Using Red Mud-based Flux in Steelmaking for High Phosphorus Hot Metal

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To smelt high phosphorus hot metal effectively, a new flux named Red Mud (RM) was applied in steelmaking to form CaO–FeO–SiO₂–Al₂O₃–Na₂O slag. Good slag fluidity and dephosphorization effects can be achieved when using RM-based flux in simulated steelmaking for high phosphorus hot metal. The dephosphorization rates of the RM-based flux were all greater than 82%. Especially, when RM:CaO=1:1.2, high dephosphorization rate (~95%) and low final [P] (~0.02%) was achieved in the situation of high [C] = 1.36%. This is of great importance for the production of clean steel. The P₂O₅ content in the P-rich phase in RM-based slag can reach 29.1 wt%, far higher than the 9.1 wt% in lime-based slag.

KEY WORDS: high phosphorus hot metal; Red Mud; CaO–FeO–SiO₂–Al₂O₃–Na₂O.

1. Introduction

To solve the crisis of resources, utilization of high phosphorus and low-grade iron ore is an urgent need. Using these high phosphorus iron ores would result in higher phosphorus content in hot metal. How to smelt high phosphorus hot metal effectively has become an increasingly important issue.⁵ To improve the dephosphorization efficiency, forming a low melting point, high basicity and good fluidity new slag is the key factor in the initial stage of the converter steelmaking process. The CaO-FeO-SiO₂-based slag formed during steelmaking generally has a high melting point. Fluxes are usually added to the slag to decrease its melting point and to enhance the kinetic efficiency of the dephosphorization process. Previous studies²-⁴ have demonstrated that Na₂O/Al₂O₃-bearing materials could be an alternative flux to improve the fluidity of CaO-FeO-SiO₂-based slag and to promote its dephosphorization performance. Bayer Red Mud (RM) is a waste tailing generated after the alumina production process, which is rich in Fe₂O₃, Al₂O₃ and Na₂O. Generally, the Fe₂O₃ concentration is as high as 35–53% in Bayer RM, which could be an ideal iron resource for ferrous metallurgy. Further, Na₂O in Bayer RM, which ranges from 5% to 10%, is a well-known strong dephosphorization agent.⁶ Therefore, Bayer RM could be an ideal new flux to form CaO–FeO–SiO₂–Al₂O₃–Na₂O slag and improve the dephosphorization efficiency of CaO–FeO-SiO₂-based slag.

In this work, experiments of using Bayer RM-based flux in simulated steelmaking for high phosphorus hot metal have been conducted. The fluxing action and dephosphorization effect in the early stage of steelmaking with the RM-based flux were studied. Finally, the enrichment of phosphorus in RM-based flux is discussed.

2. Material and Experimental Methods

The main components of the pig iron used are 4.1 wt% C, 0.2 wt% Si, 0.31–0.51 wt% P. The main chemical compositions of Bayer RM are 47.80 wt% Fe₂O₃, 20.19 wt% Al₂O₃, 12.48 wt% SiO₂, 7.62 wt% Na₂O, 6.69 wt% TiO₂, 2.15 wt% CaO. Required quantities of RM and CaO were thoroughly mixed as dephosphorizer/slagging agent.

The experiment was conducted in a 10 kg medium-frequency induction furnace (50 kW, 4 kHz). First, 5 kg of pig iron was pre-melted in the furnace. When it was completely melted and the temperature reached 1350°C, the initial iron sample was collected from the crucible using a ø6 mm tube. Then, 65–75% of the slagging agent was added into the crucible, and O₂ was blown into the top of the furnace through the ø6 mm alumina tube for 9 min. Slagging-off was performed after 9 min of O₂ blowing because the capacity of crucible was not big enough and the slag may overflow if all the slagging agent was added once. Then, another 25–35% slagging agent was added and O₂ was further blown for 16 min. Finally, the experiment was terminated and iron and slag samples were collected. Table 1 shows the specific experimental arrangements.

3. Results and Discussion

3.1. Fluidity of the Red Mud-based Flux

Figure 1 shows the conditions of the initial slag formation before oxygen blowing. When adding the RM-based slag sample, the fluidity of slag is better than the slag of lime-based slag.

<table>
<thead>
<tr>
<th>No.</th>
<th>[P]₀/%</th>
<th>RM:CaO</th>
<th>slag ratio</th>
<th>oxygen blow duration (min)</th>
<th>oxygen flow rate (m³/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.31</td>
<td>1:1.5</td>
<td>7.5%</td>
<td>9 + 16</td>
<td>0.8/0.9</td>
</tr>
<tr>
<td>2</td>
<td>0.51</td>
<td>1:1.2</td>
<td>7.5%</td>
<td>9 + 16</td>
<td>0.8/0.9</td>
</tr>
<tr>
<td>3</td>
<td>0.37</td>
<td>1:1.2</td>
<td>8%</td>
<td>9 + 16</td>
<td>0.8/0.8</td>
</tr>
<tr>
<td>4</td>
<td>0.37</td>
<td>92%CaO + 8%MgO</td>
<td>4.7%</td>
<td>9 + 16</td>
<td>0.8/0.9</td>
</tr>
</tbody>
</table>

Fig. 1. The conditions of initial slag formation before oxygen blowing: (a) No. 1, (b) No. 2, (c) No. 3, (d) No. 4.

