Research Article

Influence of B_2O_3 and Basicity on Viscosity and Structure of Medium Titanium Bearing Blast Furnace Slag

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The effects of B_2O_3 and basicity (CaO/SiO_2) on the viscous behavior and structure of medium titanium bearing blast furnace slag (MTBBFS) were investigated. High temperature viscosimeter was applied to measure the viscosities of $CaO-SiO_2-MgO-TiO_2-Al_2O_3-B_2O_3$ slag system and X-ray diffraction (XRD), NBO/T ratio, and structure parameter Q were employed to analyze its network structure. The results showed that the viscosity decreased and break point temperature increased with increasing basicity to 1.20. However B_2O_3 addition gave rise to a decrease in slag viscosity and break point temperature inspite of basicity. The more B_2O_3 content leads to the more pronounced variation, especially for the slag with larger basicity. The conventional NBO/T formula was revised to predict the structure variation of relatively complicated medium Ti bearing slag based on the work of Yanhong Gao and other researchers. The increase of B_2O_3 content in slag made parameter Q turn from Q_2 to Q_1 , suggesting that network structure became simpler. It was also noticed that the addition of B_2O_3 could suppress the formation of perovskite.

1. Introduction

Titanium resources are comparatively abundant in China, and most of them exist as vanadium-titanium magnetite ore and locate in the southwest area [1]. TiO_2 content in blast furnace slag gradually increases with the ore addition. Blast furnace slag is significant in the process of iron-making, especially titanium bearing slag, which exerts a deep influence on the reduction of ore, separating efficiency of slag-metal, gas permeability, and so on [2–10]. As one of the most important physical properties of slag, the viscosity is closely related to temperature and slag composition. So understanding the viscosity behaviors of slag with different B_2O_3 additions and basicity is beneficial for optimizing operation for blast furnace process. Although B_2O_3 is a typical acidic oxide, it can be used to modify BF slag. It has been found that the little amount of B_2O_3 remarkably enhanced the fluidity of slag with relatively high TiO_2 content and low basicity [11–13]. However, few studies have reported the effect of B_2O_3 and large basicity on the viscosity of MTBBFS. Therefore the present study was motivated. The viscosity variation of slag with B_2O_3 content from 1% to 4% and a basicity range of 1.06–1.20 was

investigated. Meanwhile the melt structure was analyzed by XRD and structure parameter Q .

It is generally known that structure of metallurgical slag is very complex and physical properties are very dependent on the level of polymerization of silicate network. We prefer the parameter, Q , to be an evaluation of the polymerization of the melt, which can be calculated by the following [14–16]:

$$Q = 4 - (NBO/T). \quad (1)$$

NBO/T is denoted as the ratio of nonbridging oxygen to tetragonal ions and is a measure of the depolymerization of the melt. Silicates are the basis of most metallurgical slags, where the types of O bonds are classified as bridging oxygen (denoted as BO or O^0), nonbridging oxygen (denoted as NBO or O^-), and free oxygen (denoted as O^{2-}), as shown in Figure 1. The structure of a slag can thus be represented by the mole fractions (X) of O^0 , O^- , and O^{2-} present. Consequently, it is customary to divide various constituents into either network formers (e.g., SiO_2) or network breakers (CaO , MgO , etc.).

TABLE 1: Composition of slag samples.

Sample number	Composition (wt, %)									Basicity CaO/SiO ₂
	TiO ₂	SiO ₂	Al ₂ O ₃	CaO	MgO	MnO	V ₂ O ₅	FeO	B ₂ O ₃	
1	18.65	27.59	13.11	29.31	8.65	1.04	0.19	1.22	0	1.06
2	18.46	27.31	12.98	30.01	8.56	1.03	0.19	1.21	0	1.10
3	18.23	26.97	12.81	30.90	8.45	1.01	0.18	1.19	0	1.15
4	17.98	26.60	12.64	31.84	8.34	1.00	0.18	1.18	0	1.20
5	18.46	27.31	12.98	29.01	8.56	1.03	0.19	1.21	1	1.06
6	18.07	26.74	12.70	29.48	8.38	1.01	0.18	1.18	2	1.10
7	17.66	26.12	12.41	30.08	8.18	0.98	0.18	1.15	3	1.15
8	17.25	25.52	12.12	30.61	8.00	0.96	0.17	1.13	4	1.20

FIGURE 1: Oxygen-silicon tetrahedron structure.

