Possibility of Hot Metal Re-Sulfurization During the Waiting Time in the Transfer Ladle

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Abstract

The investigation on the possibility of hot metal re-sulfurization during the waiting time in the transfer ladle before the BOF was carried out. According to the results, the slag was no longer a pure liquid, and different solid phases were found distributed within the slag along with small portion of liquid slag. Almost all the sulfur was found in the solid phase in the form of CaS, which is only a small fraction of slag. On the other hand, the hot metal was found to have a limited contact with the solid CaS and liquid slag which led to a very poor kinetics for re-sulfurization. Therefore, the amount of re-sulfurization in the transfer ladle was found to be very low.

Keywords

Sulfur, re-sulfurization, hot metal, calcium sulfide, calcium oxide
1 Introduction

Hot metal desulfurization is one of the most important processes in iron- and steelmaking. Several studies on the desulfurization of hot metal have been carried out by various researchers. Sulfur is a harmful impurity for steel since it strongly affects the mechanical properties and must be removed from the hot metal, except in some very specific grades. A lot of focus has been put on the hot metal desulfurization to reduce materials and energy costs before the converter. Sulfur removal from the hot metal usually starts in the blast furnace where about 90% of the total sulfur input is from coke. The remaining sulfur in the hot metal is too high for the requirements of the steel plant and additional external pretreatments are employed to further reduce the sulfur level. Such pretreatments include the injection of desulfurization agents into the torpedo ladle car or into the open ladle and the addition of desulfurization agents into the open ladle using the KR impeller stirring system. In the case of the torpedo car, the desulfurization occurs by immersing the refractory lance deeply into the hot metal while the reagents are injected at high speed using nitrogen as transport gas. Among others, calcium carbide-based reagent is commonly used due to its higher performance. After the desulfurization has finished in the torpedo, the hot metal and slag are transferred to the transfer ladle to send the liquid metal to the converter after slag removal. It often happens that the ladle is forced to wait for a long period of time because either the converter is busy or for other process reasons. In practice, despite the ladle being open to the atmosphere (leading to a contact of the melt with air that may promote an increase of oxygen potential) and experiencing a temperature drop. In such unfavorable conditions, the main concern is whether sulfur would go back to hot metal. The lack of studies in this specific case suggests the need of a systematic study. The present work aims at fulfilling this need and investigating whether sulfur would go back to the hot metal during the waiting time.

2 Industrial Trials

Hot metal desulfurization usually starts in the blast furnace as already stated, and after the process has finished the hot metal is tapped and then transferred into the torpedo car. The mass of hot metal in the torpedo may vary between 280 to 320 ton. Since the content of sulfur in the hot metal (about 0.050 mass%) is still high to satisfy the requirements of the steel plant, additional desulfurization processes before the converter are needed. At SSAB-Oxelösund, the desulfurization of hot metal takes place in the torpedo car by using CaC₂ as a desulfurization agent. The lance is immersed through the opening in the middle of the torpedo and the desulfurization agent is injected along with nitrogen as carrier gas, which also promotes turbulence in the melt. The solid flow rate is about 48-54 kg/min. Before the desulfurization starts the amount of hot metal, the content of sulfur in the hot metal and the hot metal temperature must be measured, since these factors determine the amount of desulfurization agent to be injected. In addition, all these parameters together with the desired final sulfur content in the hot metal will determine the necessary blowing time. The final sulfur content in the melt is usually below 50 ppm. After the desulfurization is complete the hot metal is poured into transfer ladle, which has the capacity of approximately 200 ton. The
pouring of hot metal from the torpedo into the transfer ladle is done carefully to minimize the amount of slag following the hot metal. The ladle is not fully filled and approximately 155-170 ton of hot metal are transferred, while the rest is kept in the torpedo. Usually the remaining hot metal is not enough for the next ladle and has to wait long time for the next torpedo (about 90 min in full operation). During the waiting time, the temperature decreases significantly. Before the hot metal in the transfer ladle is slag-skimmed and charged into the converter, an additional hot metal sample and temperature measurement are taken.

