The Effect of Magnesium Gas Injecting Conditions on the Rate of Hot Metal Desulfurization

Susumu MUKAWA,1) Yoshiyuki UESHIMA,1) Masamichi SANO,2) Jian YANG3) and Mamoru KUWABARA3)

2) Professor Emeritus, Nagoya University, Furo-cho, Chikusa-ku, Nagoya-city, Aichi 464-8601 Japan.
3) Department of Materials, Physics and Energy Engineering, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya-city, Aichi 464-8601 Japan.

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Possibility of high efficiency desulfurization of hot metal by magnesium gas was suggested from 350 g scale experiments in previous reports.1–4) The present study proves the possibility on the basis of 30 kg scale experiments. Combination of dilution of magnesium gas by argon gas and use of the injector which has 6 narrow exit holes allows to obtain magnesium efficiency of 74 % at a quantity of magnesium of 0.2 kg per ton hot metal at the initial sulfur content of 0.02 mass%.

KEY WORDS: hot metal treatment; desulfurization; magnesium.

1. Introduction

Hot metal pretreatment process is established as a key technology for mass production of high purity steel in Japanese mills. Recently, there are increasing needs for environmentally friendly processes. In steelmaking processes, reduction of slag and dust as well as recycle and treatment of these by-products are important subjects. Magnesium desulfurization of hot metal itself is a well known technology,5) but Yang et al.1–4) have shown a possibility of highly efficient magnesium desulfurization of hot metal as shown in Fig. 1. The important concept included in this diagram that to obtain high desulfurization efficiency, the partial pressure of magnesium in bubbles must be reduced to the optimum level to avoid loss of magnesium vapor released from the metal bath and/or dissolving into it without reacting with sulfur at the bubble–metal interface. The maximum efficiency may be derived from just balancing two mass transfer fluxes: mass transfer of sulfur in metal phase around bubbles, and mass transfer of magnesium in gas phase.

To prove the effectiveness of desulfurization using magnesium gas and to reveal the condition to increase efficiency at 30 kg scale furnace, experiments were performed, changing bubble formation size and dilution gas flow rate. Desulfurization with CaO base flux injection experiment were also done for comparison.

2. Experiments

The schema of experimental apparatus and the experimental conditions are shown in Fig. 2 and Table 1, respectively. Electrolytic iron was melted in a high frequency induction furnace under coexistence of graphite and a proper amount of sulfur. Metal bath temperature was maintained at

Fig. 1. Influence of magnesium content in bubble rising in hot metal bath, $N_{Mg}$, and sulfur content, [ppmS] on the efficiency of magnesium, $\eta_{Mg}$ ($d_b$: bubble diameter, $H_L$: depth of metal bath).

Fig. 2. Schematic view of experimental apparatus.
1350°C. The initial sulfur content of hot metal was 0.02%. The gas injectors used in this study are shown in Fig. 3. These are made of dense graphite.

Magnesia–aluminum pellets were used as the magnesium gas source. The pellets were made of magnesia and aluminum powders. These powders are mixed and pressed for 1 h at 150 MPa and formed in cylindrical shape of 1.5 mm diameter. These pellets produce magnesium gas in-situ by aluminothermic reactions.

\[
\begin{align*}
4\text{MgO (s)} & \rightarrow 3\text{Mg (g)} + \text{MgAl}_2\text{O}_4 (s) \quad (1) \\
3\text{MgAl}_2\text{O}_4 (s) & \rightarrow 2\text{Al (l)} + 3\text{Mg (g)} + 4\text{Al}_2\text{O}_3 (s) \quad (2)
\end{align*}
\]

As another magnesium gas source, magnesium powder having the average diameter of 0.5 mm was also used. The magnesium powder is used for hot metal desulfurization in practical operation in steel works.

After the hot-metal was melted and the temperature was stabilized, the graphite injector, in which the magnesia–aluminum pellets or the magnesium powder, was charged, was immersed after pre-heating the injector by keeping it just above the metal bath surface. Figure 4 shows the change in temperature of inner wall of the injector with time. The temperature was about 420°C before immersion. After immersion, the temperature rapidly reached bath temperature.

Hot metal samples for chemical analysis were taken by suction into quartz tube (4 mm diameter) at appropriate time intervals. In some experiments, a high speed video camera was used to measure the bubble size appearing at the bath surface.

3. Results and Discussion

3.1. Behavior of Sulfur and Magnesium

Figure 5 shows the change in sulfur content with time, when the magnesia–aluminum pellets were used as the magnesium gas source. When the 6 exit hole injector was used and the argon gas flow rate was increased and controlled, the desulfurization rate was higher and the sulfur content reached a lower level (●). Figure 6 shows the changes in sulfur content with time when the magnesia–aluminum pellets and the magnesium powder were used. In these experiments, the 6 exit hole injector was used. The initial rate of desulfurization was higher when the magnesium powder was used.