In this study, a conventional NBO/T formula has been revised to describe polymerization variation of MTBBFS, which would appear to be exceedingly useful in predicting properties since it can underline contributions of different oxides to properties.

2. Experimental

In this investigation, analytical reagents CaO and B₂O₃ were added to normal slag obtained from the blast furnace in desired proportions. Composition of slag samples is listed in Table 1. The slag viscosity was measured by rotating cylinder method and the viscosity of each sample was recorded during the cooling cycle above break point temperature of the sample. The break point temperature is the critical temperature at which the measured viscosity changes abruptly during the cooling cycle as described by Sridhar et al. [17]. A viscometer is connected to a molybdenum spindle through a molybdenum rod. The graphite crucible (50 mm in internal diameter, 100 mm in height, and 20 mm in thickness of wall and base) containing the slag sample (about 120 g of slag sample) was placed inside the furnace. The schematic diagram of the experiment apparatus and experimental procedure can be found in our previous paper [11, 18, 19].

After completing the viscosity measurements, the mineral compositions of quenched slags were acquired by XRD (X-ray diffraction). Diffraction conditions were as follows: Cu target K alpha rays, voltage of 35 kV, current of 25 mA, continuous

FIGURE 2: Effect of basicity on slag viscosity at different temperatures for samples 1-4.

scanning, the scanning range of 10~90°, and scanning speed of 0.06.

3. Results and Discussion

3.1. Effect of Basicity on Viscosity of MTBBFS. The viscosities have been presented in Figure 2 to evaluate the effects of basicity and temperature. It can be observed that increasing basicity resulted in an increase in viscosity at lower temperatures. Especially under 1623 K, the values rise sharply with basicity. However, no obvious changes are found at high temperatures (over 1623 K in this experiment). Besides, break point temperature rises linearly with basicity in Figure 3. For every 0.01 increase in basicity, it goes up around 1.4°C.

3.2. Effect of B₂O₃ on Viscosity of Medium Ti Bearing Slag. Figure 4 presents viscosity of slag containing boron or boron free slag as a function of temperature. The shapes of viscosity

FIGURE 3: Relationship of break point temperature and basicity for samples 1-4.

FIGURE 4: Comparison of viscosity-temperature curves for some samples.

FIGURE 5: Effect of B_2O_3 additions on break point temperature.

curves are similar for both slags. There are slight differences between viscosities of both slags at high temperatures. However, the value increased sharply under break point temperature. Break point temperature lowered quickly with increasing boron content from 1% to 4%. More boron in slag leads to more decrease in break point temperature. It decreases by about 20°C at 1% increase of boron content in slag, as shown in Figure 5.

As an acidic oxide with lower melting temperature, B_2O_3 can combine with basic oxides to form eutectics, such as $MgO-B_2O_3$ (988°C) and $CaO-B_2O_3$ (below 1150°C). So superheat degree of slag was increased at a fixed temperature. Ultimately, the viscosity dropped because of weak interaction among flow units.

3.3. Effect of B_2O_3 and Basicity on Viscosity of MTBBFS.

The effects of temperature on the viscosity of the $CaO-SiO_2-MgO-Al_2O_3-TiO_2$ slags at different basicities and B_2O_3 contents are plotted in Figure 6, where the slag viscosity decreases with increasing temperature. All of the viscosities are within 0.2 Pa·s at a given temperature (>1603 K), which are less than slag without boron. Break point temperature decreases from 1593 K to 1575 K with increasing B_2O_3 content from 1% to 4% and basicity from 1.06 to 1.20 (in Figure 5). The relationships of viscosity, break point temperature and basicity, and B_2O_3 content are constructed in Figures 7 and 8, respectively.

