Simultaneous Desulfurization and Deoxidation of Molten Steel with *in Situ* Produced Magnesium Vapor

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A new simultaneous desulfurization and deoxidation process of molten steel with magnesium vapor produced *in situ* by aluminothermic reduction of magnesium oxide is proposed. The pellets composed of MgO and Al are charged into an immersion tube and the magnesium vapor produced *in situ* by aluminothermic reduction of magnesium oxide is injected directly into molten steel to react with the dissolved sulfur and oxygen in it. Effects of various operating parameters on desulfurization and deoxidation are discussed.

In the case of the high initial oxygen concentration, deoxidation of molten steel proceeds preferentially, and desulfurization does not take place. When the oxygen concentration in the melt is low enough, desulfurization of molten steel with magnesium vapor can proceed.

A higher initial sulfur concentration increases the desulfurization ratio of molten steel. The sulfur concentration in the melt tends to be in equilibrium with the magnesium partial pressure in the Mg–Ar bubble rather than the dissolved magnesium concentration in the melt. Increasing pellet mass promoted desulfurization of molten steel. The maximum desulfurization ratio of molten steel can be obtained at a relatively low argon carrier gas flow rate. In both cases of the porous magnesia and the dense alumina immersion tubes with injecting holes, addition of lime onto the melt surface increases the desulfurization ratio. The desulfurization using the dense alumina tube is accompanied by resulfurization more significantly at the later stage than that using the porous magnesia tube.

KEY WORDS: desulfurization; deoxidation; magnesium vapor; pellet; magnesium oxide; aluminothermic reduction; molten steel.

1. Introduction

Desulfurization in the secondary refining process has been steadily increased for the past two decades due to the increasing demands for mass production of ultra-low sulfur steel. In most of the established desulfurization processes, the CaO-based desulfurization flux1–7) is employed but with addition of CaF₂ to improve its desulfurization rate and efficiency by decreasing its melting point. However, the environmental problems caused by use of CaF₂ make it urgent to develop an alternative desulfurization method in the secondary refining process.

It is well known that magnesium has strong affinity with sulfur and oxygen. Much work8) has shown that the sulfur concentration can be effectively reduced to a very low level during pretreatment of hot metal, on condition that magnesium is released into molten iron in a controllable manner. However, desulfurization results of molten steel with magnesium depended largely on the experimental conditions. With magnesium vapor produced in a separated furnace and blown onto the melt surface with argon carrier gas, Mori *et al.*9) found that desulfurization of molten steel with magnesium could hardly proceed at the magnesium partial pressure of 3.7×10⁻³ Pa. On the other hand, Takeyama *et al.*10) reported that the sulfur concentration in the molten steel could be decreased to 3 ppm with feeding the wire, which was a mixture of Mg, MgO and CaF₂. In a Mg–S equilibrium study for molten iron, at a temperature of 1 873 K, Nadif *et al.*11) obtained $K_{MgS} = a_S \cdot a_{Mg}/a_{MgS}$ = 2.03×10⁻⁴ from the thermodynamic calculation, while Han *et al.*12) made an experimental investigation and obtained $K_{MgS} = 2.0\times10^{-4}$.

Since the normal boiling point of magnesium, 1 363 K,13) is much lower than the temperature of the secondary refining processes, addition of magnesium metal into molten steel is usually accompanied by violent magnesium vaporization. This brings about not only a safety problem but also a drop in the magnesium desulfurization efficiency. Haddock *et al.*14) proposed a desulfurization method of molten steel with magnesium. A granular reagent, which consists essentially of fine aluminum particles encapsulated by a coating of mixture comprised of 50% MgO, 21% CaCO₃, 18% Al and 11% CaF₂ (by mass percent), was pneumatically injected into molten steel. It was expected...
that the magnesium vapor released in situ by aluminothermic reduction of magnesium oxide could be used for desulfurization of molten steel. However, it should be ascertained if the residence time of the particles in the melt is long enough for the aluminothermic reduction of magnesium oxide and if the aluminum does not react with CaCO₃ or dissolve into the melt.

