The Application of SiC in Converter Steelmaking

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\textbf{Abstract.} Silicon carbide has better deoxidization ability than ferrosilicon and recarburizer by the thermodynamic analysis, the gas of CO produced by the deoxidation reaction can agitates molten steel which could purify the molten steel. In this article, we choose HRB400 as our testing steel, it is found that the usage of SiC can reach the aim of recarburization and silicon increasing in the statistical analysis, the various properties of the testing steel are stable, and the use of Silicon carbide can further improve the economic benefits of steel plants as the price of SiC is lower.

\textbf{Introduction}

Silicon carbide with the molecular weight of 40.07 and the density of 3.209g/cm\textsuperscript{3} is a kind of synthetic compounds, molecular formula is SiC. SiC is made from high quality quartz sand and petroleum coke in the resistance furnace, it can be used as compound deoxidizer in metallurgy field as its widespread application. SiC is a new kind of compound deoxidizer with more stable physical and chemical performances and good deoxidization effect as the replacement of the traditional solid silicon powder and carbon powder. Furthermore, the usage of SiC has a cost advantage in reducing the consumption of raw materials and can improve the quality of the steel comparing with the original process.\textsuperscript{[2-5]} Since SiC has the traits of instability which is obvious under high temperature and oxidizing atmosphere, it is active in the environment of high temperature, and silicon will have the priority of reaction with oxygen in steel as silicon has stronger reducibility compared with manganese element\textsuperscript{11}, which reduces the oxygen content in steel and the loss of the manganese element caused by dyoxidation. SiC has larger affinity to oxygen compared with silicon accompanying with strong reaction, which retains the alloys of Si and Mn in the liquid steel, improving the yield rates of the Si and Mn. Therefore, the applications of SiC in the converter steelmaking process can achieve the purpose of cost decreasing and benefit increasing. Solid SiO\textsubscript{2} and gaseous CO generated continuously accompany with the deoxidization reaction of SiC in the molten steel, which can agitates the molten steel constantly, the generation and floatation of CO can promote the combination between solid SiO\textsubscript{2} and other oxides such as Al\textsubscript{2}O\textsubscript{3}, MnO etc., which will purify molten still in certain extent.

\textbf{Thermodynamic Analysis of Silicon Carbide Deoxidization Process}

We can infer from the equations\textsuperscript{11}:

\begin{align*}
\text{Si}_{(l)} + 2[O] &= \text{SiO}_2_{(s)} & \Delta G^0 &= -711489 + 202.84T, \text{ J/mol} & (2-1)
\text{C}_{(s)} + [O] &= \text{CO}_{(g)} & \Delta G^0 &= -2510 - 80.17T, \text{ J/mol} & (2-2)
\text{SiC}_{(l)} + 3[O] &= \text{SiO}_2_{(g)} + \text{CO}_{(g)} & \Delta G^0 &= -2510 - 80.17T, \text{ J/mol} & (2-3)
\end{align*}

the relationship between the temperature T and the standard gibbs free energy in above equations (2-1), (2-2), (2-3) can be drawn into a figure below:
Fig. 1 the relationship between temperature T and standard gibbs free energy in the temperature range of [1873K-2023K], the rank of deoxidization abilities of the three materials from strong to weak is that: the Silicon carbide (SiC) > Silicon (Si) > Carbon (C).

