The Effect on B_2O_3 Replacing CaF_2 of High Ti-bearing Blast Furnace Slag

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Abstract. For improving the low flowability, promoting the separation between high Ti-bearing blast furnace slag and hot metal, and replacing CaF_2 which would pollute the environment, the influence of B_2O_3 and CaF_2 on apparent viscosity were investigated from 1340°C to 1475°C by SEM, viscometer, et al. The results show that B_2O_3 has a similar effect to the CaF_2 and can decrease the apparent viscosity of high Ti-bearing blast furnace slag. When the amount of B_2O_3 and CaF_2 is equal to 1%, the B_2O_3 to CaF_2 is 1:1. With increasing the B_2O_3 from 0 to 3%, the perovskite content gradually decreases, titaniferous augite increase, and the Ti(C, N) is almost constant.

Compared with ordinary ore smelting, TiO_2 produced by vanadium-Titanium Magnet smelting process of Panzhihua Steel and Iron Group Corporation accounts for about 22% of blast furnace slag, and the viscosity is higher than ordinary slag. Especially, TiO_2 in blast furnace slag will react with the unburned coal powder because of incomplete combustion, and the materials with high melting temperature appear, such as TiC, TiN, et al. These materials will further reduce the fluidity of blast furnace slag [1-5], aggravate the difficulty of separating the hot metal from slags and lead to furnace operating difficulty. In this case, the solvent CaF_2 is used to some extent. However, CaF_2 is a strategic resource, and has relatively large environmental pollution. The price of CaF_2 gradually increases because of mineral resources decreasing, which increases the production cost. Therefore, it is necessary to do some study on how to improve the fluidity of titanium-bearing blast furnace slag and limit the use of solvent CaF_2.

Z. T. Zhang et al [6] did some research on the disappearance of B_2O_3 and Na_2O in fluoride-free slag from 1300°C to 1400°C by thermogravimetric analysis (TGA). Y. H. Lin et al [7] studied the effect and mechanism of B_2O_3 on apparent viscosity of Ti-bearing blast furnace slag, believed that B2o3 can reduce the apparent viscosity of high Ti-bearing blast furnace slag to some extent and can increase the fluidity of slag. Nakamoto et al [8] studied the evolution rule of molten silicate with B_2O_3, CaF_2 and Na_2O. S. Ren et al [9] do some research on reduction mechanism of B_2O_3 on FeO by means of EPMA and other methods under constant temperature conditions. The samples were obtained by argon quenching. G. R. Li et al [10] studied the change law of slag viscosity after environmental B_2O_3 replacing SiO_2 for CaO-BaO-SiO_2-Al_2O_3-CaF_2 system, and obtained the quantitative relationship between alkalinity and desulfurization rate. Z. H. Sun et al [11] studied the precipitation behavior of perovskite grains, and separating effect between hot metal and Ti-bearing blast furnace slag through controlling the additive amount of B_2O_3. S. Ren et al [12] analyzed the precipitation principal of Ti-bearing phase and the grain size of perovskite with high melting point which change with test temperature.

All these studies about blast furnace slag all indicate that B_2O_3 can improve flow performance of metallurgical slag. However, these researches focus on silicate slag, fluoride-free mold fluxes, et al [13-15]. There are few studies about influence of B_2O_3 replacing CaF_2. Based on this, this paper does some exploratory research on this problem.

Experimental

Materials, Apparatuses and Equipment

The experimental materials were synthesized by pure reagent according to chemical composition of Pangang slag, and then put in muffle furnace for high-temperature calcination and thermal insulation. Finally, the grain size between 50μm and 74μm was obtained.

As shown in Fig.1, the apparent viscosity of high Ti-bearing blast furnace slag is measured by means of the rotating cylinder method using digital viscometer. The 5 $MoSi_2$ elements were installed in furnace body and the maximum temperature could come up to 1550°C within an error of ±3°C. The furnace body could move up and down in vertical direction through hydraulic device. Before the start of experiment, the standard castor oil and SRM2 type slag [16] were used to calibrate viscometer at room and experimental temperature, respectively. In the experiment, the Mo crucible used for replacing graphite crucible is mainly to prevent the TiO_2 of blast furnace slag from reacting with C in graphite crucible. The basic composition of samples was listed in Table 1. The 0# sample was set as benchmark specimen, the addition amount of B_2O_3 in 1#, 3#, 6# and 8# sample were 0.5%, 1%, 2% and 3%, respectively; the addition amount of CaF_2 in 2#, 4#, 5# and 7# sample were 0.5%, 1%, 2% and 3%, respectively.