We proposed a new desulfurization method of hot metal with magnesium vapor produced in situ by carbothermic³¹ or aluminothermic reduction of magnesium oxide. The cheap magnesium oxide, instead of magnesium metal, was used as the secondary source of magnesium so that the cost of magnesium desulfurization was greatly reduced. In addition, a novel method for improving the desulfurization efficiency of magnesium (ηMg) by adjusting the initial magnesium molar ratio in the bubble through changing the argon carrier gas flow rate was also proposed.¹⁹) The mechanism of resulfurization in the desulfurization process²¹) was clarified and the prevention methods of resulfurization²¹) were also developed.

Magnesium desulfurization of hot metal is quite different from that of molten steel. The difference is caused not only by the different operating temperatures, which affect the equilibrium constants, but also by the different carbon concentrations, which affect the activity coefficient of sulfur. Furthermore, in the molten steel, since deoxidation preferentially proceeds instead of desulfurization, the deoxidation has to be taken into account in the desulfurization process of molten steel with magnesium.

As for deoxidation of molten steel with magnesium, a number of equilibrium studies²²–²⁵) were carried out in recent years. In addition, Najafabadi et al.²⁶) proposed a deoxidation method of molten steel with the immersed MgO–C porous tube, in which the magnesium vapor produced by the reaction between MgO and C, could be used for the deoxidation. Shan et al.²⁷–²⁹) developed another deoxidation method of molten steel with magnesium vapor produced in situ by carbothermic or aluminothermic reduction of magnesium oxide.

In the present paper, magnesium vapor produced in situ by aluminothermic reduction of magnesium oxide is utilized for simultaneous desulfurization and deoxidation of molten steel. The thermodynamic analysis is made to clarify the desulfurization and deoxidation ability of molten steel with magnesium vapor. The effects of initial oxygen concentration, initial sulfur concentration, pellet mass, carrier gas flow rate and addition of CaO powders onto the melt surface on the desulfurization and deoxidation are investigated experimentally.

2. Experimental Apparatus and Procedures

Figure 1 schematically shows the experimental apparatus. A high frequency induction furnace (15 kW, 100 kHz) was used to melt electrolytic iron of 350 g in a magnesia crucible of 40 mm i.d. and 100 mm in height. An inert atmosphere was maintained by blowing argon gas onto the melt surface. This argon gas had the flow rate of 1.33×10⁻⁵ m³/s, and was purified by passing through Mg(ClO₄)₂ powders at room temperature and Mg chips at 473 K. The employed dense alumina or porous magnesia immersion tube of 11 mm i.d. and 15 mm o.d. had 4 holes of 1.0 mm diameter at its lower part. Magnesium vapor together with the argon carrier gas was injected into the melt through these holes.

The pellets charged into the tube were the mixture composed of magnesium oxide powder (0.4 μm in average diameter and purity higher than 99.99%) and aluminum powder (75–150 μm in size and purity higher than 99.5%). After mixing the magnesium oxide and aluminum powders at a molar ratio of 2 : 1, the pellets were formed by use of a cold isostatic press (CIP) under a pressure of 150 MPa for 1 h, having the diameter of 3 mm and the length of 4 mm.

The initial sulfur concentration of the melt was adjusted by adding FeS powders to the molten steel. In most experiments of desulfurization, the initial oxygen concentration in the melt was reduced to the minimal level by way of deoxidation with blowing the mixture gas of hydrogen and argon onto the melt surface and subsequent addition of 0.2 g aluminum wire into the melt. Some experiments were made without pre-deoxidation to study the effect of initial oxygen concentration on desulfurization.

The refractory tube charged with the pellets was immersed into the steel melt. The magnesium vapor produced in situ by aluminothermic reduction of magnesium oxide was injected directly into the molten steel together with the argon carrier gas, to react with sulfur and oxygen dissolved in it. The desulfurization and deoxidation processes were examined by taking samples from the melt at appropriate time intervals to analyze sulfur, oxygen and magnesium contents. The sulfur content was determined by non-scattered infrared ray detector after the sample was burned in the pure oxygen gas. The analyzed sulfur concentration was calibrated by two kinds of standard samples (15 ppm and 300 ppm). The oxygen content was analyzed by non-scattered infrared ray absorptiometry and was calibrated by two kinds of standard samples (46 ppm and 437 ppm). The magnesium content in the sample was determined by induction coupled plasma emission spectroscopy (ICP) with relative scattering less than 5%.

