Effect of Additives on Melting Point and Viscosity of RH Refining Slag

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Abstract: To get suitable ladle slag which can avoid slag sticking onto the RH immersion tube during RH refining process of IF steel, the effect of composition on melting point and viscosity of RH refining ladle slag was studied by different additives which is based on CaO. The results of melting point and viscosity testing experiments indicates that, the melting point and viscosity of RH refining ladle slag would decrease effectively with the add of experimental additives. During RH refining process of IF steel, adjusting the basicity to 4~5, and the content of Al_2O_3 to 14%~15% by adding additives, it can avoid slag sticking onto the RH immersion tube efficiently, for the reason that the melting point of ladle slag is about 1280 °C, and the viscosity is only 0.65 Pa·s.

Keywords: RH immersion tube, slag buildup, viscosity, melting point, additives.

1. INTRODUCTION

RH, acting as one of the most important secondary refining processes, has been paid considerable attention in the production of high quality clean steel. The refining slag produced in the steelmaking process may have the features of high oxidizability and crystallinity, one case in point is the RH refining slag of China Panzhihua Iron & Steel Co., which is a short slag with high melting point and strong oxidizing property because of containing much TiO_2, V_2O_5 and FeO [1]. Its melting point is 1350-1400 °C, which may be 100 °C higher than common refining slag. What's more, the temperature interval from good fluidity to no fluidity is only 20-30 °C [2]. For this slag has high crystallinity, the high melting point phase maybe precipitate form molten slag during refining process. It might bond onto refractory of steelmaking device, which has many unfavorable impacts on refining operation [3]. The common solution is that altering chemical composition of ladle slag for adjusting physicochemical properties of ladle slag by additives [4-9].

When determining the viscosity of this kind of slag, it may have a lot of shortcomings by using the rotating cylinder method. Such as the slag may bond onto the refractory equipment and erode it in the laboratory, which may lead to the failure of experiment..

This article devises several kinds of additives mainly based on CaO aimed at the high crystallinity and strongly oxidizability refining slag sticking onto the RH immersion tube during RH refining process, and suitable method for viscosity determination is taken to this kind of slag. In order to get suitable ladle slag which can avoid slag sticking onto the RH immersion tube during RH refining process of IF steel, the effect of composition on melting point and viscosity of RH refining ladle slag was studied by different additives.

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2. EXPERIMENTS

2.1. Composition of Additives and Slag

Three kinds of ladle slag additives were devised which is based on CaO, showing in Table **1**. Composition of the slag shows in Table **2**. Production practice showed that the No.1 slag, which is the basic slag, can easily stick onto the RH immersion tube during RH refining process. No.2- No.10 slag were obtained by adding different quantity of additives into the basic slag No.1 so as to study the effect of additives on the properties of RH refining slag. No.2, No.3 and No.4 slag added 10% of A, B and C respectively; No.5, No.6 and No.7 slag s added 20% of A, B and C respectively; No.8, No.9 and No.10 slag added 30% of A, B and C respectively. The basicity of slag showing below,

$$R=[CaO\%+(56/78)CaF_2\%)]/SiO_2\% \tag{1}$$

where R is the basicity of slag in equation (1).

Table 1. Chemical Composition of Additives

Kinds Name	Chemical Composition		
	CaO (%)	CaF_2 (%)	Al_2O_3 (%)
A	57-68	22-35	8-14
B	65-72	14-18	13-16
C	75-80	16-22	<5

2.2. Test Method of Slag Melting Point

The hemisphere point temperature, considered as melting point, was measured by RH-05 melting point detector.

2.3. Test Method of Slag Viscosity

Based on the characteristics of slag composition, the fluid length of refining slag was measured firstly, then the viscosity was obtained with the help of relationship between viscosity and fluidity.

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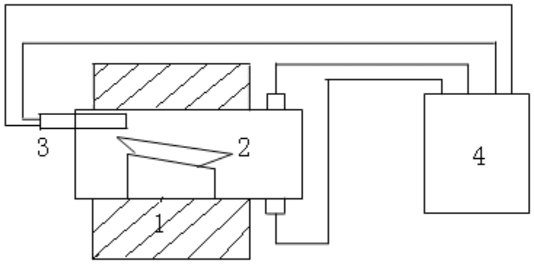
Fig. (**1**) shows the testing device for slag fluid length. Firstly, furnace temperature was held in a fixed value. Secondly, the samples were put into the furnace for a few minutes. Finally, taking out the samples and measuring its fluid length. The experimental temperature was 1500 °C.



