Sulfur Distribution Features in Metal-Slag-Gas System during Hot Metal Desulfurization with Magnesium

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ABSTRACT

A solid magnesium sulfide is formed during magnesium desulfurization of molten metal. Iron and slag structure X-ray structural analysis showed that the only one sulfide – MgS – is presented in the metal as the inclusion and is absent in ladle slag. The sulfur in the slag is mainly associated with Ca and Mn. The mechanism of formation of MnS, and CaS is thermodynamically substantiated. The ejection of the reaction product – MgS from the ladle by upward streams is considered to be a characteristic feature of the hot metal desulfurization with magnesium.

In order to clarify the mechanism of interfacial distribution and determine the balance of sulfur, the data from the full-scale experiments of magnesium desulfurization was used. While making up the sulfur balance, in addition to elements transfer from metal into the slag, the impact of the following factors was taken into the account – the change of molten metal mass in the ladle due to iron oxidation and generation the metal droplets in the slag, as well as the increase of dissolved sulfur in the iron droplets.

The calculated results are in good agreement with experimental data of the quantity of sulfur loss by upward streams. In some experiments, the amount of dissolved sulfur in the droplets has exceeded those in the slag. The dependence of sulfur loss degree from the slag amount was determined.

Introduction

Solid magnesium sulfide (T_m = 2500 K [1]) rising to the surface of the metal–slag separation is the product of hot metal desulphurization with magnesium. Various authors suggest [2, 3, 4] that magnesium sulfide is almost insoluble in hot metal. The conditions for evacuation of liquid melts of solid reaction products are determined with the physical properties (density, viscosity etc.) of the melt as well as with wettability of particles with liquid melt. It is generally recognized [4, 5] that iron-carbon melts wet the refractory materials rather poor that may be an indirect evidence of insufficient wettability of MgS with hot metal. MgS emerging in the form of liquid melt does not enter into interaction. As the authors [6] mention, only magnesium sulfide was detected in the metal as non-metal inclusion during the X-ray structure analysis of synthetic iron upon its refining with magnesium. The concentration of MgS in the melt was calculated at the level of 5·10^{-5}\% with the size of inclusion being 1.5 μm. The authors [7] confirm the occurrence of MgS in liquid melt, in which case they estimate the size of the particles to be about 1 μm.

MgS ejecting to the sub-slag layer is not absorbed by the slag. The authors [8, 9] obtained the results of experimental studies of the structure of slags formed in the ladle during hot metal desulfurization with magnesium, that prove that the ladle slag contains no MgS. Sulfur is mainly bound with Ca and Mn.

Several authors [10, 11] note that a characteristic feature of hot metal desulfurization with magnesium is the blowout of reaction product – MgS with powder-gas flows – from metal. As the analysis of waste gases has shown [7, 12] there are almost no sulfur-containing gases. Sulfur occurs
in the upward streams mainly in the form of small solid particles of MgS. The calculations of amount of S, issued with blown out with the upward-flowing gases, performed by different authors [11, 14, 15], confirmed that the amount of sulfur blown out was significant and made up to ¾ of the whole amount blown out from metal. However, when making up the sulfur balance, the authors did not take into account such significant indicators as variation of hot metal mass in the ladle related to iron oxidation to oxides and formation of metal droplets in the slag. Whereas, according to available data [13], upon refining half the slag may consist of metal droplets with a high sulfur content in them. The purpose of the present work is to adjust the mechanism of interphase distribution and determination of sulfur balance in actual industrial practice.

**Experimental**

Data of experimental treatments (i = 1÷8) of hot metal with magnesium in the factories of China were used. During the experiments the samples of metal and slag with metal droplets were taken from the ladle before and after the desulfurization of hot metal with magnesium. The samples of metal droplets were taken from the slag and dissolved in 6 fractions (j = 1÷6). The content of the elements in metal and slag phases were determined by chemical analyses.

In the course of this work the microstructure of hot metal samples after refining as well as the ladle slags before and after desulfurization with magnesium was studied. The analysis of the structure of samples of desulfurized hot metal was performed by methods of optical and scanning electronic microscopy respectively with the use of Aksiovert 200MMAT and РЭМ 106I devices. Details of the experimental method, research facilities and chemical analyses are given in the previous article [16].

**Results and Discussion**

Non-metallic inclusions formed in the samples of desulfurized hot metal have a size of about 2 μm (Fig. 1, a) that is consistent with the data provided by authors [6, 7]. The ratio of concentrations detected in the inclusions of the elements proves that non-metallic inclusions formed mainly consist of magnesium sulfide (MgS) (Fig. 1, b,c).