All of the experimental conditions are summarized in Table 1. The temperature for all experiments was 1873 K. For some experiments, the oxygen concentrations were not measured, but they were maintained for about the same level when effect of the other operating parameters on desulfurization was examined. The data of the parameters being examined are written in bold and italic characters.
3. Principle and Thermodynamic Consideration

3.1. Principle

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:

\[ 4\text{MgO(s)} + 2\text{Al(l)} = 3\text{Mg(g)} + \text{MgO·Al}_2\text{O}_3(s) \]  

\[ \Delta G^°_\text{f} = 465.6 - 0.2877T \text{(kJ/mol)} \]  

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

\[ 3\text{MgO·Al}_2\text{O}_3(s) + 2\text{Al(l)} = 3\text{Mg(g)} + 4\text{Al}_2\text{O}_3(s) \]  

\[ \Delta G^°_\text{f} = 607.7 - 0.279T \text{(kJ/mol)} \]  

The reduction efficiency of the pellet, \( \eta_R \), is defined as the ratio of the mass of magnesium oxide reduced during the experiment, \( W_R \), to the initial mass of magnesium oxide in the pellet, \( W_0 \).

\[ \eta_R = \left( \frac{W_R}{W_0} \right) \times 100 \text{(\%)} \]  

In the present refining process, the magnesium vapor produced by the above two reactions is injected directly into the molten steel. On the assumption that desulfurization and deoxidation occur on the bubble surface, the reactions proceed as follows:

\[ \text{Mg(g)} + \text{S} = \text{MgS(s)} \]  

\[ \Delta G^°_\text{f} = -404.07 + 0.16921 T \text{(kJ/mol)} \]

3.2. Thermodynamic Consideration

Since no desulfurization slag is used in the present experiment, the activity of MgS is unity. And since the carbon concentration ([%C]) is much higher than the concentrations of the other elements in the melt, the Henrian activity coefficient of sulfur is given by \( \log f_S = 0.11[\%C] \). The equilibrium relation between the magnesium partial pressure (\( P_{\text{Mg,e}} \text{(Pa)} \)) in the Mg–Ar bubble and the sulfur concentration ([ppmS]e) in the melt can be given

\[ P_{\text{Mg,e}}^{-1} \text{[ppmS]}_e = 10^{3.8-0.11[\%C]} \exp \left( \frac{-404.070 + 169.217}{8.314T} \right) \]  

Form this equation, it is seen that the equilibrium sulfur concentration is lower at a higher magnesium partial pressure and decreases with decreasing the operating temperature.

The comparison of desulfurization of hot metal and molten steel is shown in Fig. 2. For hot metal, the saturated carbon concentrations in equilibrium with graphite can be obtained from Fe–C phase equilibrium diagram, being 4.5, 4.7, 4.8 and 5.0% at 1 553, 1 613, 1 673 and 1 773 K, respectively. For molten steel, the carbon concentration is assumed to be 0. It is clear that desulfurization of hot metal proceeds much more easily than that of molten steel from the view point of thermodynamics. For example, at the magnesium partial pressure of 1.0×10⁵ Pa, the equilibrium sulfur concentration of hot metal is as low as 0.49 ppm at the temperature of 1 673 K, while the equilibrium sulfur concentration of molten steel rises to 37 ppm at 1 873 K.
Therefore the sulfur concentration of hot metal can be decreased to an ultra low level by desulfurization with magnesium vapor, but the sulfur concentration of molten steel cannot be done.

Detailed consideration of desulfurization of hot metal and molten steel indicates that the equilibrium sulfur concentration increases by about 22 times when the temperature rises from 1673 to 1873 K, and increases by approximately 3.4 times when the carbon concentration drops from 4.8% in hot metal to 0% in molten steel.