The analysis of deoxidization abilities of Silicon carbide

Theoretically, The consumption of deoxidizer can be concluded from the ratio of deoxidizing elements and the oxygen’s atomic weight combining with them. The reaction can be expressed as follows:

$$xR + yO = R_xO_y$$

It is inferred from the above formulas that when using silicon as desoxidant the calculation is that:

$$[Si] + 2[O] = (SiO_2)$$

$$\frac{\Delta[Si]}{\Delta[O]} = \frac{M_{Si}}{2M_{O}} = \frac{28}{2 \times 16} = 0.875$$

When choosing recarburizer as desoxidant:

$$[C] + [O] = CO$$

$$\frac{\Delta[C]}{\Delta[O]} = \frac{M_C}{M_O} = \frac{12}{16} = 0.75$$

When choosing the mixture of Ferrosilicon and Recarburizer by the ratio of 2 : 1 as desoxidant, The unit consumption is that:

$$0.875 \times 2 + 0.75 \times 3 = 0.833$$

When choosing silicon carbide as desoxidant:

$$[SiC] + 3[O] = (SiO_2) + CO$$

$$\frac{\Delta[SiC]}{\Delta[O]} = \frac{M_{(SiC)}}{3M_{O}} = \frac{12 + 28}{3 \times 16} = 0.833$$

It is can be included that the theoretical deoxidization consumption is identical between the mixture of Ferrosilicon and recarburizer by the ratio of 2 : 1 and Silicon carbide as desoxidant.
**Industrial Experiment**

Based on the above analysis and theoretical support, we will put silicon carbide into 120 ton converter plant to testify its effect by adding silicon carbide 250 kg per furnace, aiming to increase C to 0.08% ~ 0.10% and Si to 0.12%. Because of its effect is not clear, SiC will only be allowed to be added into the steel of HRB400, and other grades of steel are prohibited to be added into. According to the three principles of alloy adjustment in the literature, the alloy adjustment scheme is showed below.

Table 1 the alloy adjustment scheme

<table>
<thead>
<tr>
<th>Steel grade</th>
<th>the original process</th>
<th>the new process</th>
</tr>
</thead>
<tbody>
<tr>
<td>HRB400</td>
<td>FeMn+FeSi+AlMnTi+VN</td>
<td>FeSi+MnSi+SiC+SiAlBa + VN</td>
</tr>
</tbody>
</table>

The addition way of silicon carbide is that FeSiMn and SiC alloy should be added when the molten steel tap to 1/3 of the total molten steel.

When the weight percent of SiC is under 70% in Silicon carbide alloy, the (SiO₂ + Si) free is so many that will increase the contents of gases and inclusions and even lead to a sharp increase of T[O] and inclusions in molten steel, in comparison, the addition of SiC alloy which contains w(SiC) up 75% has no obvious effects on the content of gases and inclusions in molten steel, and it is uneconomical when adding the Silicon carbide alloy containing SiC up 90% in weight percent. Therefore, the physical and chemical components requirements for Silicon carbide alloy are listed as follows.

Table 2 Chemical components for Silicon carbide alloy

<table>
<thead>
<tr>
<th>w(%)</th>
<th>SiC</th>
<th>Si_free</th>
<th>C_free</th>
<th>P</th>
<th>S</th>
<th>H₂O</th>
<th>particle size/mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>82~88</td>
<td>4~10</td>
<td>≤1.50</td>
<td>≤0.05</td>
<td>≤0.05</td>
<td>≤0.50</td>
<td>≤5</td>
<td></td>
</tr>
</tbody>
</table>

Table 3 the chemical components of HRB400

<table>
<thead>
<tr>
<th>C%</th>
<th>Si%</th>
<th>Mn%</th>
<th>P%</th>
<th>S%</th>
<th>V%</th>
<th>Ceq</th>
</tr>
</thead>
<tbody>
<tr>
<td>National standard</td>
<td>≤0.25</td>
<td>≤0.80</td>
<td>≤1.60</td>
<td>≤0.045</td>
<td>≤0.045</td>
<td>≤0.12</td>
</tr>
<tr>
<td>Internal standard</td>
<td>0.17~0.25</td>
<td>0.40~0.60</td>
<td>1.20~1.60</td>
<td>≤0.045</td>
<td>≤0.045</td>
<td>0.03~0.12</td>
</tr>
</tbody>
</table>

**The experimental results and related statistics**

This experiment contains 74 furnaces, and the conditions of alloys added are listed in tables 1 to 3. The statistics of practical Si and C increased by SiC are depicted into figures below:

Fig. 2 the statistics of Si increasing

Fig. 3 the statistics of C increasing
We can see from the figure above, this experiment result is consistent with the experiment of Li Yonggang, etc.\(^2\)

Steel mechanical properties including yield strength, tensile strength and elongation are related to steel composition, technological parameters such as rolling temperature, in order to objectively analyze the affection of original technology and new process on the quality of the steel, the final point control of converter and the rolling temperature process have not changed, based on the analysis of the steel produced by the new and the original deoxidation alloying process, its mechanical performance indexes are shown in Table 4. 74 furnaces HRB400 steel are produced by new process, and the diameter of rolled steel is Φ22mm. All HRB400 steel mechanical properties are qualified, and the steel strength of HRB400 has increased about 10 MPa, just as the table 4 shows. Finally, the internal quality of the steel gets improved.

Table 4 the mechanical properties comparison of steel produced by this two processes

<table>
<thead>
<tr>
<th>Steel grade</th>
<th>items</th>
<th>average value</th>
<th>mean square error</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(R_{eL}/\text{MPa})</td>
<td>(R_{m}/\text{MPa})</td>
</tr>
<tr>
<td>HRB400</td>
<td>new process</td>
<td>481</td>
<td>658</td>
</tr>
<tr>
<td>HRB400</td>
<td>original process</td>
<td>469</td>
<td>645</td>
</tr>
<tr>
<td>HRB400</td>
<td>comparison</td>
<td>+12</td>
<td>+13</td>
</tr>
</tbody>
</table>

The steel produced by this two process are tested randomly by high and low power optical microscopes, the macroscopic examination result shows that the maximum center loose is grade 1, no other defects are found. High power microscopic examination results is showed in Table 5, from the metallographic observation, we can see that the steel group and grain size are denser and smaller. Comprehensive results show that the steel internal organization is normal, the quality is fine.

Table 5 Metallographic inclusions comparison of HRB400 produced by two process.

<table>
<thead>
<tr>
<th>Alloying process</th>
<th>Sample number</th>
<th>Sulfide thin department</th>
<th>Silicate thin department</th>
<th>Silicate coarse department</th>
<th>Globular oxide thin department</th>
<th>Globular oxide coarse department</th>
</tr>
</thead>
<tbody>
<tr>
<td>New alloying</td>
<td>10</td>
<td>0.5–1.0</td>
<td>0.5–1.5</td>
<td>0.5–1.0</td>
<td>0.5–1.5</td>
<td>0.5–1.0</td>
</tr>
<tr>
<td>process</td>
<td></td>
<td>0.7</td>
<td>0.9</td>
<td>0.6</td>
<td>0.7</td>
<td>0.6</td>
</tr>
<tr>
<td>Original alloying</td>
<td>10</td>
<td>0.5–1.0</td>
<td>0.5–2.0</td>
<td>0.5–1.5</td>
<td>0.5–2.0</td>
<td>0.5–1.0</td>
</tr>
<tr>
<td>process</td>
<td></td>
<td>0.7</td>
<td>1.0</td>
<td>0.7</td>
<td>0.8</td>
<td>0.8</td>
</tr>
</tbody>
</table>

Conclusions

The deoxidation of SiC can reduce the loss of manganese element in steel, and has a certain effect of increasing the contents of Carbon and Silicon in molten steel, improving the yield rate of Silicon and Manganese and purifying molten steel as CO generated by deoxidization reaction escapes out.

Within the scope of the steelmaking temperature, the deoxidization ability of Silicon carbide is the strongest, carbon’s deoxidization ability is the weakest.

It is reasonable when choosing silicon carbide to replace Silicon and Carburant, which can decrease the cost of deoxidation.

Various properties of the steel of HRB400 are stable when choosing silicon carbide as the deoxidizer and alloy.
References