The analysis of slags upon desulfurization of hot metal with magnesium was performed by way of point probe scanning along the linear route sweat ball – slag - sweat ball (Fig. 2). The areas corresponding to typical composition of the ladle slag CaO - SiO₂ - Al₂O₃ – MgO with variable ratio of components along the route of the probe advancement can be observed in the slag phase. Sulfur in the slag phase is mainly contained in the form of MnS, rarely – in the form of (Ca Mn)S, sulfur content along the route makes 2%. In certain areas the sulfur content reaches so much as 12-16%. On the probing route the areas representing alloys of Ca, Si, Al, Mg with different ratio of components and sulfur content of 2-4% can be observed. The obtained experimental data on non-metallic inclusions in metal and composition of ladle slag during out-of-furnace refining of hot metal with magnesium correspond to studies reported in literature [6, 7, 8]. The availability of magnesium sulfide particles in liquid metal melt proves that sulfur in hot metal interacts with gaseous or dissolved magnesium in reaction:

\[
[Mg] + [S] = MgS_s
\]  

(1)

Low density [10] and poor wettability of solid particles of magnesium sulfide allows them not only to “emerge” in metal bulk, but also to partially transfer into the coal-gas phase, breaking away from the surface of the liquid melt. Absence of MgS in the slag can be explained by occurrence of the following chemical reactions. Thus, at the metal-slag boundary – MgSs – the substitution reaction
may take place with CaS being formed:

\[ \text{MgS}_s + (\text{CaO}) = (\text{MgO}) + (\text{CaS}) \]  

(2)

Fig. 1 Non–metallic inclusions in the hot metal sample after magnesium desulfurization (a) and characteristic X-ray spectra corresponding to the NI (b) and (c).

or reaction with involvement of manganese dissolved in hot metal and slag components:

\[ \text{MgS}_s + (\text{SiO}_2) + (\text{FeO}) + [\text{Mn}] = (\text{MgO} \cdot \text{SiO}_2) + (\text{MnS}) + [\text{Fe}] \]  

(3)

\[ \text{MgS}_s + (\text{SiO}_2) + (\text{CaO}) + (\text{FeO}) + [\text{Mn}] = (\text{CaO} \cdot \text{MgO} \cdot \text{SiO}_2) + (\text{MnS}) + [\text{Fe}] \]  

(4)

The refractory compounds such as forsterite (MgO•SiO$_2$) or montichelte (CaO•MgO•SiO$_2$) [10] shift the reaction equilibrium in forward direction.

**Interfacial Balance of Sulfur**

It was offered to calculate the sulfur balance in order to determine the amount of sulfur blown out from the ladle. As the mentioned balance was being made up, not only the transfer of elements from
slag into metal was taken into account, but also the influence of such indicators as hot metal mass variation in the ladle related to iron oxidation and formation of metal droplets in the slag as well as increase of amount of sulfur dissolved in metal droplets. Due to the differences in volume of hot
Mn,%

Fig. 3 Changes in the elements composition in the slag after the ladle desulfurization defined by means of point scanning probe along the route F – G.
metal in the ladle \((Q_{\text{lad}})\) the calculation was performed in terms of a single ton of hot metal. The total amount of sulfur in the ladle before desulfurization \((Q_{\Sigma S,MG})\) and after desulfurization of hot metal with magnesium \((Q_{\Sigma S,MG})\) was compared for the purpose of determination of amount of sulfur lost with the wasted coal-gas stream.

The mass of sulfur in the ladle before desulfurization of hot metal was determined from the formula:

\[
Q_{\Sigma S} = Q_{\Sigma S,b} + Q_{\Sigma S,sl} + Q_{\Sigma S,hm},
\]

where \(Q_{\Sigma S,md}\) – total mass of sulfur in metal droplets;
\(Q_{\Sigma S,sl}\) – total mass of sulfur in slag;
\(Q_{\Sigma S,hm}\) – total mass of sulfur in hot metal including the adjustment of its mass.

Total mass of sulfur in metal droplets – \(Q_{\Sigma S,md}\) – is determined from the formula:

\[
Q_{\Sigma S,b} = Q_{hm} \times W_{sl,b} \times \sum_{j=1}^{\infty} W_{b,j} \times W_{s,b,j,}\ldots
\]

where \(Q_{hm}\) – mass of hot metal in the ladle, t;
\(W_{sl,md}\) – fraction with the metal droplets against the hot metal mass;
\(W_{md,j}\) – fraction of the metal droplets in the \(j\) fraction in \(W_{sl,b}\);
\(W_{s,md,j}\) – fraction of sulfur in the metal droplets of the \(j\) fraction.

Total amount of sulfur in the slag is determined from the equation:

\[
Q_{\Sigma S,sl} = Q_{hm} \times W_{sl,md} \times W_{s,sl},
\]

where \(W_{s,sl}\) – fraction of sulfur in the slag with metal droplets equal to \((1-W_{md})\).

