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EFFECT OF LUDWIGITE(B_2O_3) ON HIGH Al_2O_3 SLAG AND ITS MECHANISM USED AS A NEW BLAST FURNACE WELDING FLUX

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Based on the measurement of viscosities and critical temperatures of CaO-MgO-SiO_2-Al_2O_3-B_2O_3 slag system with various B_2O_3 contents, the slag with higher than 15 mas. % Al_2O_3 content has the lowest critical temperature and the widest solid-liquid coexisting region at about 2,0 mas. % B_2O_3. Furthermore, the X-ray diffractometer (XRD) result verified that bechilites whose melting point are low forms. Raman spectra revealed that the effect of network forming on viscosity is smaller than the effect of bechilites, which leads to the slag viscosity decrease with B_2O_3 addition. Base on the above research, so ludwigite can meet the requirements of a BF welding flux to decrease the critical temperature and improve the fluidity of the high Al_2O_3 slag.

Key words: blast furnace; hearth activity; high Al_2O_3 slag; B_2O_3

INTRODUCTION

Due to the continuous increase of steel production, Chinese iron ore external dependence was 84 % in 2015 [1]. A mass of iron ore with high Al_2O_3 have to be imported from foreign countries, such as Australia, India and South Africa [2], resulting in a number of blast furnaces (BF) in China have experienced accumulation of molten slag in the BF hearth, which seriously endangers the production and safety of BFs [3]. There are greater than 15 mas. % Al_2O_3 in the tapped slag due to the use of high Al_2O_3 ores, which has a certain influence on metallurgical properties of slag and BF operation [4].

In addition, when the hearth accumulation happens at the lower part of BF, ironmaking operators often use manganese ores for flushing to help furnace conditions [5]. But practice has proved that the environmental and energy saving [6]. Therefore, it is necessary to explore a new kind of BF welding flux. It has been reported that B_2O_3 could degrade the slag fluidity [7, 8], however few has explicitly investigated ludwigite as the BF welding flux and quantificationally studied the mechanism.

In this work, the high Al_2O_3 tapped slag which resulted in hearth accumulation on a 5 500 m^3 large BF in China was as the research object, so the effect of B_2O_3 on the high Al_2O_3 slag and its mechanism were researched, including the measurement of viscosity and critical temperature by rotating cylinder method, confirming the mineral phase and structure by XRD and Raman spectra. Based on the research, the ludwigite which is regarded as a new choice of BF welding flux is put forward for BF operators to restore the hearth activity.

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EXPERIMENTAL

The experimental chemical composition of the slag is shown in Table 1.

Table 1 **Chemical composition of the slags / mas. %**

No.	B_2O_3	MgO	SiO_2	Al_2O_3	CaO	CaO/SiO_2
1	0	7,35	34,72	16,96	40,97	1,18
2	0,2	7,35	34,63	16,96	40,86	1,18
3	0,5	7,35	34,49	16,96	40,70	1,18
4	0,8	7,35	34,35	16,96	40,54	1,18
5	1,0	7,35	34,26	16,96	40,43	1,18
6	2,0	7,35	33,80	16,96	39,89	1,18
7	3,0	7,35	33,34	16,96	39,35	1,18

According to the composition of the tapped slag sample, slags are prepared using reagent-grade chemicals of CaO, SiO_2, MgO, Al_2O_3 and B_2O_3. According to the desirable proportions in Table 1, the reagents are weighed 140g precisely and mixed with an agate mortar thoroughly. The molybdenum crucible (inner diameter 39 mm, high 60 mm) is used to hold the slag sample.

Based on the rotating cylinder method, the viscosity is measured by a comprehensive analyzer for physical properties of melts (RTW-10 Type). The comprehensive analyzer mainly consists of a computer, viscometer, and high temperature tubular furnace with U-shape $MoSi_2$ heating elements. After the viscosity measurements, the slag samples were reheated to 1 500 °C and quenched by water rapidly to obtain amorphous slag samples for XRD and Raman spectra.