As mentioned previously, the converter may be busy due to different process reasons and the hot metal in the transfer ladle is forced to wait for long time. In the present study the sampling of hot metal and slag took place while the transfer ladle was in this waiting stage, and three charges were assessed. Prior to each sampling, the transfer ladle was tilted for a better access of the samples. Samples were taken approximately once every 7 min, and a temperature probe was used for the temperature measurement. The sampler was immersed into transfer ladle for about 30 s to collect the hot metal, and then the hot metal sample was detached from the sampler after cooling to ambient temperature. Samples were then sent for chemical analysis. A steel scoop was employed for slag sampling and the slag was also sent for chemical analysis after cooling to ambient temperature. The sulfur contents in both slag and hot metal were analyzed by the combustion method (LECO analyzer-ASTM E1019). X-ray fluorescence (XRF) was used to analyze the final composition of slag and hot metal. Some slags were prepared and polished with a grit paper to investigate the slag structure by using a Hitachi S-3700 scanning electron microscope equipped with energy dispersive X-ray spectroscopy (EDS).

3 Results

As mentioned previously, the sampling of slags and hot metals along with temperature measurements were carried out in the transfer ladle and the results are presented in table 1. During the waiting time, the temperature decreases substantially as can be seen in the table 1 for charge 2, which is the result of a mix of two torpedoes. The contents of sulfur and hot metal temperature after the desulfurization has finished in the torpedo are also included in the table. Analysis of the hot metal indicates that the content of sulfur is almost constant in all accessed charges, whilst in the slag the content of sulfur exhibits substantial fluctuation. The slag analyses were found to be inconsistent and unreliable and so are excluded in the Table.

The morphology of slags was investigated, and the results are presented in Figure 1 and 1-C. The results show the presence of different solid phases distributed within the slag and small portion of the liquid phase. The solid phases found have been identified to be CaS, Ca$_2$SiO$_4$, CaO. Iron droplets are also found in the sample. The fraction of liquid slag is relatively small. Moreover, in some regions of slag from charge 2(B), only CaO was found and no trace of sulfur was detected as can be seen in Figure 1-C. Element mapings of slags from Charge 1 (A) and charge 2 (B) are presented in Figures 2 and 3, respectively.
Table 1. Chemical analysis of hot metal and slag collected at SSAB, Oxelösund, in the transfer ladle as well as the temperature measurement of hot metal.

<table>
<thead>
<tr>
<th>Charge</th>
<th>Time [min]</th>
<th>HM composition</th>
<th>Sulfur [mass %]</th>
<th>Temp. [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Torpedo-1</td>
<td>-</td>
<td>4.53 0.54 0.039</td>
<td>0.010 3.05</td>
<td>1351</td>
</tr>
<tr>
<td>Ladle-1</td>
<td>0</td>
<td>-   0.54 0.04</td>
<td>0.002 2.28</td>
<td>1351</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>-   0.53 0.038</td>
<td>0.002 1.90</td>
<td>1348</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>-   0.55 0.037</td>
<td>0.006 3.06</td>
<td>1346</td>
</tr>
<tr>
<td></td>
<td>21</td>
<td>-   0.54 0.039</td>
<td>0.002 1.93</td>
<td>1344</td>
</tr>
<tr>
<td>Charge-2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Torpedo-2</td>
<td>-</td>
<td>4.44 0.49 0.038</td>
<td>0.019 1.88</td>
<td>1271</td>
</tr>
<tr>
<td>Ladle - 2</td>
<td>0</td>
<td>-   0.50 0.036</td>
<td>0.002 1.60</td>
<td>1271</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>-   0.517 0.037</td>
<td>0.002 1.92</td>
<td>1266</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>-   0.479 0.037</td>
<td>0.002 1.85</td>
<td>1265</td>
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<tr>
<td></td>
<td>21</td>
<td>-   0.504 0.039</td>
<td>0.002 1.66</td>
<td>1254</td>
</tr>
<tr>
<td>Charge -3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Torpedo-3</td>
<td>-</td>
<td>4.62 0.66 0.039</td>
<td>0.012 1.49</td>
<td>1344</td>
</tr>
<tr>
<td>Ladle-3</td>
<td>0</td>
<td>-   0.65 0.038</td>
<td>0.003 2.48</td>
<td>1344</td>
</tr>
</tbody>
</table>

Figure 1. Phases present in the slag from charge 1 (A) and charge 2 (B).