Experimental Procedure

The molybdenum crucible which filled about two third with high Ti-bearing blast furnace slag was placed on Al_2O_3 base and adjusted the position of Mo spindle to make it at the center of the molybdenum crucible. For preventing the possible reactions between Ti-bearing slag and air, high purity argon was put into furnace chamber for discharging the air, and the gas flow was controlled at 0.05L/min.

The holding time, experimental temperature and heating rate were respectively set to 240min, 1475°C and 5°C/min. After reaching 1475°C, the furnace body was slowly moved along the vertical direction to pre-set position by the hydraulic device. At this moment, the Mo spindle was completely immersed in the liquid slag. After the viscosity-temperature curve was stabilized, the liquid slag was cooled down by temperature control device, and the change rule of viscosity was recorded on computer. After measuring the apparent viscosity of high Ti-bearing blast furnace slag, it was heated again to 1475°C and stabilized there for 20min, then let the furnace body move slowly down through hydraulic device until the Mo spindle was completely removed out of the liquid slag.

The cooled sample was crushed and ground, and then the mineral composition and element distribution were analyzed by MLA650.

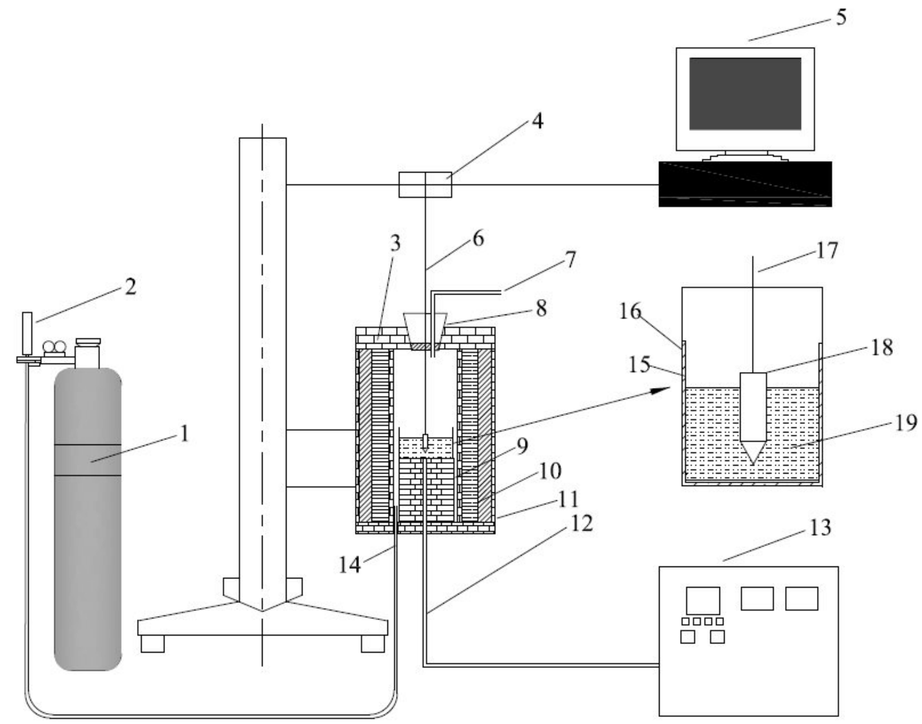

Fig. 1 Schematic diagram of experimental apparatus (1. Argon; 2. Flow meter; 3. Insulation brick; 4. Viscometer; 5. Computer; 6. Al_2O_3 shaft; 7. Air outlet; 8. Rubber stopper; 9. Al_2O_3 base; 10. $MoSi_2$ heating element; 11. Furnace shell; 12. Thermocouple; 13. Control cabinet; 14. Air inlet; 15. Molydenum lining; 16. Crucible; 17. Molydenum rod; 18. Molydenum spindle; 19. Molten slag)

Table 1 Chemical composition of samples (%)

