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Dephosphorization by Double-Slag Process in Converter Steelmaking

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Abstract: The double-slag converter steelmaking process can smelt low- and ultra-low-phosphorus steel and reduce lime and dolomite consumption and the amount of final slag simultaneously. Industrial steelmaking tests on a 150-metric ton converter at the Tangsteel Company were carried out to study this principle and its effect on the dephosphorization ratio and material consumption. The results showed that low-temperature stage could be used with a reduced amount of slag in the double-slag steelmaking process to achieve rapid and efficient dephosphorization. A low-basicity slag (~1.5–2.0) in the dephosphorization stage is required in double-slag process. The dephosphorization ratio reached a maximum of 71% when the slag basicity was 1.7. The end-point phosphorus content after the smelting process was reduced from an average of 0.018 mass% to an average of 0.011 mass% and the dephosphorization efficiency increased by more than 6%. The dephosphorization slag could be poured out rapidly when the FeO content was controlled at ~16–20 mass% in the double-slag smelting process. Based on key factors such as an efficient dephosphorization and a rapid iron–slag separation, the production efficiency was improved and the smelting cycle increased by only four minutes over the conventional process.

Keywords: double slag, dephosphorization, converter, lime consumption

Introduction

Phosphorus is an impurity element that can reduce steel performance. A high phosphorus content affects the welding performance of steel detrimentally, and it can reduce the low-temperature impact toughness of steel significantly. Phosphorus increases the brittle transition temperature of steel, and results in the formation of brittle steel at low temperature. In general, high-quality steel has a strict upper phosphorus-content limit of less than 0.015 mass%. In recent years, the reduction in lime consumption and slag quantity in the converter during ultra-low phosphorus steel production has become a research topic of great interest [1].

Extensive research has been conducted to improve the dephosphorization efficiency and to reduce smelting costs. In 2001, Ogawa et al. [2] reported that a new converter steelmaking technology MURC (Multi-Refining Converter) had been developed by Nippon Steel and tested on an 8-metric-ton converter. A new steelmaking dephosphorization process, which resulted in the development of the later double-slag process, was proposed to reduce the amount of limestone required and the slag produced. The process is divided into two stages. Desilication and dephosphorization are conducted in the first stage. Primary slag is removed at the end of this stage. Tapping is conducted after the second “decarburization” stage, and residual slag is left in the converter. Scrap and hot metal are added to the converter, and the process is repeated. In 2002, Kitamura et al. [3] conducted experiments at Nippon Steel to verify the MURC process. They found that solid-phase $2\text{CaO}\cdot\text{SiO}_2$, which exists in the slag, can absorb P_2O_5 during dephosphorization. In 2002, duplex converter dephosphorization technology and the older double-slag process were applied successfully in a 300-ton converter in Baosteel China and qualified super-low-phosphorus steel was produced for the first time. In 2003, the technological parameters of the MURC process at Nippon Steel were optimized by Kume [4]. Many reports on the application of the MURC process at Nippon Steel emerged thereafter [5, 6–10]. The amount of steel produced using the MURC process accounts for 55% of the total production at Nippon Steel and lime consumption in converter

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steelmaking decreased by more than 40 %. However, no detailed reports existed on key technologies, such as the treatment of the remaining slag, the basicity of the dephosphorization slag and oxygen blowing parameters, the dephosphorization process and deslagging. Researchers have since paid attention to and have studied this new steelmaking process [11, 12]. Posco and Korea Hyundai Company have both adopted the MURC process. As an evolution from the MURC process, Baosteel developed another process and applied independent intellectual rights of BRP (Baosteel BOF Refining Process) dephosphorization in 2004.

Although the older double-slag steelmaking process can be used to produce low- and ultra-low-phosphorus steel, an increased lime consumption and slag generation result over traditional single-slag steelmaking processes. In contrast, the double-slag process evolved from MURC has obvious advantages in the production of ultra-low phosphorus steel and it can reduce the amount of final slag, converter lime, iron and other material consumption simultaneously. Advantages of the double-slag process resulted in it achieving extensive attention from researchers in recent years [13, 14]. Typically, the P_2O_5 content in converter steelmaking slag is ~1–3 mass% [15]. The remaining slag that solidifies in the last ladle furnace usually contains some P_2O_5 , with a maximum of up to ~2–3 mass%. Because the solidified slag that remains in the converter contains a certain amount of P_2O_5 , the P_2O_5 content in the slag from the double-slag process reaches up to ~2–3 mass%. P_2O_5 usually combines with CaO as phosphate in the slag. Low-basicity slag and an improved dephosphorization efficiency should be adopted in the double-slag process to reduce dephosphorization requirements in the converter and to reduce material consumption and the amount of slag formed.