1 - resistance furnace; 2 - porcelain boat;
3 - thermocouple; 4 - temperature controlling system

Fig. (1). Schematic of testing device for slag fluid length.

2.4. Experimental Plans

Fixing Experiment Conditions

The influencing factors on fluid length are complicated, such as rake angle, samples quality, holding time and so on. For measurement purposes, it is appropriate that the fluid length of molten slag is 1/3 to 2/3 of porcelain boat length. Base on this request, the experiment conditions were fixed by many experiments.

Relationship of Viscosity and Flown Length

Measuring fluid length of the slag whose viscosity was known and similar to the refining slag in above experiment conditions, then the relationship between fluid length and viscosity is built by regression analysis.

Viscosity and Melting Point Measurement of the Slag

Firstly, on the normal operation conditions, slag was taken from the ladle before the RH refining. The slag had been picked up from many different refining ladles. Following the additives with different contents of CaO and flux were proportionally added to the slag, followed by pre-melting the mixture for homogenizing. Finally, measuring the melting point and viscosity.

The effect slag composition on melting point and viscosity were studied with above experiments for reducing the slag buildup.

The composition of additives were shown in Table **1**. The slag was prepared by adding different additives to refining slag picked up in production field, and then measuring its melting point and viscosity.

The XRD Analysis of Slag

First were the fragmentation of slag and preparation of powder test sample, then was the XRD analysis.

3. RESULTS AND DISCUSSION

3.1. Relationship Between Viscosity and Flown Length

Table **3** shows the experiment conditions under the request of fluid length. Fig. (**2**) shows the relationship of viscosity and flown length under conditions in Table **2**.

Table 2. Composition of Slag

No.	basicity	CaO/Al_2O_3	CaO/MgO	FeO	Others
No.1	2.73	1.63	2.88	15.0-18.2	10.05
No.2	3.27	1.86	3.46	14.8-16.3	11.86
No.3	3.36	1.96	3.56	14.5-17.3	10.50
No.4	3.45	2.07	3.66	14.2-16.6	10.95
No.5	3.82	2.01	4.04	12.1-14.8	13.38
No.6	4.00	2.06	4.23	13.4-15.7	10.88
No.7	4.18	2.50	4.42	12.3-14.2	11.71
No.8	4.36	2.24	4.62	11.1-13.8	14.65
No.9	4.64	2.23	4.90	10.5-14.3	11.19
No.10	4.91	2.94	5.19	12.4-13.9	12.34

Table 3. Experiment Conditions

Rake Angle (°)	Samples Diameter (mm)	Samples Quality (g)	Holding Time (min)
7	6.0	0.400±0.05	5

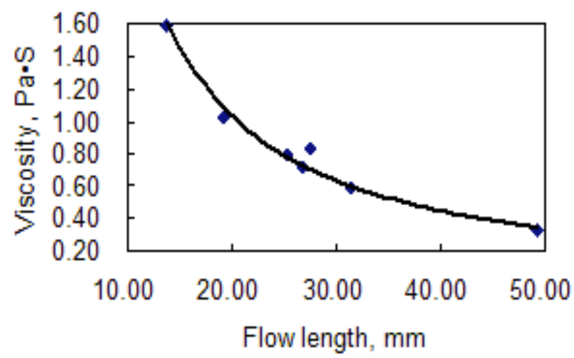


Fig. (2). The relationship of flow length and viscosity.

The relational expression built by regression analysis is

$$\eta = 36.849 \times L^{-1.1935} \tag{2}$$

where L is fluid length(mm), η is viscosity(Pa·s). The variance of equation (2) is 0.974, indicating that this equation can appropriately describe the relationship between fluid length and viscosity.

3.2. The Effect of Additives on Melting Point and Viscosity of Refining Slag

Fig. (**3**) shows the measured melting point of slag. Fig. (**4**) shows the viscosity of slag, which is calculated by the measured flow length L and equation (2).

