Research Article

Influence of Al_2O_3 , CaO/SiO_2 , and B_2O_3 on Viscous Behavior of High Alumina and Medium Titania Blast Furnace Slag

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The effect of Al_2O_3 , CaO/SiO_2 , and B_2O_3 on the viscosity of high alumina and medium titania blast furnace slag was analyzed. An increase in CaO/SiO_2 ratio from 1.14 to 1.44 resulted in higher slag viscosity and break point temperature. They also increased with increasing Al_2O_3 content but decreased with adding B_2O_3 and Al_2O_3 simultaneously at a fixed CaO/SiO_2 ratio of 1.14, which suggested that the effect of B_2O_3 on viscosity and break point temperature is predominant compared to Al_2O_3 . Apparent activation energies of $\text{CaO-SiO}_2\text{-MgO-Al}_2\text{O}_3\text{-TiO}_2\text{-B}_2\text{O}_3$ slag were found to be between 74 and 169 kJ/mol.

1. Introduction

As high-quality iron ore resources in the world decrease, vanadium-titanium magnetite ores from China or iron ores with high Al_2O_3 from Australia and India have become an alternative choice in the blast furnace (BF) smelting process [1–3]. As a result, more alumina (exceeding 15% in many enterprises) or titania (more than 10%) occur in the BF slag, resulting in higher viscosity, worse fluidity, and poor operational stability [4–10]. So it is essential to studying the viscous behavior of BF slag with more alumina (above 15%) or titania (above 10%) for optimizing the iron-making operation. It has been found that the little amount of B_2O_3 remarkably improved the properties of slag [11–15]. Influence of B_2O_3 on high titanium (above 20%) BF slag [11–13, 16], medium titanium (10%–20%) BF slag [14], and high alumina (above 15%) BF slag [17, 18] has been studied in previous reports. However, it is hard to find investigations on the viscous behavior of high alumina (above 15%) and medium titania (15%–20%) BF slag (HAMT BF slag) and the influence of B_2O_3 , Al_2O_3 , and basicity on viscous behavior. This research work appears just in this background.

In this study, the viscous behavior of the $\text{CaO-SiO}_2\text{-(13%–19%)} \text{Al}_2\text{O}_3\text{-MgO-(17%–20%)} \text{TiO}_2$ slags was

measured to clarify the effect of Al_2O_3 and C/S. In addition, B_2O_3 was added to the slag in order to improve its fluidity. A series of slags containing different Al_2O_3 , B_2O_3 content, and C/S were designed and the viscosity, break point temperature (the critical temperature at which the measured viscosity changes abruptly during the cooling cycle), and apparent activation energy were measured and analyzed.

2. Experimental

All samples were prepared by adding analytical-grade reagents CaO , SiO_2 , Al_2O_3 , and B_2O_3 to basic slag obtained from BF and analyzed by chemical processing method. Three slag series were designed with binary basicity (C/S) range of 1.14–1.44, Al_2O_3 content of 13%–19%, and B_2O_3 content of 1%–4%. The chemical compositions of the designed slag are listed in Table 1. Slag samples were put inside a molybdenum crucible and melted in a high temperature furnace.

The slag viscosity was measured by rotating cylinder method and recorded during the cooling cycle and the experiment was not ended until a steep increase in the viscosity value. The experimental setup and experimental procedure in detail can be found in our earlier studies [19, 20].

TABLE 1: Chemical compositions of slag samples (wt.%).

Number	CaO	SiO ₂	MgO	Al ₂ O ₃	TiO ₂	FeO	V ₂ O ₅	MnO	B ₂ O ₃	C/S
Basic slag	28.33	24.85	8.64	14.24	19.48	1.11	0.20	0.65	—	1.14
R1	29.76	24.04	9.27	13.77	18.84	1.07	0.19	0.63	—	1.24
R2	31.46	23.45	9.06	13.44	18.38	1.05	0.19	0.62	—	1.34
R3	33.02	22.91	8.87	13.13	17.95	1.02	0.18	0.60	—	1.44
A1	27.45	24.08	9.28	15.98	18.87	1.08	0.19	0.63	—	1.14
A2	27.12	23.79	9.18	17.00	18.64	1.06	0.19	0.63	—	1.14
A3	26.78	23.50	9.08	18.01	18.41	1.05	0.19	0.62	—	1.14
B1	27.12	23.79	9.18	16.00	18.64	1.06	0.19	0.63	1.00	1.14
B2	26.45	23.20	8.98	17.02	18.18	1.04	0.19	0.61	2.00	1.14
B3	25.80	22.64	8.78	17.97	17.74	1.01	0.18	0.60	3.00	1.14
B4	25.13	22.05	8.58	19.00	17.28	0.98	0.18	0.58	4.00	1.14