The Si and P content in hot metal of the Tangsteel Company China is usually high and fluctuates significantly. Measures such as a high lime consumption and a large amount of slag have been adopted to solve this problem in conventional smelting. However, problems such as a poor operation stability, difficulty in the production of low phosphorus steel and a high production cost have ensued. In this paper, the double-slag process was studied for a 150-metric ton converter at the Tang Steel Group. The principle of the double-slag smelting process and its influence on the dephosphorization ratio are discussed. The effect of a double-slag process on reducing converter material consumption, decreasing the slag amount and low-phosphorus steel production were analyzed.

Double-slag process principle

The double-slag smelting process is a typical clean steel-production process. This technology can reduce the material consumption and the amount of final slag compared with conventional smelting [16]. The principle of the double-slag process is that the end-point slag remains and is solidified in the converter as dephosphorization slag feed to the next furnace.

As is shown in Figure 1, the double-slag steelmaking process at Tangsteel Company China includes the following main steps. Step 1, slag solidification: the remaining slag in the converter is combined with slag splashing technology and is blown onto the lining to achieve rapid solidification of the remaining slag. Step 2, confirm: we need to confirm that there is no residue of liquid slag after slag solidification. Scrap and hot metal are added. Step 3, dephosphorization reaction stage. Step 4, residual slag after the dephosphorization reaction stage is poured out timeously. Step 5, the second blowing stage is the decarburization reaction stage, which uses blowing oxygen. Step 6, the amount of remaining slag is determined based on the hot metal content in the next furnace. Finally, tapping occurs and slag remains in the converter.

Experimental procedure

The production of SPHC (hot rolled steel plate and strip) in a 150-metric ton converter at the Tang Steel Group was the focus of this study. An industrial experiment was carried out in 100 consecutive furnaces using the double-slag process. The temperature at the end of dephosphorization, the basicity of the slag, the oxygen-blowing pressure and the smelting time were evaluated in each experiment. The hot-metal temperature and composition during production are shown in Table 1. The Si content in the hot metal affects its mobility. Fluctuations in the composition of hot metal during production can be reduced by changing the remaining amount of slag and lime according to fluctuations in $\omega[Si]$ in molten iron. A system for determining the expected residual slag quantity as used by Tangsteel Company China is shown in Table 2 and was used in the experimental design.

The oxygen content of the blowing end-point should be controlled such that $\omega[O] \leq 800$ ppm. To ensure slag splashing, appropriate measures to prolong the slag-splashing operation time were used in the experiment.

Figure 1: Schematic diagram of double-slag steelmaking process.

Table 1: Raw material condition of industrial trial with a 150 metric ton BOF.

Hot metal composition/mass%				Temperature/K
$\omega[\text{C}]$	$\omega[\text{Si}]$	$\omega[\text{P}]$	$\omega[\text{Mn}]$	
4.25~4.67	0.16~0.58	0.11~0.12	0.16~0.25	1497 ~1626

Table 2: Remaining slag quantity system.

$\omega[\text{Si}]/\text{mass}\%$	Residue slag and lime addition
$0.35 \leq \omega[\text{Si}] < 0.60$	All slag remained no lime addition
$0.60 \leq \omega[\text{Si}] \leq 0.70$	Half slag remained + 1.5~2.5 metric ton lime
$\omega[\text{Si}] > 0.70$	No slag remained + 3~4 metric ton lime

A high-low-low oxygen lance control mode was chosen for the double-slag smelting process in the dephosphorization stage. The lance height and feeding condition of the double-slag process are shown in Figure 2.

Results and discussion

If the dephosphorization reaction is insufficient during the double-slag process, the load is increased in the decarburization stage. In severe cases, this can result in an unknown end-point phosphorus content in the converter so that supplemental blowing or other remedial

Figure 2: Lance height and feeding condition of double-slag process.

measures are required. The experiment results were analyzed and we discussed the effect of the double-slag process on the dephosphorization ratio as a function of the temperature, slag basicity, blowing oxygen pressure, slag pour-out time and lance height.

