Research Article

Influence of Al_2O_3 Content on the Melting and Fluidity of Blast Furnace Type Slag with Low TiO_2 Content

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The increasing usage of iron ores with high Al_2O_3 content significantly increases the amount of Al_2O_3 in blast furnace slag and consequently affects its performance. This work uses slag sampled on site to study the effects of changes in Al_2O_3 content on the fluidity of the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-TiO}_2$ slag system that is characterized by high Al_2O_3 and low TiO_2 contents, as well as on the phase transition law during the cooling process. Slag viscosity exhibits a rising trend with an increase in Al_2O_3 content, and Al_2O_3 in the tested slag is alkaline. The viscous flow activation energy of molten slag rises from 157 kJ/mol to 172 kJ/mol with an increase in Al_2O_3 content, and the viscous flow units in the slag become large and complicated. When slag is cooled, the main precipitated phase is melilitite. Spinel, perovskite, and olivine are also observed. The crystallization amount of the melilitite phase decreases constantly with an increase in Al_2O_3 content.

1. Introduction

As mineral resources become scarce, the types of iron ore purchased by steel companies have become varied and their compositions have become complicated. Rational ore blending and cost-efficient iron making, which follow benefit-centered guidelines, are crucial for enterprises. Al_2O_3 content in slag has increased, while the grade of ores fed into most domestic blast furnaces has been raised, because of the increase in consumption of imported minerals such as Australian and Indian ores [1–6]. Consequently, the heat stability of blast furnace slag fluctuates and significantly affects blast furnace operation. Meanwhile, the quantity of blast furnace coal injection continuously increases and the amount of blast furnace slag gradually decreases given that the metallurgical method for blast furnace is reinforced constantly. Consequently, low-cost nonmetallurgical coals are used in blast furnace coal injection. Compared with traditional coals, this type of coal contains a considerable amount of gangue minerals, such as SiO_2 and Al_2O_3 , which

eventually causes the Al_2O_3 content of blast furnace slag to increase constantly.

As the Al_2O_3 content of slag increases, the high melting-point spinel phase, which is a feature of strong crystallization capacity, may occur easily in slag, thereby causing blast furnace slag to exhibit high viscosity and poor fluidity and eventually resulting in the decline of slag metallurgical performance [7–10]. Most domestic enterprises adjust the quantity of $\text{MgO/Al}_2\text{O}_3$ in blast furnace feedstock by regulating the proportion of MgO during sintering and accordingly inhibiting the negative effect of increased Al_2O_3 content on smelting. Park et al. [11, 12] demonstrated that Al_2O_3 exhibited an amphoteric character in the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO}$ slag system. When the Al_2O_3 and MgO contents of slag are low, slag viscosity initially presents a rising trend and then a declining trend with an increase in Al_2O_3 content. Kim et al. [13] reported that Al_2O_3 is an amphoteric oxide, which is either a network modifier basic oxide or a network former acidic oxide, depending mainly on the overall composition of slag. However, when blast furnace slag

FIGURE 1: Experimental setup for viscosity measurements.

FIGURE 2: Dimensions of the spindle and bob in the present work.

contains a small amount of TiO_2 , the effect of Al_2O_3 on the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-MgO-TiO}_2$ slag system remains unclear. To address this issue, the current study mainly explores the effects of increased Al_2O_3 content on the melting and fluidity of blast furnace slag with low TiO_2 content.

2. Experimental

2.1. Experimental Apparatus and Process. A rotational viscosity test system was used in the slag viscosity experiment. The experimental apparatus is shown in Figure 1. The graphite crucible used in the experiment has a diameter of 50 mm and a depth of 100 mm. The depth of the slag placed in the graphite crucible is 50 mm. The diameter of the rotational test head is 12 mm and its height is 20 mm. The rotational test head is shown in Figure 2. During the experiment, the viscosity-temperature curve was obtained by measuring viscosity

TABLE 1: Desired compositions in the present work.

Number	CaO	SiO ₂	Al ₂ O ₃	MgO	FeO	MnO	TiO ₂	CaO/ SiO ₂	MgO/ Al ₂ O ₃
(1)	37.75	32.01	15.00	9.33	0.71	0.34	3.92	1.18	0.62
(2)	36.83	31.23	18.00	9.10	0.69	0.33	3.82	1.18	0.51
(3)	35.48	30.08	21.00	8.78	0.67	0.32	3.67	1.18	0.42
(4)	34.13	28.94	24.00	8.43	0.66	0.31	3.54	1.18	0.35

FIGURE 3: Effect of Al_2O_3 content on viscosity-temperature curves.

under a decreasing temperature, and temperature reduction was controlled at $2^\circ\text{C}/\text{min}$. The viscosity-temperature test was completed when viscosity increased to 20 Poise or changed abruptly.