RESULTS AND DISCUSSION

Figure 1 shows the effect of B_2O_3 on the viscosity, the viscosities of the slag samples with various B_2O_3 contents at 0 mas. %, 0,2 mas. %, 0,5 mas. %, 0,8 mas. %, 1,0 mas. %, 2,0 mas. % are almost coincident before the inflection point, which indicates that the viscosities of high Al_2O_3 slag samples are not significantly changed during the process of increasing B_2O_3 content from 0 to 2,0 mas. % when the temperature is higher than the critical temperature, although the slag composition is somewhat different. But as soon as B_2O_3 content comes up to 3,0 mas. %, the viscosity of the slag is significantly reduced and almost unchanged in high temperature region from 1 400 °C to 1 480 °C, which indicates that the fluidity and stability of the slag with 3,0 mas. % B_2O_3 is better than the others. As shown in Figure 2, the addition of B_2O_3 significantly reduces the critical temperature of the high Al_2O_3 slags. Specifically, when B_2O_3 content was increasing from 0 mas. % to 0,8 mas. %, the rate of decrease is basically the same. During the process of increasing B_2O_3 content from 0,8 mas. % to 1,0 mas. %, the rate of decrease is accelerated. As soon as B_2O_3 content is increasing from 1,0 mas. % to 2,0 mas. %, the rate of decrease is slowing down again. When B_2O_3 content comes up to 3,0 mas. %, there is no obvious viscosity inflection point, and the fluidity of the slag is different from the general BF slag, so there is no critical temperature of the slag.

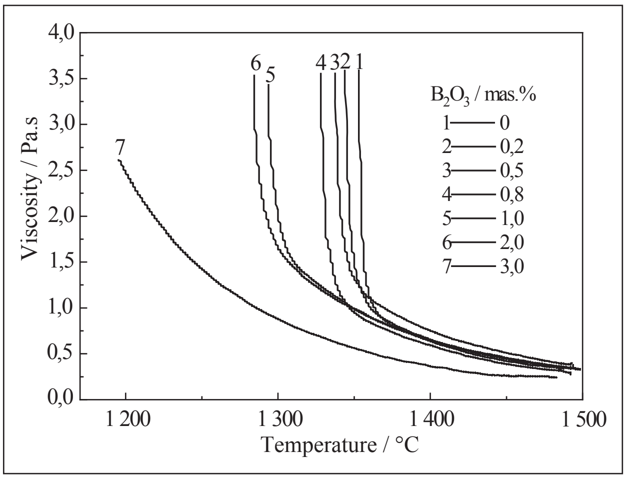

Figure 1 Effect of B_2O_3 on viscosity

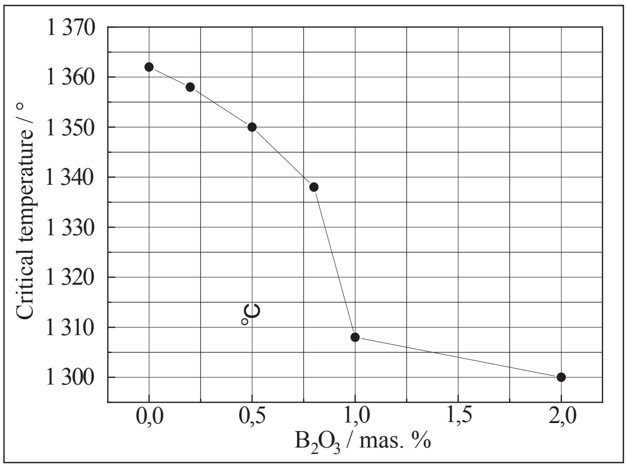

Figure 2 Effect of B_2O_3 on critical temperature

Figure 3 shows the XRD patterns of CaO-MgO-SiO_2-Al_2O_3-B_2O_3 system with various B_2O_3 contents. It can be seen that when there was no B_2O_3 addition, the mineral phase of the slag is just gehlenite. With the addition of 1,0 mas. % B_2O_3, the mineral phases of bechilite is appearing, indicating that B_2O_3 have changed the basic mineral phase in the slag after the doping process. With the increasing of B_2O_3, the diffraction peak intensity of gehlenite is weakened, on the other hand, the diffraction peak intensity of bechilite is strengthened. The XRD results indicate that the bechilite whose melting point is low really forms in the slag. With the bechilite continuously and massively forming, the critical temperature of the slag decreases as well, which is also consistent with the previous viscosity and critical temperature experiment.