Figure 7 exhibits that slag viscosity declines with B_2O_3 addition regardless of basicity, indicating the stronger effect of B_2O_3 compared to basicity. Moreover, the larger the basicity, the more intensive the curve, suggesting that B_2O_3 has more sensitive effect on slag viscosity with large basicity.

In Figure 8, break point temperature increases with basicity. At a fixed B_2O_3 content, the larger the basicity, the higher the break point temperature. Influence of B_2O_3 is exactly the opposite. When B_2O_3 content in slag is lower, in

FIGURE 6: Viscosity-temperature curves of slag samples 5-8.

FIGURE 7: Effect of CaO/SiO_2 and B_2O_3 content on viscosity (1773 K).

order to make break point temperature go up 10°C, basicity needs to increase by about 0.02 in low basicity areas. But it only needs to increase by about 0.01 in high basicity areas. But it only needs ~0.01 increase in high basicity areas. For higher B_2O_3 content in slag, different results can be found by increasing the same value of break point temperature. In low basicity areas, basicity needs to rise to ~0.03 and in high basicity areas it is ~0.015. It proves that more B_2O_3 content in slag leads to faster reduction in break point temperature and greater influences of B_2O_3 content happen for slag with large basicity.

Larger viscosity and more intensive curve after increasing basicity can be caused by gradual formation of compounds with high melting point, such as $2CaO \cdot SiO_2$. Some new compounds with low melting point were produced by adding

FIGURE 8: Effect of CaO/SiO₂ and B₂O₃ content on break point temperature. FIGURE 9: Effect of CaO/SiO₂ and B₂O₃ content on structure parameter Q before and after revision.

B₂O₃. Fluidity was effectively improved, especially to blast furnace slag with large basicity.

3.4. Effect of Basicity and B₂O₃ on Structure of MTBBFS. For a CaO-SiO₂-TiO₂-Al₂O₃-MgO-B₂O₃ slag, the conventional NBO/T ratio is given by (2) where X is the mole fraction [20–23]. The NBO/T ratio and Q are calculated based on Table 2 and (2). Relationship of basicity and Q is displayed in Figure 9. Consider

$$\text{NBO/T} = \frac{2(X_{\text{CaO}} + X_{\text{MgO}} - X_{\text{Al}_2\text{O}_3})}{X_{\text{SiO}_2} + 2X_{\text{Al}_2\text{O}_3} + X_{\text{TiO}_2} + X_{\text{B}_2\text{O}_3}}. \quad (2)$$

As observed from Figure 9(a), increasing basicity tends to make Q reduce and network turn from Si₂O₆⁴⁻ (Q₂, chain) to Si₂O₇⁶⁻ (Q₁, polyhedra). It can be concluded that silicate network becomes less polymerized. A slower drop in the parameter Q can be seen with increasing basicity after B₂O₃ addition; it suggests the opposite effect of B₂O₃ comparing with basicity, which is contrary to the facts. A reasonable explanation is that the influences of different oxides on the structure are different, for example, CaO and MgO. Bond strength is used to measure destructive capacities of alkaline oxide as an important parameter. Destructive capacity of other cations is described as the ratio of bond strength of CaO and MeO (*a_i*) assuming destructive capacity of CaO to be equal to 1 [24, 25].

TABLE 2: Composition of different slag samples (molar fraction) and Q .

