Optimization of Endpoint Control for Low Carbon and Phosphorus Steel Produced by Converter Single Slag Process

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Through field test and thermodynamic calculation of decarbonization, this paper studies the effect of endpoint control of low-carbon and phosphorus steels produced with single-slag in basic oxygen furnace (BOF) on furnace lining erosion. The study reveals that practicing step control of C% till steel tapping in lieu of the thoroughgoing blowing method can effectively reduce the tapping temperature and FeO% in final slags, thereby mitigating the effect of heat and mass transfer on the compact slag layer of furnace lining and lowering the rate of furnace lining erosion. One key point is to control the endpoint C% somewhere above the critical C% value (Ct) of C–Fe selective oxidation in the final phase of blowing, which can be accomplished effectively by shortening the press-lance time to 40 s–70 s. Another key point is to raise the control range of endpoint carbon C2 to 0.040%–0.050%. The tapping requirement for low-carbon and phosphorus steels can be satisfied through static stirring operation such that the carbon value at steel tapping C3 < 0.038%.

KEY WORDS: single-slag in BOF; low-carbon and phosphorus steels; the critical C% value; selective oxidation; endpoint control.

1. Introduction

With the surging demands for pipeline steel, high-strength steel, wear-resistant steel, steel for low-temperature pressure vessels and other low-carbon and phosphorus steels, it has become a mainstream trend to adopt BOF to smelt these types of steels. Specific to the low-carbon and phosphorus characteristics of these types of steels, new smelting processes, such as SRP (Simple Refining Process), MURC (Multi-Refining Converter), SGRS (Slag Generation Reduced Steelmaking), DRP (Double-slag Refining Process), etc., have been developed all over the world as the most commonly adopted techniques in newly established iron and steel projects.1–3)

However, the original iron and steel enterprises cannot have access to the new processes due to the restriction of smelting equipment but remain adopting the traditional single-slag smelting technique in single BOF for production. Such steels have extremely strict requirements on product constituents, the control target of carbon content is 0.048%, considering the carbon increase of 0.005%–0.01% in the other processes, so the carbon content in the tapping of molten steel from BOF shall not exceed 0.038%, otherwise, it is easy to exceed and affect the performance of the steel. In practical production, the thoroughgoing operation method, which implements deep decarbonization with the help of high temperature and high oxidizability of slags, can shorten the steelmaking cycle by 3 to 4 min as compared to the new processes, resulting in peroxidation of carbon at endpoint control, and the FeO% in the slag increased sharply, severe furnace lining erosion, and discontinuity in production.4,5)

To address this issue, it is necessary to delve into the relationship between decarbonization in the final phase of blowing and oxidizability of slags. This will help illuminate the evolutionary behaviors of endpoint C% and FeO% in slags during the production of low-carbon and phosphorus steels. Higuchi et al.6) studied the effect of bottom blowing stirring energy and \( L / L_0 \) (\( L_0 \): molten pool impact depth, \( L_0 \): liquid level) on the Ct and FeO% in slags, and the study showed that with increase in both stirring energy and \( L / L_0 \), the Ct decreases and FeO% in slags increases. Kato et al.7) studied the effect of mixed gas top blowing on the decarburization of molten steel in the low carbon range. When C% < 0.03%, the decarburization rate depends on the \( P_{CO} \) in the mixed gas.

The predecessors mainly studied the methods to improve the accuracy of endpoint composition and temperature prediction.8–11) In this paper, the effect of press-lance time on...
endpoint C% and final slags FeO% were studied through experiments, and the control range and realization method of endpoint carbon in the production of low-carbon and phosphorus steel were proposed. Summarize the law of how the operation in the final phase of steelmaking affects furnace lining erosion, so as to optimize and improve the current operation, mitigate their effect on furnace lining erosion, and attain the goal of continuous production.

2. Experimentation

2.1. Brief Introduction about the Production Process

Low-carbon and phosphorus steels are produced by the single-slag technique in single BOF, where the BOF has a nominal capacity of 150 t; the top-bottom blowing method is adopted throughout the steelmaking process in the BOF; the 5-hole laval type oxygen lance nozzle has an oxygen supply intensity of 3.3 Nm³/(t.min). See Fig. 1. for the concrete technical process.