In order to further explain the reason of viscosity variation, the room-temperature Raman spectra were investigated to obtain the structure information of molten slags with different B_2O_3 contents. The background of the measured Raman spectra was subtracted

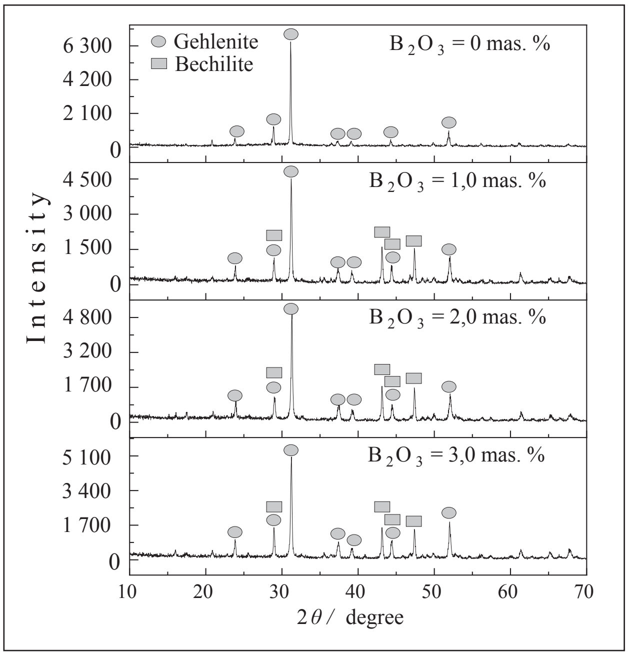

Figure 3 XRD patterns of the high Al_2-O_3 slags with various B_2O_3

Table 2 **Assignments of Raman bands for slags**

Bridging oxygen	Raman shift / cm^{-1}	Raman assignments
Q_0	840 - 870	Symmetric stretching vibrations of silicate tetrahedral with zero bridging oxygen
Q_1	900 - 930	Symmetric stretching vibrations of silicate tetrahedral with one bridging oxygen
Q_2	950 - 980	Symmetric stretching vibrations of silicate tetrahedral with two bridging oxygen
Q_3	- 1060	Symmetric stretching vibrations of silicate tetrahedral with three bridging oxygen