Figs. (**3**, **4**) show that No.1 slag has a higher melting point and viscosity. However, slag have a lower melting point and viscosity after adding additives, the more additives adding in the slag, the lower melting point and viscosity have. Especially for No.8, No.9 and No.10 slag, their melting point are less than 1300 °C. Obviously it is very favorable for avoiding slag sticking onto the RH immersion by reducing the melting point and viscosity of the slag.

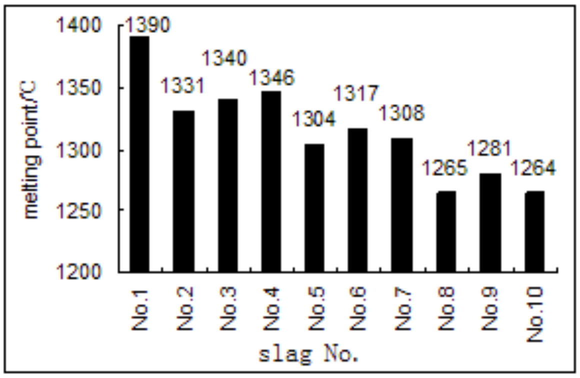


Fig. (3). Melting point of slag.

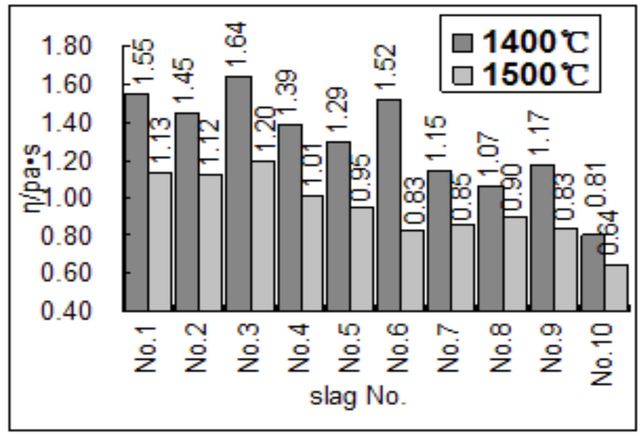


Fig. (4). Viscosity of slag.

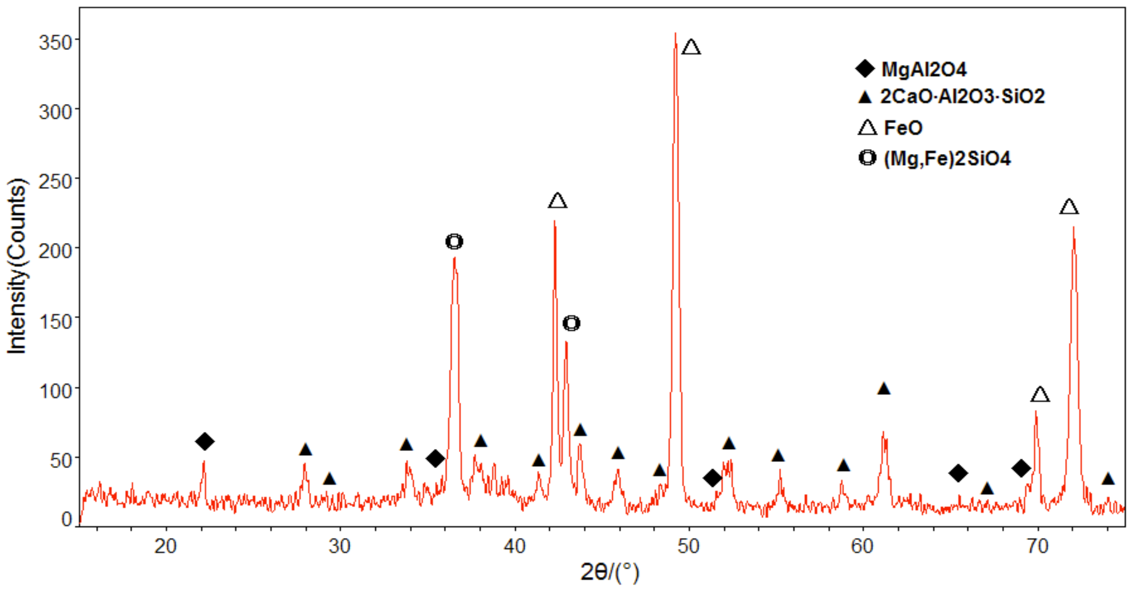


Fig. (5). XRD pattern of No.1 slag.

