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LATS refining ladle slag modifying with $CaO\text{-}CaF_2$

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Abstract: To reduce the slag sticking onto the snorkel of the ladle during the ladle alloying treatment station (LATS) process, $CaO\text{-}CaF_2$ (the mass ratio of CaO/CaF_2 is 1:1) was employed as the modifier of the LATS refining ladle slag. The effect of $CaO\text{-}CaF_2$ on the melting point, viscosity, and desulfurizing capability of the ladle slag was investigated. The melting point of the unmodified ladle slag is 1439°C. When adding 20wt% $CaO\text{-}CaF_2$, the melting point is decreased to 1327°C. At 1500°C, the viscosity of the unmodified ladle slag is 6.5 Pa·s, which can be decreased lower than 2 Pa·s by adding more than 10wt% $CaO\text{-}CaF_2$. The experimental results of desulfurization of the melts show that the desulfurizing power of the ladle slag can be enhanced by adding $CaO\text{-}CaF_2$.

Key words: LATS; ladle refining; slag; melting point; viscosity; desulfurization

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1. Introduction

To meet the increasing requirements of steel quality, the secondary refining processes have become necessary to produce high-grade steels. Among the various second refining processes, LATS (ladle alloying treatment station) as one of the considerable processes has attracted so much attention owing to many advantages including the minor initial investment, low operating cost, and multi-refining functions [1]. The main functions of LATS refining process are bottom argon stirring, alloy components adjusting, and supplementary heating *via* oxygen blowing. All these functions are carried out in a ladle with the snorkel sealed and the bottom argon bubbling. In the steelmaking plant of Shanghai's No.1 Iron & Steel Corp., Baosteel Group, the LATS refining process is employed in the production of low-alloy steels and carbon steels. During the LATS operations, the recovery rate of the alloying agents is much higher than those of the other secondary refining methods reported before [1-2]. After adopting the LATS processing, the hit ratio of the metal temperature and alloys composition is nearly up to a hundred percent, which provides qualified metal for continuous casting. However, when the ladle arrives at the refining station, there is about 300-400 kg of steelmaking slag from the converter, which is mixed with the deoxidizing products to form the ladle slag floating on the metal bath. The snorkel often thickens with a serious build up, because of the ladle slag sticking on to the refractory. So the weight and the volume of the snorkel are enhanced, which has many unfavorable impacts on the LATS operations [3]. On one side, the increased force of the gravity and thermal stress easily results in the refractory of the snorkel cracking and spalling off. So the operating life of the snorkel is greatly shortened. On the other side, the massive slag sticking onto the snorkel inevitably poses many difficulties with the operations. For example, if the slag ring is too big, the snorkel cannot be immersed into the bath of ladle. At the same time, if the snorkel is too heavy, its lifter is underpowered, which is a great potential safety hazard. So, how to reduce or even to eliminate the slag sticking onto the refining equipment has attracted great attentions of producers who adopt the same or similar secondary refining processes [3-4]. However, this problem has not been thoroughly solved because the mechanism of slag sticking on to the snorkel is very complicated.

The authors have carried out a series of studies on the physiochemical properties of the LATS refining ladle slag [5-6]. In this study, $CaO\text{-}CaF_2$ was employed as the modifier added into the LATS refining ladle slag.

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The melting point, viscosity, and desulfurizing capability of the modified ladle slag were studied, for decreasing its melting point and viscosity, aiming to reduce or even to eliminate slag sticking onto the snorkel.

2. Experimental

The melting point of slag was determined using a melting point measurer (model SJY-1700, China). First, in the normal producing conditions, some slag was taken from the ladle as soon as the LATS refining process was finished. The slag specimens picked from many different ladles were mixed up and then crushed and ground into a fine powder. Then the modifier, CaO-CaF_2 (mass ratio is 1:1) was proportionally added into the slag, followed by grinding the mixture into the homogenized fine powder. Finally, the powder was pressed in a cylindrical sampling mode to get the testing sample, whose size was ϕ2 mm×3 mm. The temperature of the sample was directly measured by a Pt-PtRd thermocouple. The accuracy of temperature control was about ±2°C. The temperature at which the height of the slag sample lowering into one-half of its original height is defined as the sample's melting point. Hence, this method for determining the melting point is called the hemisphere method [6].