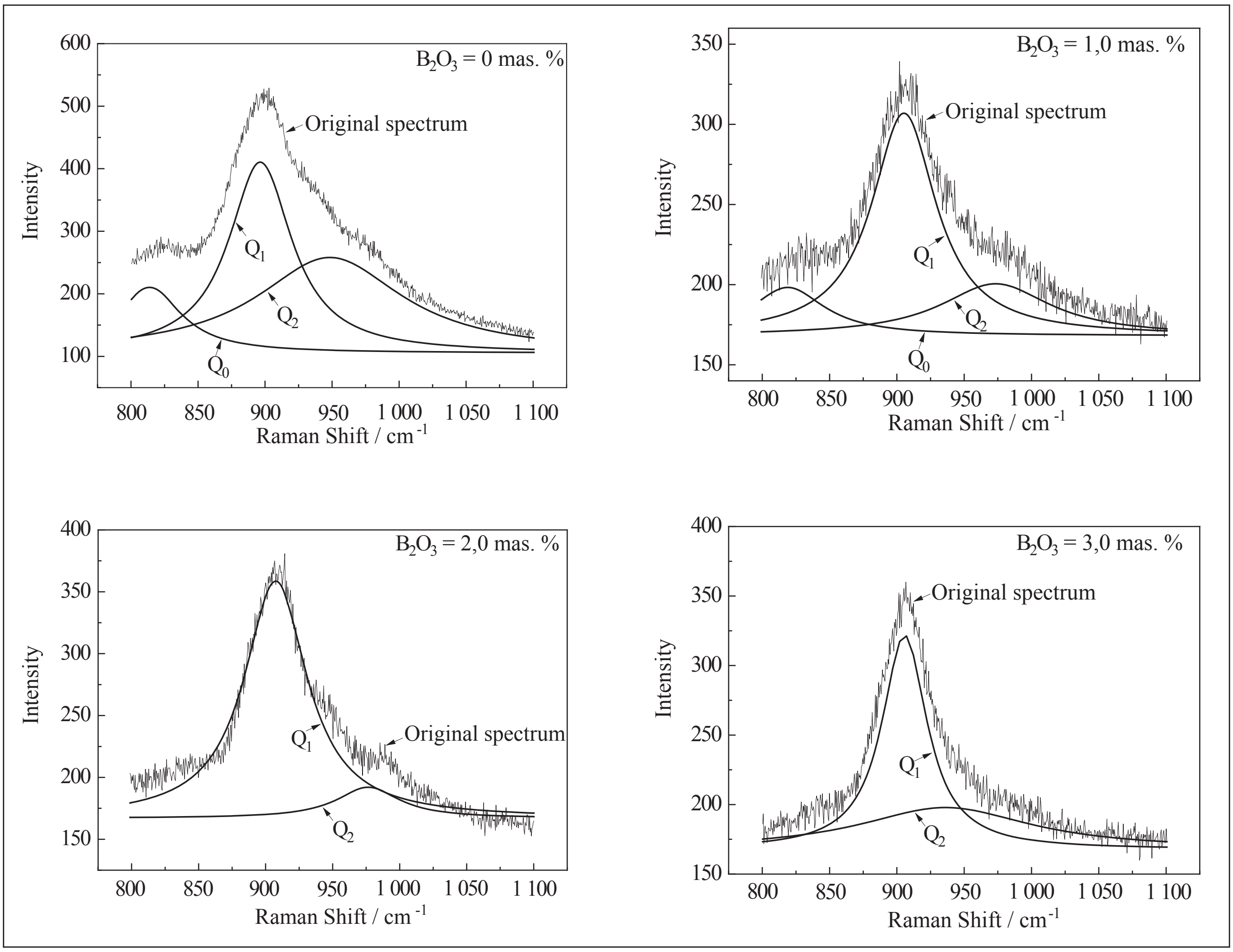

Figure 4 Raman spectra of slags with different B_2O_3

and the raw Raman spectra were deconvoluted by Gaussian-Deconvolution me-thod with the minimum correlation coefficient $r^2 \geq 0{,}99$. The assignments of Raman bands are provided in Table 2. The different Raman spectra with different B_2O_3 are showed as Figure 4.

From Figure 4, it can be seen that the band areas of Q_0 units decrease with the increase of B_2O_3 content, which is consistent with the studies of Kim et al. [10] and Wang et al. [11]. This indicates the network structure of the slags may be polymerized. On the basis of previous studies [12], a certain amount of Si-O-B bonds exist in borosilicate glasses by NMR spectroscopy analysis. Therefore, the forming of Si-O-B bonds may lead to the average number of bridging oxygen increase. Based on our structural research by Raman spectra, the degree of polymerization of the present slags are also improved by B_2O_3 that behaves as a network former to polymerize the network structure. That means the real reasons for the decrease of viscosity could not be the lower degree of polymerization. Based on this, we speculate that in spite of the new forming of B-O, but the bond energy of B-O is weaker than the bond energy of Si-O because of low melting point of B_2O_3 and B-O containing flow units are easily broken or slided [13]. The other reason is due to the formation of low-melting bechilites with B_2O_3 addition, which is advantageous to viscous flow. The effect of network forming on viscosity is smaller than the effect of low melting point compound formations, as a result, the slag viscosity is decreased with B_2O_3 addition.

PROPOSAL OF LUDWIGITE TO RESTORE HEARTH ACTIVITY IN BF

One proposal is to restore the hearth activity by the feeding of ludwigite $(Mg,Fe)_2Fe(BO_3)O_2$ as a source of B_2O_3 which is a magnetite stabilizing element(Table 3). For the BF production, the critical temperature of the tapped slag generally does not exceed 1 350 °C. Therefore, based on the experimental results, it can be known that slag with higher than 15 mas. % Al_2O_3 content has the lowest critical temperature and the widest solid-liquid coexisting region at about 2,0 mas. % B_2O_3. It is also observed that the viscosity of slag with 2,0 mas. % B_2O_3 exhibits a small enough value at higher temperature than 1 450 °C, however it does not significantly changes with varying B_2O_3 content. It is indicated that the appropriate content of B_2O_3 in the high Al_2O_3 tapped slag is 1,0 - 2,0 mas. % by the feeding of ludwigite, aiming to decrease the critical temperature and improve the fluidity of the high Al_2O_3 tapped slag, which can meet the requirements of a BF welding flux.