With the calculation similar to desulfurization, the equilibrium relation between the magnesium partial pressure ($P_{Mg,e}$ (Pa)) in the Mg–Ar bubble and the oxygen concentration ([ppmO]e) in the melt is given as

$$P_{Mg,e} \cdot [ppmO]_e = 10^9 \exp \left( \frac{-613,440 + 208,525T}{8,314T} \right)$$

This relation is plotted in Fig. 3. The comparison between desulfurization and deoxidation of molten steel with magnesium vapor reveals that the equilibrium oxygen concentration is much lower than the equilibrium sulfur concentration for the same temperature and magnesium partial pressure. At the temperature of 1873 K and the magnesium partial pressure of 1.0×10^7 Pa, the equilibrium oxygen and sulfur concentrations are 0.0060 ppm and 37 ppm, respectively. Thus deoxidation of molten steel with magnesium preferentially proceeds when both sulfur and oxygen exist.

At the same magnesium partial pressure, the relation between the equilibrium sulfur and oxygen concentrations in molten steel is sketched in Fig. 4 at different temperatures. For example, at the temperature of 1873 K, decreasing the sulfur concentration to below 50 ppm thermodynamically requires that the oxygen concentration should be decreased to below 0.008 ppm.

4. Experimental Results and Discussion

4.1. Effect of Initial Oxygen Concentration on Desulfurization and Deoxidation

Under the experimental conditions of the dense alumina immersion tube, the carrier gas flow rate of 5.0×10^-7 m^3/s and the pellet mass of 1.5 g, the desulfurization and deoxidation results of molten steel are shown in Fig. 5 in the case of the high initial oxygen concentration. When the initial oxygen concentration was 190 ppm, desulfurization of molten steel with magnesium vapor did not proceed. The initial sulfur concentration was 220 ppm and the final one was 215 ppm. On the other hand, the oxygen concentration was decreased rapidly from the initial 190 ppm to 90 ppm in 10 min. The final oxygen concentration was 100 ppm.
Namely deoxidation preferentially proceeded and desulfurization did not occur in the case of the high initial oxygen concentration.

Figure 6 presents the effect of the initial oxygen concentration on desulfurization and deoxidation of molten steel for the experiments at the carrier gas flow rate of $3.3 \times 10^{-6}$ m$^3$/s using the porous magnesia tube. In the case of the initial oxygen concentration of 330 ppm, the pellet mass was 3.0 g; in the case of the initial oxygen concentration of 28 ppm, the pellet mass was 2.0 g. When the initial oxygen concentration was 330 ppm, the sulfur concentration did not decrease even if the pellet of 3.0 g was used. But the oxygen concentration was decreased from the initial 330 ppm to the final 50 ppm. It is clear that the produced magnesium vapor was used for deoxidation. However, in contrast to the case of the dense alumina tube, the decreasing rate of the oxygen concentration with the porous magnesia tube is much slower. It is considered that the adsorption of magnesium vapor in the initial stage of the experiment and desorption of magnesium vapor in the later stage of the experiment by the porous magnesia tube are responsible for the decrease in the deoxidation rate. The details were described elsewhere.$^{17}$

In the case of the initial oxygen concentration of 28 ppm, the sulfur concentration was decreased from the initial 300 ppm to the final 210 ppm. When the oxygen concentration in molten steel was low enough, desulfurization with the magnesium vapor did take place. In the two cases, the final oxygen concentrations were as high as 50 and 25 ppm. The relatively high final oxygen concentration can be attributed to three reasons. The first reason is that the measured oxygen concentration is the total oxygen concentration including oxide inclusions. The produced MgO inclusions usually have a average diameter of about 1 $\mu$m,$^{34}$ which is so small that it takes quite a long time to float up to the melt surface. The second reason is that the oxygen concentration in the melt is not only affected by the equilibrium with magnesium concentration in the melt, but also increased with dissolution of the MgO crucible.$^{35}$ The third reason is that the aluminothermic reduction rate is rather slow at the later stage of experiment. Thus the magnesium partial pressure and magnesium concentration in the melt is so low that deoxidation can not effectively proceed.