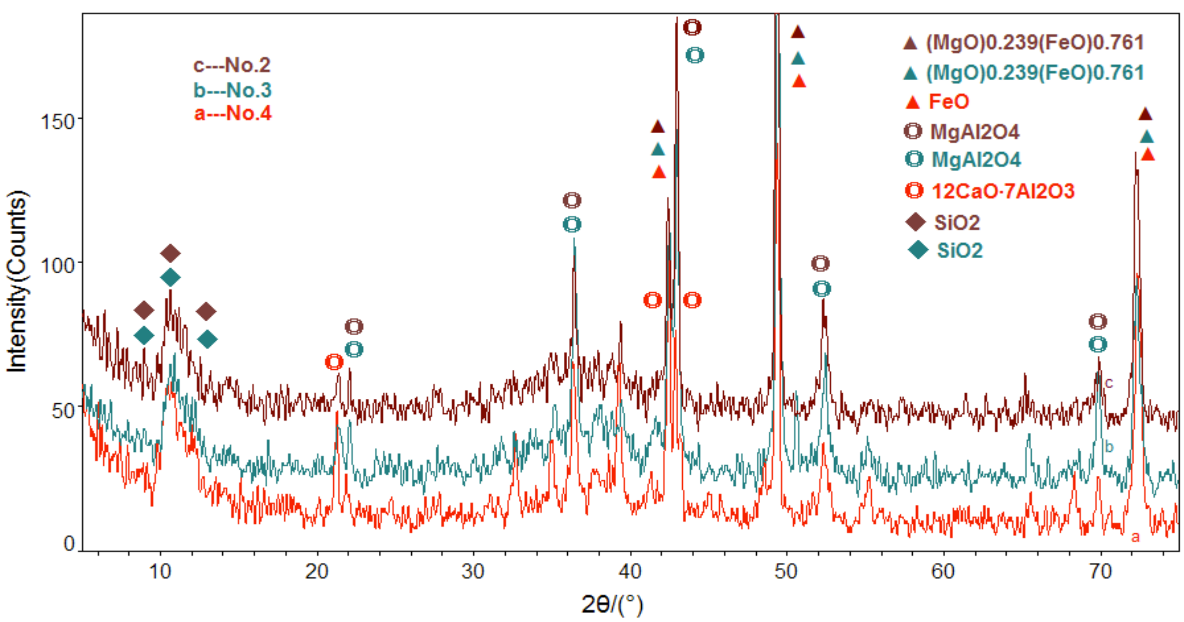


Fig. (6). XRD pattern of No.2, No.3 and No.4 slag.

