I. Kikuchi, S. Kohira, Y. Komatsu, J. Fukumi and T. Toyota: CAMP-ISIJ, 8 (1995), 105.
9) J. Hirama, K. Gennai, Y. Hiraga and Y. Nakashima: CAMP-ISIJ, 8 (1995), 104.
10) Y. Hiraga, K. Gennai, Y. Nakashima and J. Hirama: CAMP-ISIJ, 9 (1996), 225.
11) J. Yang, S. Ozaki, R. Kakimoto, K. Okumura, M. Kuwabara and M. Sano: ISIJ Int., 41 (2001), 945.
12) J. Yang, K. Okumura, M. Kuwabara and M. Sano: ISIJ Int., 41 (2001), 965.
13) J. Yang, K. Okumura, M. Kuwabara and M. Sano: ISIJ Int., 42 (2002), 595.
14) J. Yang, K. Okumura, M. Kuwabara and M. Sano: ISIJ Int., 42 (2002), 685.
15) K. Yonezawa, S. Sasakawa and S. Kitamura: CAMP-ISIJ, 6 (1993), 1070.
16) J. Yang, K. Okumura, M. Kuwabara and M. Sano: Metall. Trans. B, 34B (2003), 619.
17) K. Nakamichi, T. Tajima, T. Suzuki and F. Sudo: Tetsu-to-Hagané, 64 (1978), 1323.
18) Y. Nakamura and N. Tokumitsu: Tetsu-to-Hagané, 60 (1974), S438.
19) L. Hong, K. Okumura and M. Sano: Metall. Trans. B, 30B (1999), 1003.
20) Handbook of Iron and Steel, ed. by ISIJ, Maruzen, Tokyo, (1981), 14.
21) A. K. Biswas and G. Reginald Bashforth: The Physical Chemistry of Metallurgical Process, Chapman & Hall Ltd., London, (1962), 187.
22) M. C. Speer and N. A. D. Parlee: Cast Met. Res. J., 8 (1972), 122.
23) K. Fuji, T. Nagasaki and M. Hino: ISIJ Int., 40 (2000), 1059.
24) H. Nomura and K. Kori: Trans. Iron Steel Inst. Jpn., 13 (1973), 325.
25) K. Suzuki, K. Mori, T. Kitagawa and S. Shibayama: Tetsu-to-Hagané, 62 (1976), 42.