Table 3 **Chemical compositions of lud-wigite / mas. %**

Composition	TFe	SiO_2	MgO	P
Mas.	53,61	3,81	10,22	0,02
Composition	S	Al_2O_3	B_2O_3	
Mas.	1,0	0,27	4,53	

CONCLUSION

The slag with higher than 15 mas. % Al_2O_3 content has the lowest critical temperature and the widest solid-liquid coexisting region at about 2,0 mas. % B_2O_3. The viscosity of tapped slag with 2,0 mas. % B_2O_3 exhibits a small enough value at higher temperature than 1 450 °C, however it does not significantly changes with varying B_2O_3 content. With the addition of B_2O_3, bechilite was appearing, indicating that B_2O_3 have changed the basic mineral phase in the slag after the doping process. One proposal is to restore the hearth activity by the feeding of ludwigite as the source of B_2O_3 which is a magnetite stabilizing element. The appropriate content of B_2O_3 in the high Al_2O_3 tapped slag is 1,0 - 2,0 mas. %, aiming to decrease the critical temperature and improve the fluidity of the high Al_2O_3 tapped slag, which can meet the requirements of a BF welding flux.

REFERENCES

[1] W. Chen, Y. Lei, Y. Jiang, et al. Influencing factors analysis of China's iron import price: based on quantile regression model[J], Resources Policy 48 (2016), 68-76.

[2] X. Zhang, T. Jiang, X. Xue, et al. Influence of MgO/Al_2O_3 ratio on viscosity of blast furnace slag with high Al_2O_3 content[J], Steel Research International 87 (2016), 87-94.

[3] Z. Liu, J. Zhang, H. Zuo, et al. Recent progress on long service life design of Chinese blast furnace hearth[J], ISIJ International 52 (2012), 1713-1723.

[4] M. Nakamoto, T. Tanaka, J. Lee, et al. Evaluation of viscosity of molten SiO_2-CaO-MgO-Al_2O_3 slags in blast furnace operation[J], ISIJ International 44 (2004), 2115-2119.

[5] H. Zuo, C. Wang, C. Xu, et al. Effects of MnO on slag viscosity and wetting behaviour between slag and refractory[J], Ironmaking&Steelmaking 43 (2016), 56-63.

[6] J. B. Kim, I. Sohn. Influence of TiO_2/SiO_2 and MnO on the viscosity and structure in the TiO_2-MnO-SiO_2 welding flux system[J], Journal of Non-Crystalline Solids 379 (2013), 235-243.

[7] L. Zhang, W. L. Wang, S. L. Xie, et al. Effect of basicity and B_2O_3 on the viscosity and structure of fluorine-free mold flux[J], Journal of Non-Cry-stalline Solids 460 (2017), 113-118.

[8] X. H. Huang, J. L. Liao, K. Zheng, et al. Effect of B_2O_3 addition on viscosity of mould slag containing low silica content[J], Ironmaking& Steel-making 41 (2014), 67-74.

[9] X. B. Ai, H. Bai, L. H. Zhao, et al. Thermodynamic analysis and formula optimization of steel slag-based ceramic materials by FactSage software[J], International Journal of Minerals Metallurgy and Materials 20 (2013), 379-385.

[10] Y. Kim, Y. Yanaba, K. Morita. The effect of borate and silicate structure on thermal conductivity in the molten Na_2O-B_2O_3-SiO_2 system[J], Journal of Non-Crystalline Solids 415 (2015), 1-8.

[11] Z. Wang, Q. F. Shu, X. M. Hou, et al. Effect of substituting SiO\r, 2\r, with TiO\r, 2\r, on viscosity and crystallisation of mould flux for casting titanium stabilised stainless steel[J], Ironmaking &Steelmaking 39 (2012), 210-215.

[12] S. Wang, J. F. Stebbins. On the structure of borosilicate glasses: a triple-quantum magic-angle spinning 17O nuclear magnetic resonance study [J], Journal of Non-Crystalline Solids 231 (1998), 286-290.

[13] Z. Wang, Q. Shu, K. Chou. Viscosity of Fluoride-Free Mold Fluxes Containing B_2O_3 and TiO_2[J]. Steel Research International 84 (2013), 766-776.

Note: Y. Zhao is responsible for English language, Anhui, China