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flux into the hot metal at 1350°C, the RM-based flux was rapidly melted in 2 min in the experiments Nos. 2–3 (Figs. 1(b) and 1(c)). While it became bad when the proportion of lime increased (Figs. 1(a) and 1(d)), which was especially evident in the No. 4. The results of No. 4 show that serious agglomeration and bad slag fluidity are observed during the entire process. While the experiments Nos. 2–3 show that good slag fluidity is observed during the entire process. These results clearly show that the presence of components such as Fe₂O₃, Al₂O₃ and Na₂O in RM can act as a flux to improve the fluidity of the CaO–FeO–SiO₂ based slag and further to enhance dephosphorization in the previous stage of converter-based steelmaking.

3.2. Time Dependency of [C] and [P] in the Metal

The content of P and C in the metal as functions of time is shown in Fig. 2. Good dephosphorization results of the RM-based flux were obtained overall. The dephosphorization rate was greater than 82% for all the RM-based flux tests (Nos. 1–3). Especially, in the test of No. 3, high dephosphorization rate (~95%) and low final [P] (≈0.02%) was achieved in the situation of high [C] = 1.36%. This suggests that using Al₂O₃/Na₂O-bearing RM as a flux in steelmaking can achieve “reducing P and keeping C”. This is of great importance for the production of clean steel. In addition, No. 4 was the blank contrast test of No. 3 and they had same amount of CaO. The dephosphorization rate of the RM-based flux No. 3 was much greater than No. 4. The test of pure lime-based No. 4 showed poor dephosphorization efficiency, whose [P] in steel was decreased only to 0.17% and the dephosphorization rate was just 54.1%. This suggested adding appropriate RM into the traditional CaO-FeO-SiO₂-based slag can effectively enhance the dephosphorization effect.

Table 2 shows the chemical compositions of the pre-slag and final slag. The P₂O₅ content in the pre-slag was greater than 10% for all the RM-based flux tests. Especially, the P₂O₅ in the test No. 2 reach 15.49%, which can fully reach the phosphorus content requirements of phosphoric fertilizer for agriculture. While the P₂O₅ content in the lime-based slag No. 4 was below 5.7%. This suggests that Bayer RM may enhance the solid solubility of P₂O₅ in the slag.

3.3. The Enrichment of Phosphorus in Red Mud-based Flux

Many researchers have shown that Al₂O₃, TiO₂, and Na₂O are beneficial to the solubility, and therefore the enrichment of phosphorus in the P-rich phase. Bayer RM is rich in Al₂O₃, TiO₂ and Na₂O, which may have a positive effect on the enrichment of phosphorus. The chemical compositions of the four samples are the pre-slag shown in Table 2. And their SEM images are shown in Figs. 3(A), 3(B), 3(C) and 3(D), respectively. Table 3 shows the energy dispersive X-ray spectroscopy (EDS) results of each phase for the samples shown in Fig. 3. Figure 4 shows the corresponding slag X-ray diffraction (XRD) results of pre-slag 2–1 and 4–1.

Table 2. Chemical compositions of the four slags (wt%).

<table>
<thead>
<tr>
<th>No.</th>
<th>The slag chemical compositions (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CaO</td>
</tr>
<tr>
<td>1–1</td>
<td>(pre-slag)</td>
</tr>
<tr>
<td>1–2</td>
<td>(final slag)</td>
</tr>
<tr>
<td>2–1</td>
<td>(pre-slag)</td>
</tr>
<tr>
<td>3–1</td>
<td>(pre-slag)</td>
</tr>
<tr>
<td>3–2</td>
<td>(final slag)</td>
</tr>
<tr>
<td>4–1</td>
<td>(pre-slag)</td>
</tr>
<tr>
<td>4–2</td>
<td>(final slag)</td>
</tr>
</tbody>
</table>

Fig. 2. Time dependency of [P] and [C] in the metal during the experiments: (a) No. 1, (b) No. 2, (c) No. 3, (d) No. 4.
Combined the EDS and XRD results help identifying the deep-black phase 1 in slag as a P-rich phase of a \(n\text{C}_2\text{S}-\text{C}_3\text{P}\) solid solution. The white phase 2 is the RO phase mainly containing iron oxide and magnesium oxide. Light gray phase 3 is the liquid phase matrix. The \(\text{P}_2\text{O}_5\) content in P-rich phase in the RM-based slags (slags A–C) was 27.4 wt%, 29.1 wt% and 20.4 wt%, respectively. However, the \(\text{P}_2\text{O}_5\) content in P-rich phase in the lime-based slag (slag D) was only 9.1 wt%. Hence, the degree of P enrichment in the RM-based slags is far greater than in the pure lime-based slag. This change is mainly attributed to the fact that \(\text{Al}_2\text{O}_3\), \(\text{TiO}_2\), and \(\text{Na}_2\text{O}\) in the RM-based flux can increase the phosphorus enrichment of the P-rich slag phase.

### 4. Conclusions

Good slag fluidity and dephosphorization effects can be achieved when using Bayer RM-based flux in simulated steelmaking for high phosphorus hot metal. Especially, when the RM:CaO ratio was 1:1.2, high dephosphorization rate (~95%) and low final [P] (~0.02%) was obtained in the situation of high [C] = 1.36%. The \(\text{P}_2\text{O}_5\) content in P-rich phase in the RM-based slag can reach as high as 29.1 wt%, far higher than the 9.1 wt% in lime-based slag.

### Acknowledgements

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### REFERENCES