Lance height is varied within the range 1.3 m–2.0 m during the blowing process in BOF. A subsidence is adopted for measuring temperature and sampling in the carbon catching process. Subsequently, the blowing continues till tapping of steel below the target carbon content. The auxiliary materials which include lime, light-burned dolomite and some sintered ores are charged as slagging material in two batches in an earlier phase of blowing. See Table 1. for the concrete ingredients.

2.2. Test Method

To delve into the effect of endpoint control of low-carbon and phosphorus steels produced by the single-slag technique in single BOF on furnace lining erosion, the study is carried out in the following three respects, provided that the production condition and process are the same.

(1) Decarbonization thermodynamic calculation is adopted to figure out the C–Fe selective oxidation in the final phase of blowing. Statistics on the tapping temperature and sampling in the carbon catching process in BOF, the C and Fe in the molten pool undergo the following C–O reaction towards being oxidized.12)

\[ \Delta G^{\text{G}}_{1} = -22 200 - 38.34T \] J/mol

(2) During the blowing process, samples are taken to analyze the decrement of carbon content C x% in distinct endpoint C% and FeO% in final slags.

(3) A press-lance time optimization test is carried out by sampling and analyzing the effect of press-lance time on endpoint C% and FeO% in final slags.

(4) A static stirring test is carried out by sampling and analyzing the decrement of carbon content C x% in distinct endpoint C% at fixed time and fixed bottom blowing flow.

3. Results and Discussion

3.1. Calculation and Application the C x of C–Fe Selective Oxidation in the Final Phase of Blowing in BOF

As the C–O reaction in the molten steel verges to equilibrium in the final phase of blowing, the C–O concentration product becomes basically constant. The endpoint C% value has a great effect on the oxidizability of final slags. In particular, during the production of low-carbon steels, the selective oxidation of C and Fe is hardly avoidable in the final phase of blowing. To this end, decarbonization thermodynamic calculation is adopted to figure out the C x during selective oxidation. In the final phase of blowing in BOF, the C and Fe in the molten pool undergo the following reaction towards being oxidized.12)

\[ [C] + [O] = CO_{(g)} \] (1)

The standard Gibbs free energy of reaction Eq. (1) is:

\[ \Delta G^{\text{G}}_{1} = -22 200 - 38.34T \] J/mol (2)

Assume that Eq. (1) is in equilibrium: that is, \( \Delta G_{1} = 0 \)

\[ \ln K_{1} = -\frac{\Delta G^{\text{G}}_{1}}{-RT} = \frac{\Delta G_{1}}{RT} = \frac{\Delta G_{1}}{RT} \] (3)

\[ \ln K_{1} = -\frac{\Delta G^{\text{G}}_{1}}{-RT} = \frac{\Delta G_{1}}{RT} = \frac{\Delta G_{1}}{RT} \] (4)

The reaction equation of molten iron and oxygen is:

\[ [\text{Fe}]_{(l)} + [O] = (\text{FeO})_{(s)} \] (6)

The standard Gibbs free energy of reaction Eq. (6) is:

\[ \Delta G^{\text{G}}_{2} = -117 700 + 49.83T \] J/mol (7)

From reaction Eqs. (1) and (6), we can get (9); and from the standard Gibbs free energy (2) and (7), we can get (10):

\[ \Delta G^{\text{G}}_{x} = 95 500 - 81.8T \] J/mol (10)

![Fig. 1. Schematic diagram of converter single slag steelmaking process. (Online version in color.)](image)
Where, R: Gas constant, 8.314 J/(mol.k);
T: Thermodnamic temperature, at 25°C, T=298 k;
K: Equilibrium constant;
P_{CO}: Partial pressure, atm;
o: Activity;
f: Activity coefficient;
w: Mass concentration;
P^o: Standard atmospheric pressure, 1 atm;

The reaction verges to equilibrium in the final phase of blowing, the content of other elements in the molten Fe is already dilute enough, so the activity of Fe can be approximately 1.\(^{13}\) The activity coefficient of C and O are calculated by Eqs. (12) and (13), The result are all approximate to 1. With the decrease of C%, the decarbonization rate at the end of blowing decreased significantly.\(^{14-16}\) In actual steel-making, P_{CO}/P^o < 1 atm, when the bottom blowing amount is small, P_{CO}/P^o should take the value of 0.88 atm–0.96 atm at the reaction interface, and the low carbon steel should be calculated with the lower limit of 0.88 atm. See Table 2 for calculation results, the C_t of C–Fe selective oxidation corresponding to the a_{FeO} value in different slags, as the temperature of the molten pool rises from 1 500°C to 1 700°C.