**4.2. Effect of Initial Sulfur Concentration on Desulfurization and Deoxidation**

Figure 7 shows the effect of the initial sulfur concentration on desulfurization and deoxidation. The porous magnesia immersion tube was used, the temperature was 1873 K and the carrier gas flow rate was 0 m$^3$/s. Because the carrier gas was not used, the interior part of the immersion tube above the pellets was sealed with a refractory chip closely in order to ensure all the produced magnesium vapor was injected into the melt. When the initial sulfur concentrations were 370, 200 and 70 ppm, the sulfur concentrations decreased to 210, 80 and 20 ppm, respectively, at the end of the corresponding experiments. The differences between the initial and the final sulfur concentrations were 160, 120 and 50 ppm, and the desulfurization efficiencies of magnesium were 4.2, 3.1, and 1.3%, respectively. The larger was the initial sulfur concentration, the higher was the desulfurization efficiency of magnesium. In addition, even though the initial sulfur concentration was adjusted to as low as 70 ppm, the final sulfur concentration was about 20 ppm, which was close to the equilibrium value of 37 ppm at 1873 K under the magnesium partial pressure of $1.0 \times 10^5$ Pa. It is confirmed that the ultra-low sulfur concentration is difficult to be obtained by desulfurization of molten steel with magnesium vapor.

In contrast to the previous studies, Mori et al.$^{9}$ indicated that desulfurization of molten steel with magnesium could hardly proceed at the magnesium partial pressure of $3.7 \times 10^5$ Pa and the temperature of 1873 K. The present thermodynamic calculation shows that the equilibrium value of sulfur concentration is as high as about 1000 ppm, which is much higher than the initial sulfur concentration of
300 ppm in their case. Thus desulfurization did not proceed. On the other hand, Takeyama et al.\textsuperscript{10} reported that the sulfur concentration in the molten steel could be decreased to 3 ppm with feeding the wire, which was a mixture of Mg, MgO and CaF\textsubscript{2}. The ultra low sulfur concentration resulted from the integrated effect of these additives because addition of CaF\textsubscript{2} promoted the formation of slag and might decrease the activity of MgS.

When the initial total oxygen concentrations in Fig. 7 ranged from 30 to 40 ppm, the final ones dropped to 15–25 ppm. The magnesium concentrations in the melt are also shown in the same figure, all the values being below 20 ppm.

Zhang et al.\textsuperscript{36} investigated the dissolution equilibrium of magnesium vapor in molten steel by the vapor pressure method using a two-temperature zone furnace. By use of their experimental data, a regression equation can be obtained for 1 873 K as follows:

\[ [\text{ppmMg}]_e = 530 P_{\text{Mg,e}} / \text{H11005} \]

where \( P_{\text{Mg,e}} \) is the magnesium partial pressure in the atmosphere (Pa).

By combination of Eqs. (10) and (12), the solubility product of Mg and S in molten steel is given as

\[ [\text{ppmMg}]_e \cdot [\text{ppmS}]_e = 5.3 \times 10^6 \exp \left( \frac{-404070 + 169.21 T}{8.314 T} \right) \]

Similarly, combination of Eqs. (11) and (12) gives the solubility product of Mg and O in molten steel as follows:

\[ [\text{ppmMg}]_e \cdot [\text{ppmO}]_e = 5.3 \times 10^9 \exp \left( \frac{-613440 + 208.525 T}{8.314 T} \right) \]

It should be noted that Eqs. (13) and (14) are valid only at the temperature of 1 873 K, and the calculated solubility products are \([\text{ppmMg}]_e \cdot [\text{ppmS}]_e = 19600\) and \([\text{ppmMg}]_e \cdot [\text{ppmO}]_e = 3.2\).

The relations between \([\text{ppmMg}]_e \) and \([\text{ppmS}]_e \), and between \([\text{ppmMg}]_e \) and \([\text{ppmO}]_e \) are illustrated in Fig. 8. The equilibrium results are plotted with inclined straight lines, and the experimental results are depicted with marks linked by lines. For the various initial sulfur concentrations, the magnesium concentrations increased with decreasing the sulfur and the oxygen concentrations at first and reached the peak values, and then decreased with further decreasing the sulfur and the oxygen concentrations.

The experimental results of \([\text{ppmMg}]_e \) versus \([\text{ppmS}]_e \) are far below the equilibrium line. This indicates that the desulfurization results with magnesium vapor can not be explained from the equilibrium relation between the dissolved sulfur and magnesium. As aforementioned, because the lowest value of \([\text{ppmS}]_e \) of about 20 ppm is close to the sulfur concentration in equilibrium with the magnesium vapor of the partial pressure of \(1.0 \times 10^5\) Pa at 1 873 K, desulfurization with magnesium vapor should take place on the surface of the Mg-containing bubble rather than in the melt.