To determine the total amount of sulfur in hot metal it is necessary to determine the mass of metal in the ladle first and to adjust it with due account of part of metal that transferred into the slag as oxides of iron and metal droplets from the below equation:

\[
Q_{hm}' = Q_{hm} - Q_{Fe,sl} - Q_{md}
\]

where \(Q_{hm}\) – basic mass of hot metal in the ladle;
\(Q_{Fe,sl}\) – amount of iron that transferred into the slag as oxides;
\(Q_{md}\) – amount of iron that transferred into the slag as the metal droplets.

The amount of hot iron being oxidized and transferred into the slag as iron oxides FeO and \(Fe_2O_3\) - \(Q_{Fe,sl}\) is determined from the below equation:

\[
Q_{Fe,sl} = Q_{sl,md} \times W_{sl} \times \left(\frac{(W_{FeO,sl} - W_{FeO,furn,sl}) \times X_{Fe}}{M_{FeO}} + W_{Fe_2O_3,sl} \times \frac{2X_{Fe}}{M_{Fe_2O_3}}\right)
\]
where \( W_{FeO,sl} \), \( W_{FeO,furn,sl} \) – fraction of FeO in the experimental and in the furnace slag respectively;
\( W_{FeO_{2},sl} \) – fraction of Fe\(_2\)O\(_3\) in the slag of certain sample;
\( W_{sl} \) – slag fraction in the slag with metal droplets;
\( X_{Fe} \) – atomic mass of iron,
\( M_{FeO} \), \( M_{Fe_{2}O_{3}} \) – molecular mass of FeO and Fe\(_2\)O\(_3\), respectively.

The mass of iron that transfers from the hot metal into the metal droplets is calculated from the equation:

\[
Q_{md} = Q_{sl,b,i} \times W_{md}
\]  

where \( W_{md} \) – fraction of metal droplets in the slag with metal droplets. Thus, upon calculation of final mass of hot metal from the equation (8) the concentration of sulfur in it is determined:

\[
Q_{\Sigma s,hm} = Q'_{hm} \times W_{s,hm}
\]  

where \( W_{s,hm} \) - fraction of sulfur in hot metal.

In the same way the total amount of sulfur in the ladle upon desulfurization with magnesium is determined:

\[
Q_{\Sigma s,Mg} = Q_{\Sigma s,md,Mg} + Q_{\Sigma s,sl,Mg} + Q_{\Sigma s,hm,Mg}
\]

where \( Q_{\Sigma s,md,Mg} \) – total amount of sulfur in the metal droplets upon desulfurization;
\( Q_{\Sigma s,sl,Mg} \) – total amount of sulfur in the slag upon desulfurization;
\( Q_{\Sigma s,hm,Mg} \) – total amount of sulfur in hot iron upon desulfurization with due account of its mass adjustment.

The specific mass value is to be used for the purpose of correct comparison of total amount of sulfur in the ladle before and after desulfurization, that means the mass of sulfur per one ton of hot metal shall be determined:

\[
\begin{align*}
W_{\Sigma S} &= \frac{Q_{\Sigma S}}{Q_{hm}} & \text{after treatment} \\
W_{\Sigma S,Mg} &= \frac{Q_{\Sigma S,Mg}}{Q_{hm,Mg}}
\end{align*}
\]

In case the correlation value of total specific amount of sulfur in the ladle before and after hot metal desulfurization with magnesium does not exceed one \(\frac{W_{\Sigma S,Mg}}{W_{\Sigma S}} < 1\), the part of sulfur is therefore released from the ladle with the upward streams. In such a case the concentration of sulfur released to the gas phase for certain experiment shall make:

\[
\Delta S_i = (1 - \frac{W_{\Sigma S,Mg}}{W_{\Sigma S}}) \times 100\%
\]

The results of calculation shall be fixed in the Table.

When analyzing the table it should be noted that in spite of the different capacity of ladles in every single sample, sulfur mass as per ton of hot metal were slightly different.

According to the table data the concentration of sulfur blown released from the ladle with the gas for every experiment is calculated. Mass fraction of every experiment is taken into account. The calculation is performed according to the below formula:

\[
\Delta S_s = \sum_{i=1}^{8} \Delta S_i \times W_{mass,i}
\]