2.2. Sample Preparation. The slag used in the experiment was semisynthetic. Compositional variation was achieved after on-site slag was blended with chemical reagents. All chemical reagents used were of analytical grade with a purity over 99%. The details of the experimental scheme are provided in Table 1. In the experiment, 250 g slag was heated to 1500°C in a blast furnace for 3 h. During this period, the slag was churned every 15 min to ensure its even composition. After performing the viscosity test, temperature was raised to 1450°C and maintained for 30 min. Then, the molybdenum crucible was removed immediately from the furnace and quenched with water to obtain a glassy state slag and to fix the structure of the slag that formed under high temperature.

3. Result and Discussion

3.1. Effect of Al_2O_3 Content on Viscosity. Figure 3 shows the viscosity-temperature curve of blast furnace slag under

FIGURE 4: Effect of Al_2O_3 content on break point temperature.

different Al_2O_3 contents. As shown in the figure, the viscosity of blast furnace slag exhibits a constant declining trend as temperature increases, and a turning point occurs in the viscosity-temperature curves under different Al_2O_3 contents. These results indicate that the low TiO_2 - CaO - SiO_2 - Al_2O_3 - MgO - TiO_2 slag is acidic. Blast furnace viscosity demonstrates a rising trend with an increase in Al_2O_3 content. This rising trend is apparent when temperature is lower than 1400°C mainly because Al_2O_3 becomes acidic with the gradual decrease in $\text{MgO}/\text{Al}_2\text{O}_3$ content of blast furnace slag. This condition causes the microstructure of blast furnace slag to transform into a complicated network structure and consequently increases slag viscosity.

The break point temperature under different Al_2O_3 contents (Figure 4) was obtained by setting the temperature at the turning point of the viscosity-temperature curve as the break point temperature of blast furnace slag. The tangent point temperature of the 135° tangent line was obtained as “break point” when the curve transition from low viscosity to rapidly increasing viscosity is not very sharp. As shown in Figure 4, the break point temperature of blast furnace slag exhibits a linear rising trend with an increase in Al_2O_3 content, thereby indicating that the minimum temperature at which the slag can flow freely increases gradually. Therefore, hearth temperature should be raised during smelting to exceed the melting temperature of slag at the moment to ensure the smooth operation of the blast furnace and the normal discharge of slag.

3.2. Effect of Al_2O_3 on Apparent Activation Energy. The viscous flow of blast furnace slag is hindered by its internal structure. The distance and interaction among particles in molten slag are similar to those in crystal. Each particle is affected by the bonding force of adjacent particles. That is, every particle encounters a certain potential barrier. In case of a balanced state, the potential energy of a particle is low. Thus, sufficient energy is necessary to overcome a potential barrier, activate particles, and make them flow. The viscous flow of slag will not result in bond fission but may cause atoms to

move from one balanced position to another. Therefore, the activation energy shall act as the force that drives the molten particles to move in a linear manner [11]. In a silicate slag system, silica complex ions are significantly larger than positive ions. That is, the activation energy of viscous flow should be increased. Therefore, $\text{Si}_x\text{O}_y^{z-}$ becomes the main viscous flow unit in molten slag. The change in slag composition leads to the disintegration or aggregation of $\text{Si}_x\text{O}_y^{z-}$. Hence, when the structure changes, the viscosity of molten slag may decline or increase accordingly. Although temperature does not change the activation energy of viscous flow, an increased temperature and an increased kinetic energy of particles enable the number of particles with viscous flow activation energy to increase. Simultaneously, complex ions may probably disintegrate to become small flow units because of the intensified thermal vibration and bond fission of particles. Accordingly, viscosity decreases.

The viscosity of molten slag can be expressed in the form of an Arrhenius relation [14] as follows:

$$\eta = A_w e^{E/RT}, \quad (1)$$

where η is the viscosity of molten slag, A_w denotes the preexponential factor, T is the temperature of molten slag, E refers to the activation energy of viscous flow, and R is the ideal gas constant.