The dephosphorization ratio (η_P) is defined as [17–19]:

$$\eta_P = \frac{w[P]_0 - w[P]_e}{w[P]_0} \times 100\% \quad (1)$$

where $w[P]_0$ is the initial phosphorus content in liquid steel before dephosphorization and $w[P]_e$ is the end-point phosphorus content in molten steel.

Efficient dephosphorization by double-slag process

Temperature at the end of the dephosphorization stage

Figure 3 shows the change principles of the dephosphorization ratio versus temperature. With an increase in temperature, the dephosphorization ratio also increased to achieve an average of 51.74 % over this period ($T < 1660$ K/1387 °C). Above 1723 K (1450 °C), the effect of temperature on the dephosphorization reaction became key. The dephosphorization ratio decreased with increase in temperature during this period ($T > 1723$ K/1450 °C), and the average dephosphorization ratio was 52.29 %. A temperature between 1660 K (1387 °C) and 1723 K (1450 °C), which is the low-temperature range for converter smelting, was conducive to the dephosphorization reaction. The average dephosphorization ratio reached a maximum of 57.3 %. The dephosphorization reaction at the interface of the steel slag-smelting time can be expressed by eqs (2)–(4) [20, 21]:

Figure 3: Effect of temperature on dephosphorization ratio.

$$\Delta G_T^\ominus = -832384 + 632.65T \quad (3)$$

$$\log k_p = \log \frac{a(P_2O_5)}{a_{[P]}^2 a_{[O]}^5} = \log \frac{x_{P_2O_5} \gamma_{P_2O_5}}{w[P]^2 f_{[P]}^2 w[O]^5 f_{[O]}^5} \quad (4)$$

$$= \frac{43492}{T} - 33.056$$

Equation (3) indicates that the dephosphorization reaction is exothermic. Equation (4) shows that the dephosphorization reaction equilibrium constant k_p increases with a decrease in reaction temperature, which indicates that a low temperature is conducive to dephosphorization. The

basic principle of double-slag steelmaking is to make full use of a low temperature during the early stage, which is a conducive thermodynamic condition for dephosphorization. Figure 4 shows that the reaction equilibrium constant during the primary blowing period is $\sim 10^2$ – 10^5 times the end point of blowing. The end-point slag, which almost lost its dephosphorization ability at high temperature, was reused for dephosphorization in the low-temperature stage of the subsequent furnace (because of the low temperature, the slag dephosphorization ability is restored) in the double-slag smelting process. Before the smelting temperature increased above that which is not conducive to dephosphorization, the slag of the dephosphorization stage was poured out rapidly.

Rapid and efficient dephosphorization was achieved during the low-temperature period after using the double-slag smelting process. After adopting double-slag smelting, the end-point phosphorus content with an average of 0.018 mass% was reduced to an average of 0.011 mass% and the dephosphorization efficiency increased by more than 6

Figure 4: Relationship between dephosphorization reaction equilibrium constant and temperature.

Slag basicity

As shown in Figure 5, the dephosphorization ratio increased with increase in slag basicity. Because the CaO is also left in the re-used slag by slag-splashing technology in the double-slag process, the basicity of the slag (R) should be controlled precisely. Equation (3) shows that the phosphorus in the steel after oxidation can bind rapidly with basic oxides in the slag to form stable phosphates. The increase in basic oxide content in the slag will decrease the activity coefficient of the P_2O_5 in slag, and $w[P]$. An increase in slag basicity can

Figure 5: Influence of basicity on dephosphorization ratio.

improve the dephosphorization ratio. However, if this value is too high, it will lead to a worsening slag fluidity. The slag viscosity normally decreases with increasing slag basicity due to the breakdown of the silica network formed in the fully liquid slag. On the other hand, the slag melting point increases with increasing basicity. When the slag basicity increase to the point the solid phase become saturated, the slag viscosity will increase sharply so that its fluidity will be worsen. Or more seriously, slag cannot be poured out smoothly. Therefore, the slag basicity should be controlled within a suitable range. When $R < 1.5$, the dephosphorization ratio increased rapidly as the basicity increased. When the slag basicity reached 1.7, the dephosphorization ratio reached a maximum of 71%. Therefore, the ideal dephosphorization slag basicity for the double-slag smelting process should be controlled between 1.5 and 2.0.