3. Results and Discussion

3.1. Effect of CaO/SiO₂ on Viscous Behavior. The effect of C/S on viscosity at different temperatures is shown in Figure 1. As clearly observed, the viscosity strongly depends on the temperature for each sample. The viscosities of all slag samples are under 0.5 Pa·s at above 1460°C. As temperature reduces to 1440°C, the viscosity of sample R3 (C/S = 1.44) goes up to 0.92 Pa·s and the viscosities of sample R2 (C/S = 1.34) and sample R3 both exceed 1.0 Pa·s with temperature continuous decreasing to 1420°C. When temperature further drops to 1400°C, the viscosity of sample R1 (C/S = 1.24) increases sharply to 3.38 Pa·s and that of sample R2 or R3 is even higher. For basic slag sample (C/S = 1.14), its viscosity does not reach 0.91 Pa·s until 1360°C because of low basicity. It illustrates that these slags are short slags. When the temperature is lower than break point temperature, the viscosity increases sharply in a narrow temperature range. Meanwhile, the fluidity and the stability of slags become worse. Besides, with an increase of the CaO/SiO₂, the change of viscosity is much sharper, and the viscosity becomes more sensitive to the temperature change, resulting from the precipitation of phases with the high melting point [21, 22].

Figure 2 indicates that break point temperature raises with increasing C/S and shows relatively gentle change at the stage where C/S varies from 1.24 to 1.34. As we all know, although CaO can modify the melt structure effectively by providing additional free oxygen ions (O²⁻) as a typical basic oxide, more addition of CaO exerts a negative effect on the viscosity and the break point temperature because of its high melting temperature.

3.2. Effect of Al₂O₃ on Viscous Behavior. Figure 3 shows the effect of Al₂O₃ on the viscosity of CaO–SiO₂–MgO–Al₂O₃–(18%–19%) TiO₂ slag at various temperature and a fixed C/S of 1.14. It is noted that the viscosity increases with increasing Al₂O₃ content from 14.24% to 18.01%. When temperature is 1360°C, the viscosity goes up rapidly, especially as Al₂O₃ content is more than 16%. Viscosity of sample A1 is more than 1.5 Pa·s and the value of sample A3 goes up to

FIGURE 1: Viscosity isotherms for slag series R and basic slag.

FIGURE 2: Break point temperature for slag series R and basic slag.

FIGURE 3: Viscosity isotherms for slag series A and basic slag.

FIGURE 4: Break point temperature for slag series A and basic slag.

5.5 Pa·s. When temperature decreases to 1340°C, viscosity of basic slag reaches up to 3.5 Pa·s. It is inferred that these slags also take on the characteristics of short slag and more Al₂O₃ responds to larger viscosity. With an increase of the Al₂O₃ content, viscosity varies more quickly in a narrow temperature range and the fluidity deteriorates rapidly, attributing to the precipitation of phases with the high melting point [21, 22]. The break point temperature shows a similar tendency, as marked in Figure 4. When Al₂O₃ content in slag exceeds 17%, it dramatically increases. It is reported that Al₂O₃ behaves as an amphoteric oxide and initially Al³⁺ cations can replace Si⁴⁺ to form [AlO₄]⁵⁻ tetrahedral units [23–25]. However, after further addition of Al₂O₃, it behaves as a network modifier and exists in the [AlO₆]⁹⁻ octahedral configuration [3]. Thus complex structure corresponds to higher break point temperature and larger viscosity. In this investigation,

Al₂O₃ behaves as a network former and increases the slag viscosity, agreeing with previous study [3].