The measurements of viscosity were conducted using a rotating viscometer (model RTW-08, China). The slag specimens were picked up from different ladles as soon as the LATS refining processes were finished. Then the ladle slag mixture was respectively added with 0, 5wt%, 10wt%, 15wt%, and 20wt% CaO-CaF_2 (mass ratio is 1:1) to get five slag specimens. To every slag specimen, about 120 g was charged into a graphite crucible with the size of ϕ40 mm×90 mm. The graphite crucible was put into the furnace, whose temperature was controlled by a computer. After the slag was melted completely, the temperature was kept constantly for about 20 min. Then the viscosity of the slag was continuously measured keeping its temperature at a downward speed of 10°C/min.

The experiments on desulfurization were conducted in a tubular mode $MoSi_2$ furnace. Both metal and slag specimens were taken from the ladles as soon as the LATS processes were finished. The initial composition of the metal was analyzed using a spectrum analyzer (model GS-1000, Germany). To every slag specimen, CaO-CaF_2 was added to the extent of 10wt% of the ladle slag. The metal and the modified slag specimens were charged in a corundum crucible, which was protected by the graphite. Then the specimens were melted at 1600°C for 30 min. The metal samples were taken after melt-down for the analysis of the final composition.

3. Results and discussion

The composition of the experimental slag is similar to the final composition of the modified slag of LATS processing. It is assumed that the modified slag in LATS operation behaves similar to the slag of the test.

3.1. Effect of CaO-CaF_2 on the melting point of LATS refining ladle slag

Fig. 1 indicates the effect of adding CaO-CaF_2 on the melting point of the ladle slag. It is seen that the CaO-CaF_2 acting as the modifier takes on the remarkable effect of decreasing the melting temperature of the ladle slag. The melting point of the unmodified ladle slag is 1439°C whereas when the additional level of CaO-CaF_2 is up to 20wt%, the melting point of the modified ladle slag is decreased to 1327°C, which is lower than the temperature of the snorkel at the end of the LATS refining process. So the ladle slag will be still in a molten state till the snorkel is hoisted. So the slag sticking will be reduced.

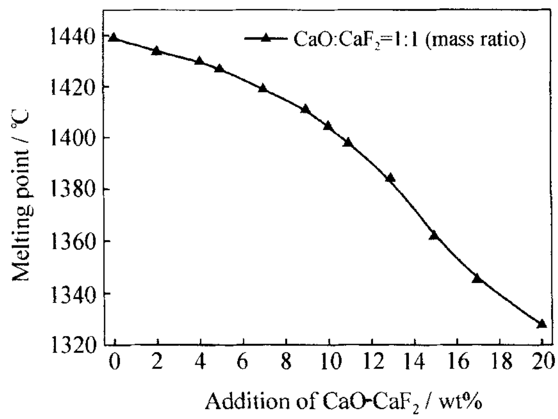

Fig. 1. Effect of adding CaO-CaF_2 on the melting point of the LATS refining ladle slag.

The ladle slag composition was analyzed by the chemical method. The slag specimens were picked from the sticking slag layer on the snorkel and from the ladle before and after LATS respectively. Table 1 shows the main composition of the slag in a quasi-ternary system Al_2O_3-SiO_2-CaO. Other components of the slag were converted to CaO, SiO_2, or Al_2O_3 accordingly, as basic, acidic, or amphoteric oxides. The composition points of the ladle slags are marked on the concentration triangle of Al_2O_3-CaO-SiO_2, as shown in Fig. 2. The melting points of the ladle slags are indicated according to the phase diagram of the Al_2O_3-CaO-SiO_2 ternary system, which are higher than the hemisphere point temperatures of the actual slags [4]. As some other fluxing oxides existed in the actual slag, for example, MgO and Fe_tO, its melting point was lowered somewhat.