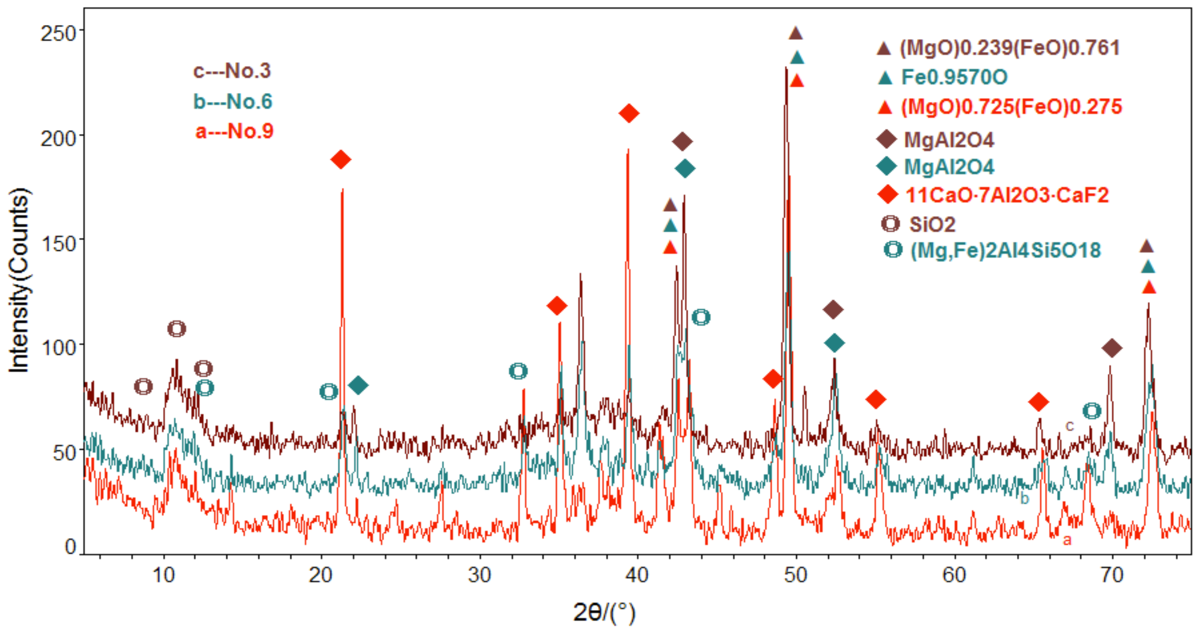


Fig. (7). XRD pattern of No.3, No.6 and No.9 slag.

Figs. (**5-7**) show the XRD pattern of slag samples. Table **4** shows the analysis results of phase composition of slag.

The melting point and viscosity of the slag have changed after adding additives because there is a direct relationship to the slag phase. Fig. (**5**) shows that MA exists in No.1, which is a phase with high melting point. However, a large number of $11CaO{\cdot}7Al_2O_3{\cdot}CaF_2$ appear in No.9-obtained by adding 30% additives B into No.1, which is a phase with low melting point. Physical properties of slag changed with the adding of additives, that is why No.1 has a higher melting point and viscosity than No.9.

Fig. (**6**) shows that when the same amount of additives is added, the MA reduces and $12CaO{\cdot}7Al_2O_3$(or$11CaO{\cdot}7Al_2O_3{\cdot}CaF_2$), non-crystalline substance increase with the increase of CaO content.

Fig. (**7**) shows that when the same content of additives is added, the MA reduces with the increase of additives amount. MgO combines with FeO to form oxide solid solution, and Al_2O_3 forms $12CaO{\cdot}7Al_2O_3$ mainly. Especially, $12CaO{\cdot}7Al_2O_3$ or $11CaO{\cdot}7Al_2O_3{\cdot}CaF_2$ increases and the non-crystalline substance increase Significantly in the slag with the increase of slag basicity.

As stated previously, the composition of RH slag can adjust by adding additives, then the precipitation phases of MA can be efficiently inhibited, so as to improve the physical properties related to the slag sticking. It can be concluded that No.4, No.7, No.9 and No.10 have a better property-changing.

3.3. The Effect of Basicity on Melting Point and Viscosity of Refining Slag

Fig. (**8**) shows the effect of basicity on melting point, and Fig. (**9**) shows the effect of basicity on viscosity at 1500 °C. It can be found that, with slag basicity increasing, melting point and viscosity would decrease deeply. The main reason

Table 4. Phase Composition of Slag

Slag No.	Main Phase	Micro Phase
No.1	FeO, (Mg, Fe)$_2$SiO$_4$, MA	gehlentie
No.2	(MgO)$_{0.239}$(FeO)$_{0.761}$, MA, SiO$_2$	non-crystalline substance
No.3	(MgO)$_{0.239}$(FeO)$_{0.761}$, MA, SiO$_2$	non-crystalline substance
No.4	FeO, $12CaO{\cdot}7Al_2O_3$	Portland phase, non-crystalline substance
No.5	Fe$_{0.942}$O, Portland phase, MA	non-crystalline substance
No.6	Fe$_{0.9570}$O, Portland phase, MA、 11CaO·7Al2O3·CaF2	non-crystalline substance
No.7	(MgO)$_{0.593}$(FeO)$_{0.407}$,$11CaO{\cdot}7Al_2O_3{\cdot}CaF_2$	Portland phase, SiO$_2$, non-crystalline substance
No.8	(MgO)$_{0.432}$(FeO)$_{0.568}$,$11CaO{\cdot}7Al_2O_3{\cdot}CaF_2$	spinel, (SiO$_2$)$_x$, non-crystalline substance
No.9	(MgO)$_{0.725}$(FeO)$_{0.275}$,$11CaO{\cdot}7Al_2O_3{\cdot}CaF_2$	SiO$_2$, non-crystalline substance
No.10	Fe$_{0.942}$O, $11CaO{\cdot}7Al_2O_3{\cdot}CaF_2$	(SiO$_2$)$_{72}$, non-crystalline substance