Figure 1-C. Presence of CaO in the slag from charge 2 (B).
Figure 2. Element mapping of slag from charge 1.

Figure 3. Element mapping of slag from charge 2 (B).
4 Discussion

As stated previously, the compositions of slags were analyzed, found to be inconsistent and are therefore not included in the table. The reason of inconsistency of the slag analysis and the trend of sulfur could be explained from the slag morphology (Figure 1). According to the results, slag is no longer molten and different solid phases were found distributed within the slag along with a small portion of liquid slag. Sulfur was found in the solid phase and is not uniformly distributed within the slag as can also be seen from element mapping (Figures 2 and 3). As an example, the morphology of some areas of the slag from charge 2(B) was investigated, only CaO was present (Figure 1-C). The presence of CaO could be explained by the oxidation of the remained CaC\textsubscript{2} in the slag which is injected in excess during the desulfurization in the torpedo car. Sampling was performed at different times and positions, which may also contribute to inconsistency in the results of the slag analysis. A significant number of iron droplets were found in the slag which could also contribute on the inconsistency of the slag analysis. Thus, although the effect of FeO on the hot metal desulfurization will not be addressed in the present study, it worthwhile to mention that its presence in the slag would slightly increase the oxygen potential at the interface between the slag and hot metal.\textsuperscript{[10, 12]}

In the present work, the possible re-sulfurization of hot metal in the transfer ladle during the waiting time was investigated. During the waiting time, it was expected that sulfur would go back to the hot metal due to the decrease in temperature and a possible increase in oxygen potential (the ladle is in contact with air, although the hot metal is protected by a thin layer of slag on top, which restricts the increase), according to equation (3). Rath and Hüsken,\textsuperscript{[18]} claimed that when the hot metal is in contact with air, re-sulfurization will take place.

\begin{equation}
\frac{1}{2}O_{2(\text{gas})} + S_{\text{metal}} \rightarrow \frac{1}{2}S_{2(\text{gas})} + O_{\text{metal}}
\end{equation}

\begin{equation}
\log K_1 = -\frac{935}{T} + 1.375 \quad [1, 20, 21]
\end{equation}

\begin{equation}
L_s = \frac{C_s \times f_s \times K_1}{a_o}
\end{equation}

In addition, the amount of sulfur expected in the slag decreases as the temperature drops. This, along with the increase in oxygen potential is expected to lead to re-sulfurization, according to equation (3). In practice, although the oxygen potential could be somewhat increased, and the temperature of the melt had decreased significantly (especially for charge 2), the level of sulfur in the hot metal did not increase, contrary to expectations. With respect to the oxygen potential, despite the contact of the melt with air, the oxygen activity is controlled by carbon in the hot metal. The slag morphology in Figure 1 shows that the slag is no longer completely molten in the transfer ladle and consists of a mix of different solid phases and small portion of liquid slag. Most of the sulfur in the slag was found in the solid phase in the form of CaS, which is only a small volume fraction of the slag. The presence of
CaS is due to the desulfurization practice using CaC\textsubscript{2}. From Figure 1A and B, it can be observed that the liquid slag and solid CaS have a limited contact with the hot metal. The limited contact area between the hot metal and the sulfur-containing phases in the “slag” leads to very sluggish kinetics for the transfer sulfur back to the hot metal. Therefore, the amount re-sulfurization that is observed in the hot metal due to the temperature drop and oxidation in the ladle is very low.

5 Summary

Industrial trials were carried out to investigate the possibility of hot metal re-sulfurization during the waiting time in the transfer ladle before being sent to the BOF. From the slag morphology, it was found that the slag is no longer completely molten. almost of the sulfur in the slag was found in the form of CaS and in the solid phase, which represents only a small volume fraction of the slag. The hot metal was found to have a limited contact with the solid CaS and liquid slag which led to very poor kinetics for re-sulfurization. Therefore, the degree of re-sulfurization that is observed in the transfer ladle was found to be very low.

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Reference