\[
\log f_c = \log f_c^0 + \log f_c^0 \equiv \log f_c^0 = 0.243(\%C)^{17} \quad \ldots \quad (12)
\]

\[
\log f_c = \log f_c^0 + \log f_c^0 \equiv \log f_c^0 = -0.421(\%O)^{17} \quad \ldots \quad (13)
\]

According to the normal ionic solution model, calculate the value of a_{FeO}, the reference state of FeO activity in the model is taken to the hypothetical stoichiometric FeO, in which the regular nature of the solution is satisfied. However, the reference state of conventional iron oxide activity is the pure iron oxide in equilibrium with metallic iron.\(^{18}\) According to previous research, when the slag system (CaO-MgO-SiO\(_2\)-Al\(_2\)O\(_3\)-P\(_2\)O\(_5\)-MnO-FeO,Fe) satisfied FeO<30% and MnO<13%, there is the following conversion relationship:

\[
a_{FeO} = 0.864a_{FeO,RS}^{19} \quad \ldots \quad (14)
\]

\[
a_{FeO,RS} = \gamma_{FeO,RS}X_{FeO}^{19} \quad \ldots \quad (15)
\]

<table>
<thead>
<tr>
<th>Slag system</th>
<th>FeO</th>
<th>CaO</th>
<th>MnO</th>
<th>SiO(_2)</th>
<th>MgO</th>
<th>P(_2)O(_5)</th>
<th>a_{FeO}</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-1</td>
<td>27.76</td>
<td>45.08</td>
<td>3.63</td>
<td>12.39</td>
<td>8.40</td>
<td>2.74</td>
<td>0.29</td>
</tr>
<tr>
<td>S-2</td>
<td>22.76</td>
<td>48.20</td>
<td>3.88</td>
<td>13.25</td>
<td>8.99</td>
<td>2.92</td>
<td>0.25</td>
</tr>
<tr>
<td>S-3</td>
<td>17.76</td>
<td>51.32</td>
<td>4.13</td>
<td>14.11</td>
<td>9.57</td>
<td>3.11</td>
<td>0.20</td>
</tr>
<tr>
<td>S-4</td>
<td>12.76</td>
<td>54.44</td>
<td>4.38</td>
<td>14.96</td>
<td>10.15</td>
<td>3.31</td>
<td>0.15</td>
</tr>
</tbody>
</table>

From Table 2, in the following two cases, the C_t decreases gradually: (1) When the a_{FeO} value in slags is the same, the temperature of the molten pool rises; (2) When the molten pool temperature is the same, the a_{FeO} value in slags increases.

The higher the temperature of the molten pool and the higher the a_{FeO} value in slags in the final phase of blowing, the lower of the C_t and the easier to implement deep decarbonization. In practical production, the temperature and oxidizability of slags should be regulated to an appropriate degree as per the technical requirement for the type of steel to be smelted, so as to implement precise catch carbon.

There is a great variance of the C_t calculated at distinct temperatures and a_{FeO} value in different slags. See Fig. 2 for the details.

The tapping temperature of steelmaking is typically controlled within the range 1 600°C–1 700°C. This temperature interval is subject to appropriate adjustment to various conditions of endpoint catch carbon. Statistics on the production of pipeline steel in 26 experiments were gathered; the average tapping temperature is 1 681.2°C, the tundish average C% value is 0.0253%, the average C% increase in the LF process is 0.0051%, so the C% value in actual tapping of steel from BOF is estimated below 0.02%. It can be reckoned that the endpoint C% value is lower than the C_t of this type of steel, and the oxidizability of slags is stronger than S-1. The endpoint C% of pipeline steel is at point Z1 behind the right side of point f. See Fig. 2.