On the other hand, the experimental results of \([\text{ppmMg}]_e \) versus \([\text{ppmO}]_e \) are above the equilibrium line of \([\text{ppmMg}]_e \) and \([\text{ppmO}]_e \). Therefore the magnesium concentration in molten steel is strongly affected by the dissolved oxygen concentration in the melt rather than is determined merely by the equilibrium between the dissolved oxygen and sulfur concentrations.

The difference of \([\text{ppmO}]_e \) between the experimental results and the equilibrium ones is mainly caused by the inclusions of MgO, SiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3}. The formation of SiO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3} inclusions was confirmed in our other article,\textsuperscript{37} and it resulted from the quartz sample tube and the impurities in the crucible.

Under the experimental conditions of using the porous magnesia immersion tube, the carrier gas flow rate of \(5.0 \times 10^{-7} \text{ m}^3/\text{s}\) and the pellet mass of 1.5 g, the desulfurization results are given in Fig. 9 with the initial sulfur concentrations of 410 and 270 ppm. The desulfurization ratio, which is defined as the ratio of the difference of the sulfur concentrations between the initial and certain time value to the initial one, is shown in the right diagram. When the initial sulfur concentration increased from 270 to 410 ppm, the maximum desulfurization ratio was increased from 24 to 38%. It is evident that the mass transfer of sulfur in the melt is one of the rate controlling steps in the desulfurization of molten steel with magnesium vapor.

4.3. Effect of Pellet Mass on Desulfurization

Figure 10 shows the influence of the pellet mass on desulfurization. The porous magnesia immersion tube was used, the carrier gas flow rate was \(1.7 \times 10^{-7} \text{ m}^3/\text{s}\) and the temperature was 1 873 K. The differences between the initial and the final sulfur concentrations were 120 and
170 ppm with the pellet masses of 2.0 and 3.0 g, respectively. This indicates that increasing the pellet mass can effectively promote desulfurization.

### 4.4. Effect of Carrier Gas Flow Rate on Desulfurization

As mentioned in our previous paper, a little argon carrier gas can greatly increase the aluminothermic reduction rate of magnesium oxide. On the other hand, the argon carrier gas decreases the magnesium partial pressure in the Mg–Ar bubble. This is unfavorable to the desulfurization of molten steel from the viewpoint of thermodynamics.

**Figure 11** indicates the influence of the carrier gas flow rate on desulfurization. The porous magnesia immersion tube was used, the pellet mass was 3.0 g, and the temperature was 1 873 K. When the argon carrier gas flow rate was increased a little from 0 to $1.7 \times 10^{-7}$ m$^3$/s, the ratio of desulfurization of molten steel was increased. This is because the aluminothermic reduction of magnesium oxide was greatly promoted and the produced Mg vapor was smoothly injected into the melt with a little argon carrier gas.

However, when the argon carrier gas flow rate was further increased to $3.3 \times 10^{-6}$ m$^3$/s, the desulfurization of molten steel was inhibited. The result is shown in **Fig. 12**. The porous magnesia immersion tube was used and the pellet mass was 2.0 g. With further increasing the carrier gas flow rate, the aluminothermic reduction rate of magnesium oxide was not markedly increased, but the magnesium partial pressure was pronouncedly decreased. Therefore, the desulfurization of molten steel was inhibited and the desulfurization efficiency was decreased from the thermodynamic point of view.

On the other hand, the oxygen concentration is affected...
by the inclusions formed during the deoxidation process when the oxygen concentration is rather low. In our previous article, it was pointed out that the deoxidation efficiency is increased with decreasing the magnesium partial pressure through increasing the carrier gas flow rate. This is because some of the magnesium vapor leaves the metal surface without reacting with oxygen in the melt when the magnesium partial pressure is high. However, the inclusions formed during the deoxidation process is easily evolved into the melt at the larger carrier gas flow rate. As a result, the carrier gas flow rate did not affect the deoxidation results greatly under the present experimental conditions.