Desulfurization by CaO powder injection was performed for comparison. The results are shown in Fig. 7. It is seen that quite a large amount of CaO is needed to desulfurize the hot metal to a very low sulfur level.

Figure 8 shows the relationship between flux consumption and degree of desulfurization under various experimental conditions. The degree of desulfurization is defined as follows:

<table>
<thead>
<tr>
<th>Experimental conditions.</th>
</tr>
</thead>
<tbody>
<tr>
<td>hot metal amount</td>
</tr>
<tr>
<td>temperature</td>
</tr>
<tr>
<td>crucible</td>
</tr>
<tr>
<td>dia. of crucible</td>
</tr>
<tr>
<td>initial [%S]</td>
</tr>
</tbody>
</table>

Table 1. Experimental conditions.

<table>
<thead>
<tr>
<th>hole</th>
<th>material</th>
<th>amount</th>
<th>Ar flow rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>MgO+Al(3:2)</td>
<td>1.13kg/t</td>
<td>unchanged</td>
</tr>
<tr>
<td>1</td>
<td>MgO+Al (4:2)</td>
<td>2kg/t</td>
<td>1Nl/min</td>
</tr>
</tbody>
</table>

Fig. 3. Schematic view of graphite injectors.

Fig. 4. Change in temperature of injector inner wall with time.

Fig. 5. Change in sulfur content with time.

Fig. 6. Change in sulfur contents with time.
Degree of desulfurization

\[ \frac{[\%S_i] - [\%S_f]}{[\%S_i]} \times 100(\%) \quad \text{.........(3)} \]

\[ [\%S_i] : \text{ initial sulfur content (mass\%)} \]

\[ [\%S_f] : \text{ final sulfur content (mass\%)} \]

In the experiment with using the magnesium powder and the 6 exit hole injector and changing the argon gas flow rate, only 0.2 kg/t magnesium was needed to obtain a degree of desulfurization of 80%.

In Fig. 9, the relationship between magnesium and sulfur content during treatment are shown. At the early stage of treatment, magnesium content remained low. At the middle stage, the highest magnesium content was attained and the sulfur content was decreased. At the later stage, the magnesium content was decreased and the sulfur content tended to increase, so that the re-sulfurization reaction occurred. Finally, the relationship approached the equilibrium.\(^6\)

### 3.2. Magnesium Efficiency

Figure 10 shows the material balance of magnesium. The total amount of magnesium is calculated using the pellet mass changed in the graphite injector. The amount of magnesium, contributing to the desulfurization, is calculated from Eq. (4) on the assumption of reaction (5).

\[ W_{\text{Mg}}^{(s)} = \Delta[\%S] \times M_{\text{Mg}} / M_S \times W_m / 100 \quad \text{.........(4)} \]

\[ \Delta[\%S] = [\%S_i] - [\%S_f] \]

\[ M_{\text{Mg}}, M_S \]: magnesium and sulfur molecular weight (g/mol)

\[ W_m \]: weight of hot metal (g)

\[ \text{Mg} + \text{S} = \text{MgS} \quad \text{.........(5)} \]

The amount of magnesium remaining in hot metal was calculated from the magnesium content of the melt. The amount of magnesium, remaining in the graphite injector was calculated from analysis of remaining pellets and mass balance of aluminum and magnesia.

At the low argon gas flow rate of 1 NL/min, a large amount of magnesium seems to be released from the bath as magnesium gas. Under the condition of increased and controlled argon gas flow rate, the amount of magnesium, which contributed to the desulfurization, was almost the same as the above case of a lower and constant argon gas flow rate, in spite of the small total amount of pellets. In the case of magnesium powder, none of the magnesium remained in the graphite injector. The desulfurization efficiency of magnesium is shown in Fig. 11. In this report, two kinds of definitions of desulfurization efficiency of magnesium are used: The over-all desulfurization efficiency of magnesium, \( \eta_{\text{S,Mg,ov}} \), is defined as

\[ \eta_{\text{S,Mg,ov}} = \text{Mg used for desulfurization (g)} / \text{Total Mg in the charged pellets or magnesium (g)} \]

and the desulfurization efficiency of generated Mg gas, \( \eta_{\text{S,Mg}} \), is defined as

\[ \eta_{\text{S,Mg}} = \text{Mg used for desulfurization (g)} / \text{Amount of generated Mg gas (g)} \]

The overall desulfurization efficiency of magnesium reached 74%, when the magnesium powder and the 6 exit
3.3. Investigation of Bubble

Figure 12 shows one shot of high speed video images, taken during the experiment under the condition of argon gas flow rate of 1 NL/min and using the 6 exit hole injector. In this case, the bubble diameter at the bath surface was about 10 mm.

At a higher gas flow rate, the bubble size could not be determined owing to successive arrival, accumulation and rupture of bubbles at the bath surface. Therefore, water model experiments were performed to observe the behavior of bubble formation.