In practical production of low-carbon and phosphorus steels by thoroughgoing operation method by the single-slag technique in single BOF, it takes slags with higher temperature and stronger oxidizability to decarbonize endpoint product to a lower C% value in BOF before steel tapping. Given that the furnace lining is situated in a high-temperature high-oxidizability environment, its compact slag layer will likely be located in an unstable region under the effect of heat and mass transfer, such that the rate of overall furnace lining erosion will increase due to the dissolution of the magnesia particles in magnesia carbon bricks and the oxidation of graphite at high temperature.\(^{20-23}\)

In combination with the real control condition of endpoint
C% value and decarbonization thermodynamic theoretical analysis, the following optimization solution is proposed for the control of endpoint C% value: (1) First, move the control point of endpoint C% value from point Z1 (where C(Z1) < 0.02%) forward to above point a (where C(Z1) ≥ 0.038%), control Z1 in the C 2 area between line L 1 and L 2; (2) next, move downward to point b, c and its neighborhood (where C(Z1) < 0.038%) before steel tapping, control Z1 in the C 3 area between line L 2 and L 3 . Improve the endpoint control objective and perform bottom blowing static stirring operation, so that the tapping temperature drops from the original interval 1650°C–1700°C to the interval 1600°C–1650°C, and that the final slags FeO% drop from ultrahigh ferrous slag system and above to near high ferrous slag system (FeO% = 27.76%). Perform step control on endpoint C% value by blowing to C 2 before bottom-blowing and static-stirring to C 3 , so as to effectively reduce the tapping temperature and FeO% in final slags.

3.2. Effect of Press-lance Operation on Furnace Lining Erosion in the Final Phase of Blowing in BOF

In practical blowing process, it is hard to have an accurate grasp of the variation law of FeO% in slags and C content in steels, on account of the effects of a myriad of factors such as temperature, steel type, charging, quality requirement, etc. However, as the reaction verges to equilibrium in the final phase of blowing, the law of interaction between final slags FeO% and endpoint C% can be analyzed by sampling. See Table 4 for the sampling results in different phases (use manual and sublance sampling), and Fig. 3, for the correspondence between endpoint C% value and FeO% in slags.

From Table 4 and Fig. 3, the slags FeO% in the earlier phase are somewhere between medium ferrous slag system (15% < (FeO) < 20%) and medium-to-high ferrous slag system (20% < (FeO) < 25%), while the slags FeO% in the later phase are somewhere between high ferrous slag system (25% < (FeO) < 30%) and ultrahigh ferrous slag system ((FeO) > 30%); in the final phase of blowing, the C content in steels further decreases while the FeO% in slags keeps rising, and the C1 at which the C and Fe in steels undergo selective oxidation gradually decreases. Controlling the endpoint C% value to be higher than the C1 can effectively decrease the FeO% in slags and mitigate furnace lining erosion. Set the carbon values to be C1, C2, and C3 in the TSC phase, TSO phase, and at endpoint steel tapping, respectively. The duration between points g and h corresponds to the adjust-slag press-lance stage, and the duration between points h and i corresponds to the stop-blowing static stirring stage. The ideal control point should be such that the value is above the Ct, i.e., C2 ≥ Ct, when press-lance is over in the final phase of blowing. If C2 < Ct then the FeO% in slags tends to surge drastically, causing anomalies in blowing under the effects of temperature, ingredients, operation, and other factors in practical production. Two types of the problems are serious: One is the overall rise of FeO% in the slag system due to twice or more point-blowing operations, at which time the duration between points i and j corresponds to the secondary press-lance stage and the duration between j and k corresponds to the secondary static stirring stage. This circumstance is a remedial measure in abnormal conditions. C4 and C3 are the carbon values after the secondary press-lance and static stirring, respectively, with C4 < Ct in this circumstance, meaning the carbon reduction result of static stirring operation is poor. The other is overlong press-lance time, in which circumstance the case C2 < Ct can be avoided by optimizing the press-lance operation. Either of the above two circumstances results in C2 < Ct, so that the temperature of the molten pool rises and that the FeO% in slags resides above the ultrahigh ferrous slag system. Under the effect of heat and mass transfer, the slag layer of furnace lining enters an unstable region of Zx, thereby increasing the

| Table 4. Sampling situation of low-carbon and phosphorus steel during smelting. |
|---------------------------------|----------------|----------------|----------------|----------------|----------------|
| FeO%   | Initial | Early-5 min | TSC* -12 min | TSO* -14 min | End |
| C%     | C4      | C5      | C3      | C2      | C1      |
| FeO%   | 0.00    | 0.00    | 0.00    | 0.00    | 0.00    |
| C%     | 4.79    | 4.79    | 4.79    | 4.79    | 4.79    |
| T/°C   | 1333    | 1333    | 1333    | 1333    | 1333    |
| *: Sublance measurement with Temperature, Sample, using carbon type probe and oxygen type probe. |
3.3. Optimization of Press-lance Time in the Final Phase of Blowing in BOF