	CaO	SiO_2	MgO	Al_2O_3	TiO_2	C	B_2O_3	CaF_2	R
0#	27.55	26.20	9.19	14.89	21.85	0.22	0	0	1.05
1#	27.33	26.02	9.19	14.89	21.85	0.22	0.5	0	1.05
2#	27.33	26.02	9.19	14.89	21.85	0.22	0	0.5	1.05
3#	27.02	25.73	9.19	14.89	21.85	0.22	1.0	0	1.05
4#	27.02	25.73	9.19	14.89	21.85	0.22	0	1.0	1.05
5#	26.51	25.24	9.19	14.89	21.85	0.22	0	2.0	1.05
6#	26.51	25.24	9.19	14.89	21.85	0.22	2.0	0	1.05
7#	26.00	24.75	9.19	14.89	21.85	0.22	0	3.0	1.05
8#	26.00	24.75	9.19	14.89	21.85	0.22	3.0	0	1.05

Results and Discussion

The Effect of B_2O_3 and CaF_2 on Apparent Viscosity of Ti-bearing Slag

The change rule of B_2O_3 and CaF_2 on apparent viscosity is shown in Fig.2. The ordinate is the apparent viscosity of Ti-bearing blast furnace slag, and the horizontal axis is the experimental temperature. The 0# sample was set as benchmark specimen, the addition amount of B_2O_3 in 1#, 3#, 6# and 8# sample were 0.5%, 1%, 2% and 3%, respectively; the addition amount of CaF_2 in 2#, 4#, 5# and 7# sample were 0.5%, 1%, 2% and 3%, respectively.

Compared to 0# sample, the apparent viscosity of high Ti-bearing blast furnace slag gradually decreased with increasing the B_2O_3 amount from 0 to 0.5%, 1%, 2% and 3%. All the same to 0#, 2#, 4#, 5# and 7# sample, the apparent viscosity was also decreased with the increase of CaF_2 from 0 to 0.5%, 1%, 2% and 3%. But different type of additives will have different effects. When the two additives were equal to 1%, B_2O_3 and CaF_2 almost have the same effect and the two curves shown in Fig.2 were the same. At this point, the substitution ratio of B_2O_3 and CaF_2 was equal to 1:1.

When the amount of B_2O_3 and CaF_2 additives were all less than 1%, the effect of CaF_2 on apparent viscosity of Ti-bearing slag was more obvious. Compared to CaF_2, it is necessary to add more quantity of B_2O_3 for having the same effect. At this moment, the substitution ratio of B_2O_3 to CaF_2 was more than 1:1. When the amount of B_2O_3 and CaF_2 additives were all more than 1%, the effect of B_2O_3 on apparent viscosity was better than CaF_2 additive. The substitution ratio of B_2O_3 to CaF_2 was less than 1:1. That was less B_2O_3 additive could achieve the modified effect of CaF_2, and the results was shown in Fig.2. If a straight line perpendicular to the ordinate axis was drawn to intersect nine curves, it could be found that experimental temperature decreased with increasing the B_2O_3 and CaF_2 additives at the same apparent viscosity. That is the high Ti-bearing blast furnace slag with B_2O_3 or CaF_2 additive had lower apparent viscosity at the same experimental temperature.

Therefore, when the amount of B_2O_3 and CaF_2 is equal to 1%, the effect of B_2O_3 and CaF_2 on apparent viscosity is almost the same, and the substitution ratio is 1:1; When the amount of B_2O_3 and CaF_2 is more than 1%, the substitution ratio of B_2O_3 to CaF_2 is less than 1:1 for same modified effect; When the amount of B_2O_3 and CaF_2 is less than 1%, the substitution ratio of B_2O_3 to CaF_2 is greater than 1.

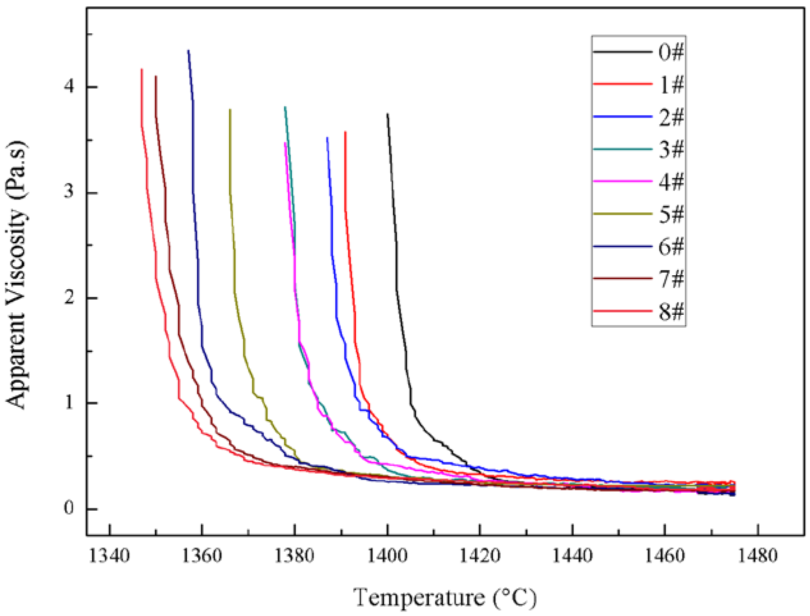

Fig. 2 The relationship between apparent viscosity and temperature with B_2O_3 or CaF_2 additives