MA：$MgAl_2O_4$.

is that the activity of O^{2-} rises sharply with the contents of CaO increasing. This change is good for the dissolution of Al_2O_3, which can remarkably decrease the slag melting point and viscosity. Under the present condition, the slag basicity is about 2.7, its melting point is about 1400 °C and viscosity is about 1.10 Pa·s at 1500 °C respectively. However, the refining slag melting point and viscosity has a large decrease when adjusting the basicity to 4-5 by additives which is a benefit for reducing immersion tube buildup.

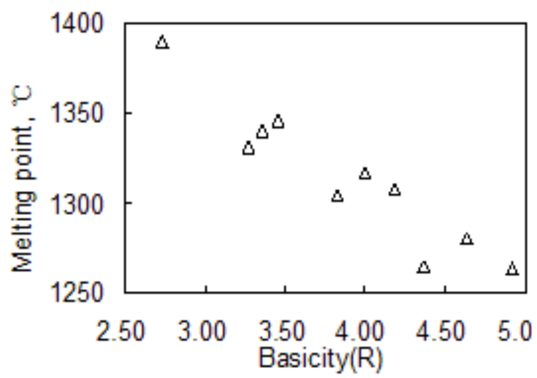


Fig. (8). Effect of basicity on slag melting point.

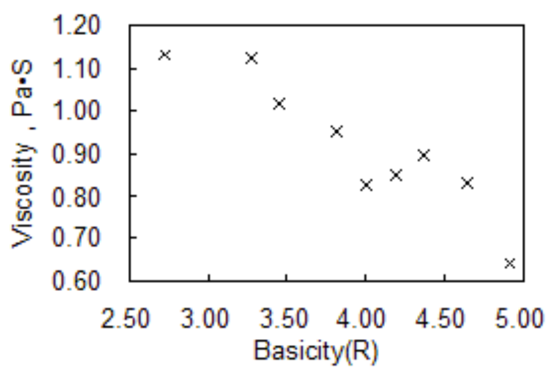


Fig. (9). Effect of basicity on slag viscosity.

3.4. The Effect of Al_2O_3 on Melting Point and Viscosity of Refining Slag

Fig. (**10**) shows the effect of Al_2O_3 on melting point, and Fig. (**11**) shows the effect of Al_2O_3 on viscosity at 1500 °C. We can see from those two figures that, with the contents of Al_2O_3 increasing, slag melting point and viscosity would rise sharply. The primary reason is that, with the contents of Al_2O_3 increasing, the crystallizing rate of high melting point phase, such as $CaO{\cdot}Al_2O_3$ and $CaO{\cdot}6Al_2O_3$, would increase and may generate many multiple oxides. Therefore, the contents of Al_2O_3 should be appropriate for reducing amount of slag building-up. As can be seen from Figs. (**10**, **11**), slag has proper melting and viscosity when the mass fraction of Al_2O_3 is 15%.

3.5. The Effect of CaF_2 on Melting Point and Viscosity of Refining Slag

Fig. (**12**) shows the effect of CaF_2 on melting point, and Fig. (**13**) shows the effect of CaF_2 on viscosity at 1500 °C. It can be found from Figs. (**12**, **13**) that, with slag basicity increasing, melting point and viscosity would decrease sharply. The reason is that CaF_2 has a low melting point. Meanwhile, some low melting point eutectics would appear by the reaction of CaF_2 and other oxides. For example, one of these eutectics is $CaF_2{\cdot}Al_2O_3$, whose eutectic temperature is about 1400 °C. The appearance of these low melting point eutectic can reduce the free high melting point phases, at the same time, F^- can improve the slag fluidity by spuring the composite anion on to decomposing.