To study the effect of press-lance time on endpoint C% and FeO% in final slags, a comparative test is carried out between two groups as follows:

Test scheme for Group I: The press-lance test is carried out at equal lance position among a total of 6 experiments as samples under test within 40 s–160 s press-lance time. See Table 5 for the test conditions and results.

From Table 5, the endpoint C% value of the 6 experiments under test fluctuates within the range 0.0222%–0.0685%, the press-lance time ranges from 40 s to 155 s, and the FeO% in slags fluctuates within the range 21.52%–32.98%. In the low-carbon region (C ≤ 0.0439%), the longer the press-lance time, the higher the FeO% in final slags, thereby the lower the endpoint C% value of the experiment, that is, the endpoint C% value is inversely proportional to the FeO% in final slags. In the high-carbon region (C > 0.0439%), the longer the press-lance time, the lower the FeO% in final slag, and vice versa. The difference between them is whether selective oxidation occurs. The C-Fe selective oxidation has taken place in experiments H1-1 and H1-2 in the final phase of blowing, with the FeO% in final slags near and above high ferrous slag system, endpoint C% values both lower than 0.030%, and press-lance time being 155 s and 94 s, respectively. Compared with the furnace H1-3, the overlong press-lance time is identified as the root cause for this problem, as shown in Fig. 4.

Test scheme for Group II: The press-lance test is carried out on low-carbon and phosphorus steel types under the condition of equal press-lance position among a total of 6 experiments as samples under test within 40 s–70 s press-lance time. See Table 6 for the test conditions and results.

From Table 6, the endpoint C% value of the 6 experiments under test fluctuates within the range 0.0306%–0.0383%, the press-lance time ranges from 40 s to 70 s, the FeO% in slags fluctuates within the range 27.9%–30.3%, and the P% at the endpoint did not increase due to the decrease of FeO% in slags, the fluctuation range was 0.0092%–0.0126%, the average value was 0.0109%. When the fluctuation of endpoint C% value is stably controlled within 0.010%, the fluctuation of FeO% in final slags is stably controlled within 2.4%. At this moment, the correspondence between press-lance time length and FeO% in final slags is significant. As the press-lance time shortens the FeO% in final slags decreases; otherwise, it increases. C–Fe selective oxidation is supposed not to have occurred in each experiment in the final phase of blowing, and the FeO% in slags in each is controlled between somewhere near high ferrous slag system and ultrahigh ferrous slag system. Evidently, shortening press-lance time can effectively control the endpoint carbon value above C and FeO% in final slags below ultrahigh ferrous slag system, as shown in Fig. 5.

Table 5. Test conditions and results for Group I.

<table>
<thead>
<tr>
<th>NO.</th>
<th>Low Carbon and Phosphorus Steel</th>
<th>FeO%</th>
<th>C%</th>
<th>Time/s</th>
<th>Position/m</th>
</tr>
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<tbody>
<tr>
<td>H1-1</td>
<td>X70-4</td>
<td>32.98</td>
<td>0.0222</td>
<td>155</td>
<td>1.4</td>
</tr>
<tr>
<td>H1-2</td>
<td>X80-3</td>
<td>31.60</td>
<td>0.0290</td>
<td>94</td>
<td>1.4</td>
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<tr>
<td>H1-3</td>
<td>Q345SP-3</td>
<td>27.85</td>
<td>0.0439</td>
<td>40</td>
<td>1.4</td>
</tr>
<tr>
<td>H1-4</td>
<td>A</td>
<td>25.00</td>
<td>0.0472</td>
<td>53</td>
<td>1.4</td>
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<tr>
<td>H1-5</td>
<td>S355J-1</td>
<td>21.52</td>
<td>0.0595</td>
<td>84</td>
<td>1.4</td>
</tr>
<tr>
<td>H1-6</td>
<td>LR-A36</td>
<td>23.10</td>
<td>0.0685</td>
<td>40</td>
<td>1.4</td>
</tr>
</tbody>
</table>

Table 6. Test conditions and results for Group II.