Titanium Distribution in the Slag

It can be easily found that the change rule between apparent viscosity and temperature with B_2O_3 additive were 1#, 3#, 6# and 8# curves as shown in Fig.2. The change values of B_2O_3 additive were 0.5%(1# to 3#), 1%(3# to 6# and 6# to 8#) respectively. As seen in Fig.2, the variation degree of 6# to 8# curve was not obvious compared to variation degree of 3# to 6# curve. Therefore, the 0#, 3# and 6# curves were only chosen to analyze.

The area surface scanning of 0#, 3# and 6# samples was carried out by the metallographic microscope(MLA) and the results were shown in Figure 3-5. According to Fig.3, Fig.4 and Fig.5, the materials which was pointed by the red arrow were perovskite phase. The perovskite particles in samples became smaller and more dispersed with increasing the amount of B_2O_3 additive. With increasing the B_2O_3 additive from 0 to 2% as listed in Table 2, the Ti distribution in perovskite phase decreased from 42.35% to 32.11%, Ti(C, N) increased little, while titaniferous augite increased from 47.48% to 54.07%.

According to the above analysis, the titanium distribution of high Ti-bearing blast furnace slag appeared obvious migration with the addition of B_2O_3. The B_2O_3 additive could promote Ti element to migrate from the high melting point phase to the low melting point (titaniferous augite) and decreased the proportion of high melting point phase. It is also one of the reasons why the apparent viscosity of high Ti-bearing blast furnace slag decreased with the addition of B_2O_3.

It can be seen from Fig.3, Fig.5 and Fig.5 that the perovskite with high melting phase was in the form of solid particles at experimental temperature (1475°C). Therefore, the high Ti-bearing blast furnace slag belonged to non-Newtonian fluid containing suspended particles. At this moment, the apparent viscosity of high Ti-bearing blast furnace slag was only related to its own character.

Fluid was affected by the solid particles itself, which needed to consume additional energy to overcome solid interference for keeping the identical rate as before. Then the apparent viscosity of suspension or Sol was generally higher than viscosity of the full liquid state. This is also one of the reasons that the existence of high melting point phase caused higher the apparent viscosity. But according to generalized Einstein-roscoe [16], the apparent viscosity of suspension liquid decreased with the decrease of the solid volume fraction. As listed in Table 2, the volume fraction of perovskite gradually decreased with increasing the B_2O_3 amount.

Therefore, the addition of B_2O_3 modifier prevented the perovskite formation of high Ti-bearing blast furnace slag and promoted the Ti elements migration to the low melting point phase (titaniferous augite).