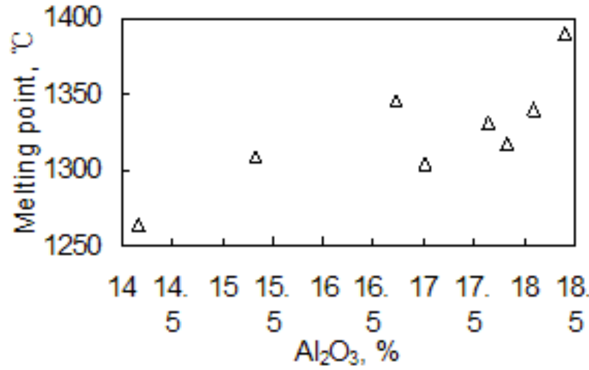


Fig. (10). Effect of Al_2O_3 on slag melting point.

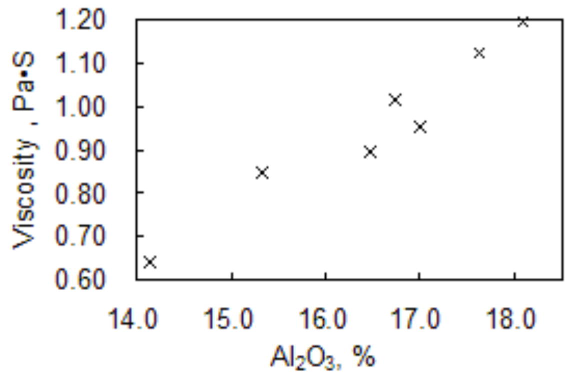


Fig. (11). Effect of Al_2O_3 on slag viscosity.

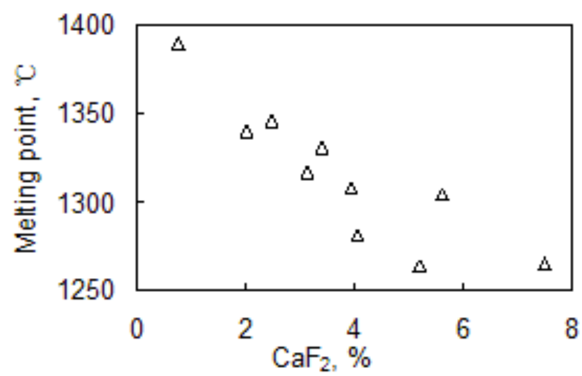


Fig. (12). Effect of CaF_2 on slag melting point.

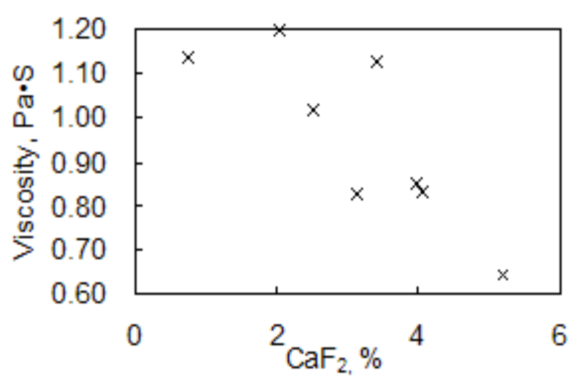


Fig. (13). Effect of CaF_2 on slag viscosity.

However, the mass fractions of CaF_2 should be no more than 5%, for guaranteeing refining effectiveness, and considering manufacture cost and environmental protection.

4. CONCLUSIONS

(1) The melting point and viscosity of high oxidizability refining slag can be easily determinated. The relationship between viscosity η and fluid length L is

$$\eta = 36.849 \times L^{-1.1935}$$

(2) It is found that, within the composition range determined by the experiment, the added additives based on CaO can effectively reduce the melting point and viscosity of RH refining ladle slag, so as to improve slag sticking onto the RH immersion tube.

(3) For the problem of slag building-up onto RH immersion tube of Panzhihua Steel during RH refining process, the results of experiments indicate that, altering the basicity to 4-5, mass fractions of Al_2O_3 to 15% by additives under present condition, the refining slag melting point is 1280 °C, and the viscosity is 0.65Pa·s at 1500 °C. The slag has a lower melting point and good fluidity which can reduce amount of slag building-up effectively.

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