Sample number	Composition (mol, %)									Q	Q_{correct}
	TiO ₂	SiO ₂	Al ₂ O ₃	CaO	MgO	MnO	V ₂ O ₅	FeO	B ₂ O ₃		
1	0.15	0.29	0.08	0.33	0.14	0.01	0.00	0.01	0	2.65	2.22
2	0.14	0.29	0.08	0.34	0.13	0.01	0.00	0.01	0	2.61	2.17
3	0.14	0.28	0.08	0.35	0.13	0.01	0.00	0.01	0	2.56	2.11
4	0.14	0.28	0.08	0.36	0.13	0.01	0.00	0.01	0	2.51	2.05
5	0.14	0.29	0.08	0.33	0.13	0.01	0.00	0.01	0.01	2.69	2.21
6	0.14	0.28	0.08	0.33	0.13	0.01	0.00	0.01	0.02	2.69	2.15
7	0.14	0.27	0.08	0.34	0.13	0.01	0.00	0.01	0.03	2.68	2.07
8	0.14	0.27	0.07	0.34	0.13	0.01	0.00	0.01	0.04	2.68	2.00

FIGURE 10: XRD patterns of 1[#] slag (a) and 3[#] slag (b).

This study presumes that the dominant structure associated with Al-O arrangements is AlO₄ tetrahedra based on the report from McMillan [26, 27]. B₂O₃ is thought to be a network breaker for its function of improving slag fluidity. Therefore, (2) is corrected as follows:

$$\text{NBO/T} = \frac{2(a_{\text{MeO}}X_{\text{MeO}} + a_{\text{Me}_2\text{O}}X_{\text{Me}_2\text{O}} + a_{\text{B}_2\text{O}_3}X_{\text{B}_2\text{O}_3})}{X_{\text{SiO}_2} + 2 \times 0.66X_{\text{Al}_2\text{O}_3} + 0.71X_{\text{TiO}_2}} \quad (3)$$

The results of parameter Q versus CaO/SiO₂ and B₂O₃ are shown in Figure 9(b). As clearly observed, Q decreases with increasing CaO/SiO₂ from 1.06 to 1.20 and adding B₂O₃ from 0% to 4%, which encourages change in slag structure from complexity to simpleness. Furthermore, all values fall off remarkably after revising (2), indicating that the dominant structural unit associated with B-O arrangements can be BO₃ triangular, which is a simpler and less structural two-dimension (2D) structure compared to three-dimension (3D) structures, BO₄ tetrahedra [13]. Although B-O bond in BO₃ triangular is stronger than Si-O bond in a layer, layer and adjacent one link by weaker molecular bonds. The viscosity

and melting temperature of the slag are intimately associated with its structure, whereas structure depends upon its composition. SiO₂ forms framework for sample as the network former. The increase of B₂O₃ content makes large tetrahedron clusters break. As a result, its melting temperature is low and chemical stability is poor. It is easy to form irregular network structure when cooling, implying that glass phase tends to precipitate more easily and suppress the formation of perovskite (melting temperature: 2243 K, in agreement with results from Figures 10 and 11). In addition, boron can capture oxygen from silicate-oxygen chains to produce boron clusters. Thus silicate-oxygen chains were broken and the network structure became simpler. Therefore, viscosity and break point temperature reduced. However a larger basicity corresponds to a higher O/Si ratio, which gives rise to a change in the connecting mode of oxygen-silicon tetrahedron from layer (O/Si = 2.5) or chain (O/Si = 3.0) to individual silica tetrahedra (O/Si = 4.0). That is to say, parameter Q decreases. Thus viscosity of slag reduces. However, dicalcium silicate (melting point: 2614°C) or other compounds with high melting point are produced steadily due to excessive CaO, which leads to a rise in viscosity and break point temperature.

FIGURE 11: XRD patterns of 5[#] slag (a) and 7[#] slag (b).

4. Conclusions

The role of basicity and B_2O_3 in $CaO-SiO_2-MgO-TiO_2-Al_2O_3-B_2O_3$ slag system was studied by measuring viscosity combined with structure parameter Q and XRD results. The experimental results were summarized as follows:

- (1) Slag viscosity and break point temperature both decrease with increasing B_2O_3 at each basicity. The more B_2O_3 content leads to the more pronounced variation, especially for the slag with larger basicity.
- (2) Increasing basicity from 1.06 to 1.20 makes viscosity and break point temperature of MTBBFS rise.
- (3) It is found that B_2O_3 addition changes network structure of MTBBFS from complex to simple based on the revised NBO/T formula and XRD results.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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