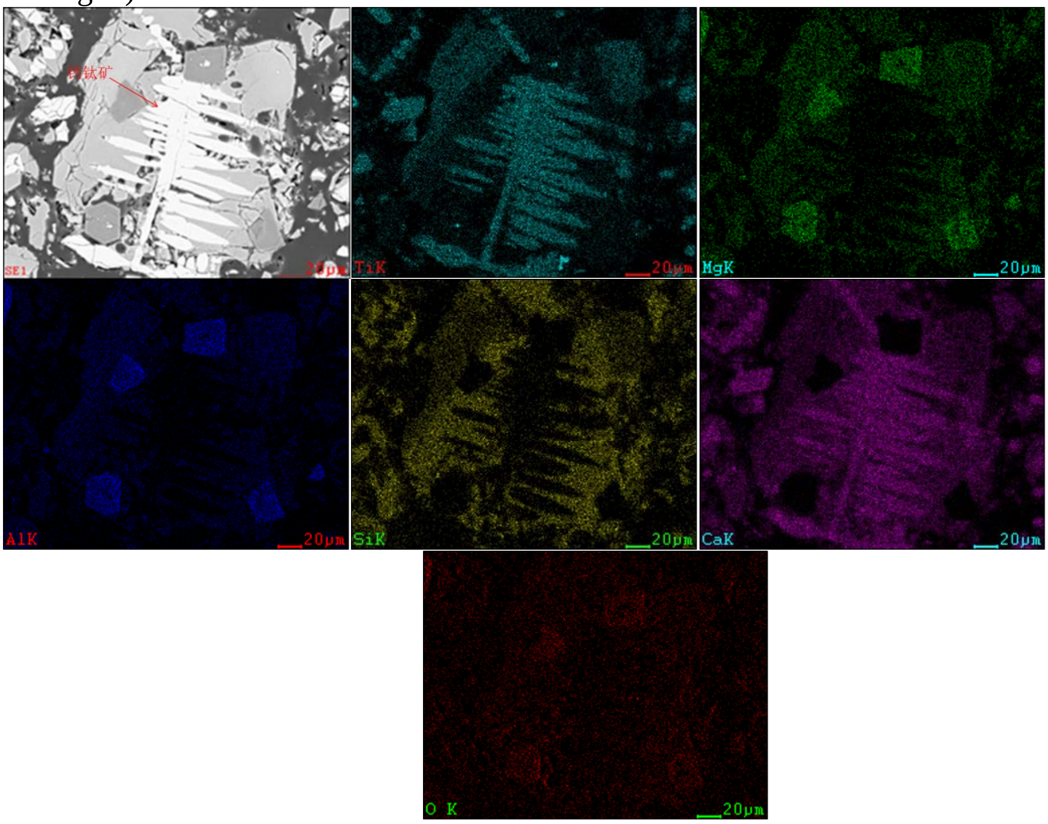

Fig. 3 The elemental distribution of Ti element for 0# sample

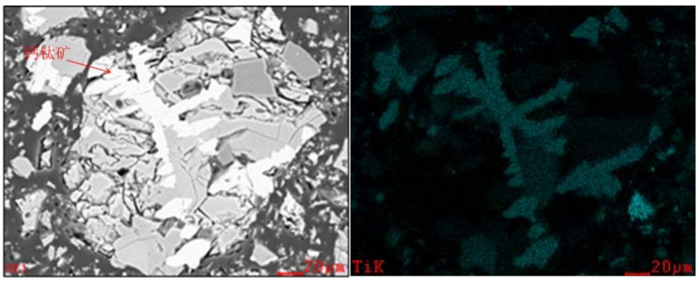

Fig. 4 The elemental distribution of Ti element for 3# sample

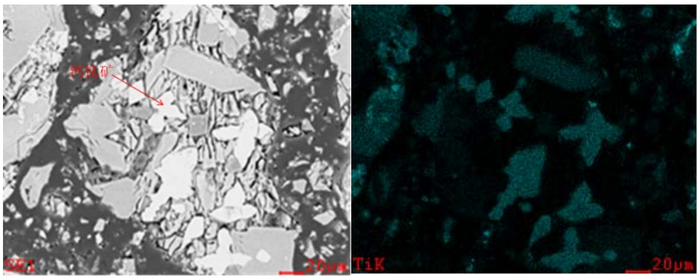

Fig. 5 The elemental distribution of Ti elemental for 6# sample

Table 2 The elemental distribution (%)

	perovskite	Ti(C,N)	Titaniferous augite
0#	42.35	7.15	47.48
3#	35.51	7.68	50.68
6#	32.11	7.82	54.07

Conclusions

The influence of B_2O_3 and CaF_2 on the apparent viscosity of Ti-bearing slag was studied from 1340°C to 1475°C. Some important results are as follows:

(1) When the two additives are equal to 1%, B_2O_3 and CaF_2 almost have the same effect and the substitution ratio of B_2O_3 and CaF_2 is equal to 1:1; When the amount of B_2O_3 and CaF_2 additives are all more than 1%, it needs to add more quantity of B_2O_3 for having the same effect and the substitution ratio of B_2O_3 to CaF_2 is less than 1:1; When the amount of B_2O_3 and CaF_2 additives are all less than 1%, the substitution ratio of B_2O_3 to CaF_2 is greater than 1:1 for having the same modification effect.

(2) The B_2O_3 modifier can promote the Ti element of high melting point phase transferred to low melting point phase (titaniferous augite). With increasing the mass fraction of B_2O_3 from 0 to 2%, the Ti distribution in perovskite phase decreases from 42.35% to 32.11%, but in titaniferous augite increases from 47.48% to 54.07%.

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