Blowing oxygen pressure and lance

The blowing dephosphorization ratio decreased with an increase in oxygen pressure (Figure 6). The main reason for this behavior is that the molten bath temperature increased rapidly after the blowing oxygen pressure was enhanced, which led to a significant shortening of the low-temperature dephosphorization period. This resulted in a decrease in dephosphorization ratio.

The dephosphorization reaction occurs mainly at the slag/metal interface and in the slag. Accordingly, weak stirring with blowing in the bottom became limiting factors for dephosphorization. A key parameter in double-slag smelting processing is the lower lance position,

Figure 6: Effect of blowing oxygen pressure on dephosphorization ratio.

which can enhance stirring in the bath and promote mass transfer of [P] in molten steel [22, 23]. The lance height system is shown in Figure 2. Compared with the single-slag process, the oxygen lance height in the prior period was reduced by $\sim 0.1\text{--}0.2\text{m}$ so that stirring could be enhanced. Combined with a high-low-low lance height system, [P] in the molten bath was stirred fully and transferred to the slag/metal interface where [P] reacted with FeO entering slag. The lance height system overcame the insufficient kinetic conditions in the single-slag smelting process. The double-slag process can inhibit increases in splash, strengthen stirring and promote [P] transfer to the slag/metal interface.

Deslagging time

As shown in Figure 7, when the blowing time was less than 4 min, the dephosphorization ratio showed an increasing trend with increase in reaction time. When the blowing time exceeded 6 min, the carbon-oxygen reaction became violent, the FeO content in the slag and the steel temperature both increased. The dephosphorization ratio showed a clear downward trend at this time. For a blowing time between 4 and 6 min, the dephosphorization ratio was higher and more stable than at other times and the dephosphorization ratio reached 54% on average. The dephosphorization ratio increased first and then decreased under a combined influence of temperature, basicity and FeO content in the slag. Therefore, deslagging should be carried out after the peak in the dephosphorization ratio curve. The optimal time for the slag to be poured out was at a blowing time of ~ 6 min.

Figure 7: Effect of blowing time on dephosphorization ratio.

Figure 8: Relationship between iron fraction in slag and slag basicity at the end of dephosphorization.

Slag–iron separation and rapid deslagging

Grinding slag is usually weighed after magnetic separation to determine the amount of metal in the slag. This method is one of the most effective means to evaluate the effect of slag–iron separation. Rapid slag–iron separation would influence the smooth running of production in the double-slag process. To ensure rapid slag–iron separation, the following measures were taken:

High-pressure N_2 blowing on the slag surface

After lance withdrawal at the end of dephosphorization, high-pressure N_2 was used as a purge to reduce slag foaming and gravity sedimentation. This was an ideal method to facilitate slag–iron separation.

Slag basicity (R)

As shown in Figures 8 and 9, the metal amount carried by the slag increased gradually with slag basicity, which provided a positive correlation trend. In contrast, the amount of slag decreased with increase in slag basicity, which presented a negative correlation trend. As mentioned in 4.1.2, the increase in slag basicity will lead to a sharp increase in slag viscosity, which could worsen the slag fluidity significantly. Slag–iron separation became more difficult and the amount of metal that was carried by the slag was enhanced. When the slag basicity reached 2.3, the metal proportion in the slag reached 44 %. The iron loss was large and affected the smelting

Figure 9: Relationship between deslagging amount and slag basicity at the end of dephosphorization.

time in the double-slag steelmaking process. Based on the impact of slag basicity on the dephosphorization ratio and the slag viscosity, the slag basicity should be controlled from 1.5 to 2.0.

FeO content in slag

The slag dries easily, which can lead to rephosphorization at the end of the converter smelting period. A key point in double-slag smelting is that the slag is poured out rapidly after dephosphorization and the FeO content in the slag is supplemented by secondary slagging and a reasonable lance height. The target is to inhibit

rephosphorization at the end of the converter smelting period. If enough slag could be poured out rapidly early during smelting it would affect the effect of dephosphorization directly. If the deslagging were insufficient, the basicity would increase, which would make it more difficult to pour the slag out. Thus, the slag fluidity would initiate a vicious cycle, and even result in an increase in the metal amount carried by the slag.

From the results in Figure 10, when the content of FeO in slag used in the double-slag smelting process was < 16 mass%, the slag was of inferior fluidity and the deslagging time was longer (5.5 min). These conditions are unfavorable for rapid deslagging and prolong the smelting period. With increase in FeO content in the slag, the slag fluidity improved gradually and the amount of slag increased.