In the case of one exit hole injector, diameters of bubbles are about 50 mm at an argon gas flow rate of 1 NL/min. With increased gas flow rate of 10 NL/min, larger bubbles were formed and dispersed in a narrow region. In the case of the 6 exit hole injector, smaller bubbles were observed and dispersed widely even at the increased gas flow rate.

3.4. Evaluation of the Effect of Bubble Size and Argon Gas Flow Rate

A evaluation by a model calculation to estimate the effect of bubble diameter reduction and argon gas flow rate. Considering both mass transfer of sulfur in hot metal side and magnesium in gas phase, the rate of desulfurization reaction may be described as Eq. (6), assuming the equilibrium at the interface, and $\alpha_{MgS}=1$, as shown Eq. (7).

$$n_s = k_m A (\%S) - \%S \frac{P_m}{100M_s}$$

$$E_s = 1/(\%S) \frac{P_{Mg*}}{RT}$$

$$K = \exp(-\Delta G^*/RT)$$

$$\Delta G^* = -414636 + 174.55T \quad (J/mol) \quad (9)$$

$K$ is an equilibrium constant of reaction (5). The mass transfer coefficients are expressed as Eqs. (9) and (10).

$$k_m = 2(D_s/\pi r)^{1/2}$$

$$k_g = 2(D_g/\pi r)^{1/2}$$

$$\tau = \frac{d_B}{V_m}$$

$$V_m = (g d_B/2)^{1/2}$$

$D_s$ was estimated as $3 \times 10^{-5}$ (m$^2$/s) at 1350°C from the literature. $D_g$ is estimated by Chapman–Enskog’s method.

These equations are numerically solved for one bubble floating from the position of injection to free surface position by 4th-order Lunge–Kutta method. Change in sulfur content of hot metal is calculated from Eq. (13). Reaction during the bubble formation and resulfurization by MgS decomposition at the bath surface were not considered.

$$-d(\%S)/dt = f_B \frac{A_{n_s} 100 M_s}{W_m}$$

The diameter of bubble at a formation was estimated by Eq. (14). In these calculations, $\sigma$ and $\theta$ is assumed to be 1.5 N/m$^2$ and 135$^{\circ}$ respectively, and inner nozzle diameter was used as $d_{no}$ in Eq. (14). When a 6 exit hole injector was used, $N_c$ is 27 and $d_B=0.011$ cm is obtained at 1 NL/min and showed a good agreement with the result shown in Sec. 3.3. In contrast, when a 1 exit hole injector was used, $N_c$ is less than unity.

$$d_B = \left[ (\alpha \sigma d_{no}/\rho g)^2 + 0.241 (V_g^2 d_{no})^{0.867} \right]^{1/6}$$

$\alpha=6$ ($N_c<1$), $\alpha=6N_c$ ($1<N_c<9$), $\alpha=55$ ($N_c>9$)
The calculated and the experimental results showed a good agreement as experiment, was shown by the thick solid line. From these results, both calculated results, assuming another conditions are shown. From Fig. 9, maximum magnesium content in hot metal was attained at 4 min after start of treatment.

In Fig. 14, an experimental result and calculated results for four cases are shown. The experimental result was shown by open circle. A calculated result, assuming same condition as experiment, was shown by the thick solid line. The calculated and the experimental results showed a good agreement, although there was no fitting parameter. The calculated results, assuming another conditions are shown with dotted, broken and thin line. From these results, both conditions for smaller bubble formation and dilution of magnesium gas by argon gas have considerable effect on the rate of desulfurization.

Fig. 14. Change in sulfur content with time. Comparison of the experimental result and calculated results of 4 cases.

\[ N_c = 4V_r \Delta p g \sin \theta \pi d_w^2 (P_0 + p_m \theta h) \] \hspace{1cm} (15)

All the magnesium was assumed to vaporize at a constant rate during initial 4 min. From Fig. 4, only after 1 min, temperature exceed 1,100°C, which means vapor pressure of magnesium exceed 1.01325 \times 10^5 Pa. Moreover, from Fig. 9, maximum magnesium content in hot metal was attained by increasing the flow rate of argon carrier gas.

4. Conclusion

30 kg scale experiment were performed to examine the conditions of efficient desulfurization of hot metal with magnesium, the source of which was magnesia–aluminum pellets or magnesium powder.

Main results obtained through this study were as follows:

(1) The desulfurization efficiency of magnesium as high as 74% was obtained when the 6 exit hole injector was used and the carrier gas flow rate was increased and controlled.

(2) This high desulfurization efficiency was attributed to the effect of smaller bubble formation or dilution of magnesium partial pressure in the bubble, which was attained by increasing the flow rate of argon carrier gas.

(3) When the magnesia–aluminum pellet was used as magnesium gas source, the argon carrier gas contributed to promote desulfurization reaction in two ways. One is decreasing the magnesium partial pressure in the bubble and the other is enhancing the MgO reduction.

(4) Using magnesium gas, the possibility that the slag quantity can be substantially reduced compared with the CaO base flux, was shown.

REFERENCES