<table>
<thead>
<tr>
<th>NO.</th>
<th>Low Carbon and Phosphorus Steel</th>
<th>FeO%</th>
<th>C%</th>
<th>P%</th>
<th>Time/s</th>
<th>Position/m</th>
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<tr>
<td>H2-1</td>
<td>X80-3</td>
<td>28.80</td>
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<td>0.0095</td>
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<td>H2-2</td>
<td>X80-3</td>
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<tr>
<td>H2-6</td>
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<td>30.11</td>
<td>0.0383</td>
<td>0.0113</td>
<td>50</td>
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</table>

Average 29.33 0.0342 0.0109 58
3.4. Effect of Static Stirring Operation in BOF on Tapping Carbon Content

To implement step control of endpoint C% value, choose appropriate bottom blowing static stirring parameters after stopping blowing, without increasing the temperature of the molten pool and oxidizability of the slags, and decrease the carbon content C in some of the molten steel, with carbon value at steel tapping C = C – C.

Sampling scheme for field test: (1) To prevent excess drop in temperature of the molten pool during stirring, fixed bottom blowing flow is planned to be adopted within 200 Nm³/h–300 Nm³/h; (2) fluctuation of the endpoint C% value in the sampled furnaces for test shall be controlled within the interval of low-carbon and phosphorus steels; (3) to prevent the test samples from impacting the production rhythm, the bottom blowing static stirring time shall be controlled within 360 s. The C content in steels shall be analyzed by sampling before and after the static stirring test. The test condition is shown in Table 7.

From Table 7 and Fig. 6, the C% value of the test furnaces is controlled between 0.0315% and 0.0727%, the average static stirring time is 311 s, the decrement of carbon content C through static stirring ranges within 0.0052%–0.0173%, and the rate of decarbonization is 22% on average. Among the experiments with C < 0.040%, the rate of decarbonization is below 20%, and 17% on average, and the decrement of carbon content C% through stirring is 0.0158% on average. From the above analysis, the decrement of carbon content C% increases as endpoint C% value increases. For C > 0.040%, the rate of decarbonization through static stirring operation is approximately 24%, basically maintaining the balance. When the endpoint C% value is controlled below 0.050%, the tapping requirement for low-carbon and phosphorus steels can be met through static stirring operation such that the carbon value at steel tapping C < 0.038%.

4. Conclusion

Practicing step control of C% till steel tapping in lieu of the thoroughgoing blowing method can effectively reduce the tapping temperature and FeO% in final slags, mitigate the effect of heat and mass transfer on the compact slag layer of furnace lining, and lower the rate of furnace lining erosion. Controlling the C value in the steel above C when press-lance is over in the final phase of blowing, i.e., C ≥ C, can effectively decrease the FeO% in slags. Overlong press-lance time can cause C < C, so that the temperature of the molten pool rises and that the FeO% in slags resides above the ultrahigh ferrous slag system; shortening press-lance time to 40 s–70 s can effectively control the endpoint C value above C, leading the FeO% in final slags to drop to the high ferrous slag system. Decrement of carbon content C% through static stirring operation increases as C increases. When C > 0.040%, the rate of decarbonization is approximately 24%, namely for 0.040% < C < 0.050% the tapping requirement for low-carbon and phosphorus steels can be met through static stirring operation such that the carbon value at steel tapping C < 0.038%.

Acknowledgements

We thank the directors of Nangang Zhou Guicheng and Zhou Hehe for their support to this work.

Nomenclature

Cᵢ: Decrement of carbon content during static stirring operation (%)
Cᵢ: Critical C% value of C–Fe selective oxidation (%) Cᵢ(θ): Average carbon content of pipeline steel (%) Cᵢ: Carbon values in the TSC phase (%) Cᵢ: Carbon values in the TSO phase (%) Cᵢ: Carbon values at endpoint steel tapping (%) Cᵢ: Carbon values after the secondary press-lance (%) Cᵢ: Carbon values after the secondary static stirring (%)

REFERENCES