4.5. Effect of Addition of Lime on Desulfurization and Deoxidation

Figure 13 shows the changes in the sulfur and oxygen concentrations, and the desulfurization and deoxidation ratios with time, with and without addition of lime onto the melt surface. The porous magnesia immersion tube was used, the carrier gas flow rate was 1.7×10⁻³ m³/s, the temperature was 1 873 K, and the pellet mass was 2.0 g. It is seen that both desulfurization and deoxidation of molten steel were promoted with addition of lime. The reason of the improvement of desulfurization is that the desulfurization product of MgS can react with CaO to produce CaS and MgO, in which CaS has much higher stability than that of MgS. The improvement of deoxidation is perhaps because the inclusions produced in the deoxidation process are liable to adhere to the CaO phase on the melt surface, and thus the total oxygen concentration in the melt tends to be decreased. This should be further studied in the future.

By use of the dense alumina immersion tube, the effect of addition of lime on desulfurization and deoxidation was further studied, and the results are presented in Fig. 14. The experiments were conducted under the conditions of the carrier gas flow rate of 5.0×10⁻³ m³/s, the pellet mass of 3.0 g and the temperature of 1 873 K. With adding lime of 1.75 g onto the melt surface, the desulfurization was greatly promoted.

However, the desulfurization using the dense alumina tube was accompanied by resulfurization more significantly at the later stage than that using the porous magnesia tube. When the dense alumina immersion tube is used, the reaction of the dissolved magnesium in the melt with the alumina immersion tube can be described as

\[
\text{Al}_2\text{O}_3(s) + 3\text{Mg} = 3\text{MgO}(s) + 2\text{Al} \quad \text{...........(15)}
\]

It is also possible to form spinel according to

\[
4\text{Al}_2\text{O}_3(s) + 3\text{Mg} = 3(\text{MgO} \cdot \text{Al}_2\text{O}_3)(s) + 2\text{Al} \quad \text{...........(16)}
\]

Therefore the dissolved magnesium is liable to be consumed by the reaction with alumina immersion tube. The decomposition of the desulfurization product of MgS is therefore promoted and the resulfurization rate becomes fast in the case of the dense alumina immersion tube.

5. Conclusions

A new simultaneous desulfurization and deoxidation process of molten steel with magnesium vapor produced \textit{in situ} by aluminothermic reduction of magnesium oxide has been developed. Effects of initial oxygen and sulfur concentrations, pellet mass, argon carrier gas flow rate and addition of lime onto the melt surface on desulfurization and deoxidation were discussed. The main conclusions are drawn as follows:

(1) In the case of the high initial oxygen concentration, deoxidation preferentially proceeded, and desulfurization could not take place because the equilibrium oxygen concentration with magnesium vapor is much lower than the equilibrium sulfur concentration under the same experimental conditions. When the oxygen concentration was low enough, desulfurization of molten steel with the magnesium vapor did take place.

(2) Because increasing the initial sulfur concentration increased the desulfurization rate and ratio, the mass transfer of sulfur in molten steel is one of the rate-controlling steps for desulfurization. Since the magnesium concentration in the melt was strongly affected by the oxygen concentration in the melt, the dissolved magnesium concentration in molten steel was much lower than that in equilibrium with the sulfur concentration in the melt. Therefore desulfurization should take place on the bubble surface rather than in the melt. The obtained lowest sulfur concentration was close to the value in equilibrium with the magnesium partial pressure of 1.0×10⁵ Pa in the Mg–Ar bubble in the present experiment.

(3) Addition of more pellets into the immersion tube
improved desulfurization of molten steel because more magnesium vapor was produced. A little argon carrier gas promoted desulfurization of molten steel because aluminothermic reduction of magnesium oxide was promoted and the produced Mg vapor was smoothly injected into the melt. However, further increasing carrier gas flow rate decreased the desulfurization ratio because of decreasing the magnesium partial pressure in the bubble.

(4) Since MgS can react with CaO, and changes into CaS that is of the higher stability, in both the cases of the porous magnesia and the dense alumina immersion tubes, addition of lime onto the melt surface promoted desulfurization of molten steel. However, the desulfurization using the dense alumina tube was accompanied by resulfurization more significantly at the later stage than that using the porous magnesia tube. This is because the dissolved magnesium was consumed by the reaction with the dense alumina immersion tube, and decomposition of MgS was promoted.

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