The relationship between the content of FeO in the slag, the amount of slag poured out and the deslagging time was taken into account. When the content of FeO in the slag reached 16 mass%, the deslagging time reached a minimum (3.24 min). Therefore, the FeO content in the slag should be controlled from 16 mass% to 20 mass% in the double-slag smelting process so that a suitable dephosphorization ratio can be ensured and so that the dephosphorization slag could be poured out rapidly at the same time.

Figure 10: Relationship between (FeO) at the end of dephosphorization and deslagging amount and time.

Applied effect

Advantages in the dephosphorization effect or in the consumption of lime and slag materials were achieved in the double-slag smelting process compared with the conventional smelting (single-slag) process.

As shown in Figure 11, in the conventional smelting process, the end-point content of phosphorus was 0.012 mass%–0.021 mass% and the mean value was 0.018 mass%. After adopting the double-slag process, the end-point content of phosphorus was reduced to 0.006–0.016 mass% with a mean value of 0.011 mass%. The dephosphorization efficiency increased by more than 6%.

A comparison of the slag material consumption between the conventional single-slag smelting process and the double-slag process is shown in Figure 12. The slag material costs were reduced significantly after adopting the double-slag process. The lime consumption decreased by an average of 9.14 kg per metric ton of steel. The average saving of light-burned dolomite and dolomite were 1.91 kg per metric ton steel and 1.25 kg per metric ton steel. The average cost saving of slag material was up to 11.68 kg per metric ton steel.

Figure 11: Comparison of end-point phosphorus content between single- and double-slag process.

Figure 12: Comparison of slag material cost between single- and double-slag process.

The use of scrap was reduced by 3.05 kg per metric ton steel, and the consumption of other metal materials in the double-slag process increased slightly as shown in Figure 13.

As shown in Figure 14, the smelting time of the single-slag process and double-slag process were compared. The test results show that the smelting cycle of the double-slag process increased by 4.77 min. Deslagging at the end of dephosphorization in the double-slag process can lead to an increase in smelting cycle. Therefore, efficient production organization and scheduling is particularly important. The efficient dephosphorization and rapid iron-slag separation technology led to an accelerated production speed and improved production efficiency after using the double-slag smelting process. The total smelting cycle of the double-slag process increased by only 4 min.

Figure 13: Comparison of metal material cost between single- and double-slag process.

Figure 14: Comparison of smelting time between single- and double-slag process.

Conclusions

Industrial tests were conducted using a double-slag process in a 150-metric ton converter at the Tang Steel Group. The principle of a double-slag smelting process and its influence on the dephosphorization ratio were discussed. Conclusions are summarized as follows:

1. The double-slag steelmaking process uses a low temperature during the early stages, which is a conducive thermodynamic condition for dephosphorization. The end-point slag, which had almost lost its dephosphorization ability at high temperature was solidified to the inner lining surface and re-used for dephosphorization in the low-temperature stage of the subsequent furnace (because of the low temperature, the slag dephosphorization ability was restored) in the double-slag smelting process.
2. To form a good fluidity and moderately foamed slag, a low basicity should be used in the dephosphorization stage (R ranges from 1.5 to 2.0) in the double-slag process. Rapid and sufficient deslagging could be achieved and problematic high amounts of metal iron in the slag could be solved by using the double-slag process. When the slag basicity reached 1.7, the dephosphorization ratio reached a maximum of 71%.
3. A key factor of the double-slag smelting process is to enhance the stirring intensity strength in the molten bath and to promote the mass transfer of $[P]$ in molten steel. A low oxygen lance height was used in the dephosphorization stage in the double-slag smelting process to intensify bath agitation and to promote the dephosphorization reaction. The phosphorus end-point content was reduced from an average of 0.018 mass% to an average of 0.011 mass%, and the dephosphorization efficiency was increased by more than 6%.
4. Rapid deslagging after dephosphorization could reduce rephosphorization in the later smelting stage. Dephosphorization slag could be poured out rapidly when the FeO content in the slag was controlled from 16 mass% to 20 mass%. The production speed was accelerated and the production efficiency improved after using the double-slag smelting process. The double-slag process smelting cycle increased by only 4 min. The cost of the slag material and the metal material were reduced.

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