3.3. Combined Effect of B₂O₃ and Al₂O₃ on Viscous Behavior. The viscosity-temperature curves of the slag samples are shown in Figure 5. Viscosity is closely related to temperature for each sample and B₂O₃ addition decreases the viscosity and improves the fluidity of slags regardless of Al₂O₃ content in slag. The viscosity of CaO–13% Al₂O₃–SiO₂–MgO–18% TiO₂–B₂O₃ slags decreases with increasing B₂O₃ addition in our previous investigation [14]. Similar results are obtained by Sun et al. [11], Fox et al. [26], and Wang et al. [27] despite different compositions. Besides, the break point temperature of slag was decreased by the addition of B₂O₃, as shown in Figure 6. The more B₂O₃ in slag, the faster break point temperature drops.

According to some studies on boron bearing multicomponent slag [28, 29], B₂O₃ exists mainly in the form of [BO₃]⁻ triangle and [BO₄]⁻ tetrahedral units; B₂O₃ additions could decrease the [AlO₄]⁻ tetrahedral structural units and transformed the 3D network structures such as pentaborate and tetraborate into 2D network structures of boroxol and boroxyl rings by breaking the bridged oxygen atoms (O⁰) to produce nonbridged oxygen atoms (O⁻) leading to a decrease in the slag viscosity.

The isoviscosity curves of boron containing HAMT BF slag are constructed in Figure 7 and its iso-break point temperature curves are plotted in Figure 8. As can be seen, viscosities and break point temperatures decrease gradually with the addition of B₂O₃ and Al₂O₃, which suggests that the B₂O₃ effect is predominant compared to the Al₂O₃ additions. The isoviscosity curves become closer and closer as the B₂O₃ content decreases and the Al₂O₃ content increases, which indicates that the thermal stability of slag starts to deteriorate. However, increase of Al₂O₃ must be accompanied by decrease of B₂O₃ to maintain constant viscosity (in Figure 7) in several domains where B₂O₃ is greater than 3.5 or Al₂O₃ is more than 18.5%. Furthermore, these domains where increase of Al₂O₃ should be accompanied by decrease of B₂O₃ for constant break point temperature are more widespread in Figure 8. Significantly, in present study, break point temperatures are all under 1350°C after adding B₂O₃, which can meet the requirement of BF operation.

3.4. Effect of B₂O₃ on the Apparent Activation Energy for Viscous Flow. Temperature dependence of viscosity (η) is given by the Arrhenius equation (see (1)), from which the apparent activation energy can be derived.

$$\ln \eta = \ln A + \frac{Ea}{RT}, \quad (1)$$

where η is viscosity of the slag; A is constant; Ea is the apparent activation energy; R is molar gas constant; T is absolute temperature. Variations in Ea can reveal changes in the frictional resistance of viscous flow and suggest a change in the structure of the molten slag. The variation of apparent activation energy is constructed in Figure 9 based on (1). It decreases with an increase of B₂O₃ content

FIGURE 5: Viscosity changes of the slag with temperature at different B_2O_3 content.

and Al_2O_3 content, which indicates that the resistance for viscous flow becomes smaller. So the slag structure becomes simpler and less complex. This is attributed to a weakening of the bond energy by increasing of B–O bonds in the network structure of BO_4 and BO_3 units [30]. In other words, although increasing Al_2O_3 can make the network of slag melts complex, it was modified by adding B_2O_3 .

4. Conclusions

In the present study, viscous behavior of HAMT BF slag was analyzed when Al_2O_3 content and B_2O_3 content in slag varied. The important results were summarized as follows:

- (1) The thermal stability of the slag is better at higher temperature. Viscosity begins to deteriorate rapidly when temperature is below 1420°C and C/S varies from 1.14 to 1.44. For HAMT BF slag with fixed C/S of 1.14, the temperature is 1360°C .

- (2) Break point temperature increases faster with Al_2O_3 content in high aluminum and medium titanium slag; Al_2O_3 content especially exceeds 17%. Therefore, Al_2O_3 content in slag should be under 17% during iron-making process.
- (3) B_2O_3 addition can improve fluidity of HAMT BF slag and decline significantly break point temperature regardless of Al_2O_3 content.
- (4) Apparent activation energy decreases with an increase of B_2O_3 content and Al_2O_3 content.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

Authors' Contributions

The authors contributed equally to this work.

FIGURE 6: Break point temperature of the slag with B₂O₃ content. FIGURE 7: Effects of Al₂O₃ and B₂O₃ content on viscosity. FIGURE 8: Effects of Al₂O₃ and B₂O₃ content on break point temperature. FIGURE 9: Relationship of apparent activation energy and B₂O₃ and Al₂O₃ content in slag.

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