where \( W_{mass} \) – mass fraction.
The average value makes 50.02%. Thus, the reduction of sulfur mass in the content of ladles after desulfurization reaches half of its initial value. As it follows from the analysis of the study results (Table), the reduction of slag mass upon treatment of hot metal with magnesium slightly increases the concentration of sulfur released with the waste gases. The highest value of 66.5% corresponds to the minimum amount of slag of 0.12%. The calculations performed comply with the experimental data on amount of sulfur released with the upward streams [15].
<table>
<thead>
<tr>
<th>Experiment (i)</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass of hot metal in the ladle $Q_i$, t</td>
<td>140</td>
<td>59</td>
<td>50</td>
<td>58</td>
<td>45</td>
<td>45</td>
<td>46</td>
<td>46</td>
</tr>
<tr>
<td>Mass fraction of experiment(i) $W_{mass,i} = \frac{q_i}{\sum_{i=1}^{8} q_i}$, fractions of unity</td>
<td>0,2863</td>
<td>0,1207</td>
<td>0,1022</td>
<td>0,1186</td>
<td>0,0920</td>
<td>0,0970</td>
<td>0,0941</td>
<td>0,0941</td>
</tr>
<tr>
<td>The ratio of slag mass to hot metal mass, mass%</td>
<td>2,85</td>
<td>1,21</td>
<td>0,72</td>
<td>0,49</td>
<td>0,49</td>
<td>0,49</td>
<td>0,12</td>
<td>2,44</td>
</tr>
<tr>
<td>Mass of S in the ladle before treatment $Q_{\Sigma S} \times 10^4$, t</td>
<td>528,76</td>
<td>136,498</td>
<td>111,070</td>
<td>227,19</td>
<td>90,822</td>
<td>177,619</td>
<td>147,489</td>
<td>218,918</td>
</tr>
<tr>
<td>S specific gravity (per ton of hot metal) before treatment $Q_{\Sigma S} \times 10^{-4}$, t</td>
<td>3,7769</td>
<td>2,3135</td>
<td>2,2214</td>
<td>3,9171</td>
<td>2,0183</td>
<td>3,9471</td>
<td>3,2063</td>
<td>4,7591</td>
</tr>
<tr>
<td>Mass of S in the ladle after treatment $Q_{\Sigma S,Mg} \times 10^4$, t</td>
<td>229,851</td>
<td>60,203</td>
<td>63,091</td>
<td>89,720</td>
<td>44,926</td>
<td>137,860</td>
<td>49,3874</td>
<td>160,160</td>
</tr>
<tr>
<td>S specific gravity (per ton of hot metal) after treatment $Q_{\Sigma S,Mg} \times 10^4$</td>
<td>1,6418</td>
<td>1,0204</td>
<td>1,2618</td>
<td>1,5469</td>
<td>0,9984</td>
<td>3,0636</td>
<td>1,0736</td>
<td>3,4817</td>
</tr>
<tr>
<td>Mass of blown out S (per 1 ton of hot metal) from the ladle $\Delta Q_{\Sigma S} \times 10^4$, t</td>
<td>-2,1351</td>
<td>-1,2931</td>
<td>-0,9596</td>
<td>-2,3702</td>
<td>-1,0199</td>
<td>-0,8835</td>
<td>-2,1327</td>
<td>-1,2774</td>
</tr>
<tr>
<td>Sulfur masses ratio after and before treatment $\frac{Q_{\Sigma S,Mg}}{Q_{S}}$, fractions of unity</td>
<td>0,4347</td>
<td>0,4411</td>
<td>0,5680</td>
<td>0,3949</td>
<td>0,4947</td>
<td>0,7762</td>
<td>0,3349</td>
<td>0,7316</td>
</tr>
<tr>
<td>Sulfur amount blown out from the ladle $\Delta S_i$, mass% -</td>
<td>56,53</td>
<td>55,89</td>
<td>43,20</td>
<td>60,51</td>
<td>50,53</td>
<td>22,38</td>
<td>66,51</td>
<td>26,84</td>
</tr>
</tbody>
</table>
Conclusion

Using methods of optical and scanning electron microscopy, the microstructure of hot metal and slag samples after desulfurization with magnesium was studied. Magnesium sulfide particles of about 2 μm were detected in the samples of desulfurized hot metal. The analysis of slag has shown that these particles are considerable heterogeneity. Sulfur in the slag was found in the form of magnesium sulfide and a compound (CaMnS).

The sulfur balance in metal-slag-gas system was calculated. Taking into account the features of production experiments, while building a model the following factors were considered:
- the change in hot metal mass in the ladle, connected with the oxidation of iron to oxides and the formation of metal droplets in the slag;
- substantial change of sulfur in the droplets, caused by the resulfurization process.

According to calculation, on the average the half of the sulfur amount removed from hot metal is blown by gas flow out from the ladle. With a minimal amount of the slag in the ladle, the maximum amount of blown out sulfur was received – 66.5%. While conducting other experiments, a clear dependence of this parameter on the slag amount was not found.

Thus, the calculated data and results of laboratory research lead to a better understanding of the phenomena of sulfur interfacial distribution during hot metal ladle treatment.

References