At this point, molten slag is composed of discrete ion structure units, and its viscous flow activation energy is closely associated with ions, ionic compounds, and the force acting among ions. An increased kinetic energy of particles enables the number of particles also to change with temperature because ion type and size may change with temperature. The Wayman-Frankel relation is frequently used to reflect changes, and considerable experimental data show that this relation is more applicable than an Arrhenius relation. The Wayman-Frankel relation [14] is presented as follows:

$$\eta = A_W \cdot T \cdot e^{E_W/RT}. \quad (2)$$

The logarithm is calculated for both sides of the preceding equation as follows:

$$\ln \eta = \ln A_W + \ln T + \frac{E_W}{RT}. \quad (3)$$

When T changes slightly, $\ln T$ nearly does not change, and $\ln \eta$ is linearly correlated with $1/T$. After fitting is conducted over the fixed viscosity and temperature reciprocal, the activation energy of the viscous flow of a slag component was obtained according to the slope.

Figure 5 shows the $\ln \eta$ and $1/T$ fitting results and the changes in the calculated viscous flow activation energy along with Al_2O_3 content when the binary basicity is $R = 1.18$ in the CaO - SiO_2 - Al_2O_3 - MgO - TiO_2 slag system. In addition, the linear fitting relevancy is $R^2 \geq 0.94$. From the slope of the fitted curve, the activation energies of slag viscous flow are 157, 166, 168, and 172 kJ/mol when the Al_2O_3 content of slag changes from 15% to 24%. This finding indicates that activation energy exhibits a rising trend with a decline in $\text{MgO}/\text{Al}_2\text{O}_3$ content mainly because the quantity of MgO is

FIGURE 5: Effect of Al₂O₃ content on apparent activation energy.

insufficient to balance Al₂O₃ when Al₂O₃ content increases. Consequently, Al₂O₃ becomes alkaline and forms Al_xO_y^{z-} and other complicated agglomerates with negative ions. The viscous flow units in slag become large and complicated, and an increase in viscous flow activation energy is required for movement.

3.3. Effect of Al₂O₃ on the Crystallization Behavior. The Equip module of the thermodynamic calculation software Factsage 6.5 is adopted for the thermodynamic calculation of crystallization in blast furnace slag. In addition, two databases, namely, Fact53 and FToxide, are used during computation. Diffusion is extremely fast during computation, and the entire system is balanced.

Figure 6 shows the phase precipitation during the cooling crystallization process of the CaO–SiO₂–Al₂O₃–MgO–TiO₂ slag system under different Al₂O₃ contents. This figure indicates that the major precipitated phase is melilitite. In addition, spinel, perovskite, and olivine are observed. The change in solid fraction was shown in Table 2 with temperature $[d(\text{fraction solid})/dT]$ at break point temperature. The crystal phases of experimental slag system were analyzed by XRD as shown in Figure 7. It can be seen that the phase information of the experimental slag system is 2CaO·Al₂O₃·SiO₂.

Figure 8 illustrates the changes in major phase crystallization temperature with Al₂O₃ content in the CaO–SiO₂–Al₂O₃–MgO–TiO₂ slag system. The crystallization temperatures of melilitite, perovskite, and olivine exhibit a rising trend, particularly that of perovskite. By contrast, the crystallization temperature of spinel presents a declining trend. These results are mainly attributed to several low melting-point phases transforming into high melting-point phases and the melilitite phase turning into the Al₂O₃-rich spinel phase with an increase in Al₂O₃ content.

TABLE 2: Solid fraction at break point temperature.

Al ₂ O ₃ content/%	15	18	21	24
Break point temperature/°C	1358	1370	1378	1386
Solid fraction/%	53	45	42	39

According to the thermodynamic calculation, it can be found that the major precipitated phase is melilitite during the cooling crystallization process of the CaO–SiO₂–Al₂O₃–MgO–TiO₂ slag system. Figure 9 shows the changes in the crystallization amount of the melilitite phase along with temperature under different Al₂O₃ contents of slag. As shown in the figure, the crystallization amount of melilitite increases continuously and can reach up to 80% when temperature decreases. The crystallization speed of melilitite is extremely fast when temperature ranges from 1325°C to 1450°C, but afterward the crystallization rate becomes stable. Moreover, temperature exhibits a rising trend with an increase in Al₂O₃ content when the crystallization rate of the melilitite phase slows down. When temperature is below 1380°C, the crystallization amount of the melilitite phase presents a rising trend with an increase in Al₂O₃ content if temperature remains unchanged. When temperature is above 1380°C, the crystallization amount of the melilitite phase presents a declining trend with an increase in Al₂O₃ content if temperature remains unchanged.

4. Conclusions

This study applies the rotational viscometer method to measure the viscosity of the CaO–SiO₂–Al₂O₃–MgO–TiO₂ blast furnace slag system and investigates the effects of changes in Al₂O₃ content on the fluidity of blast furnace slag and on the phase transition law during the cooling crystallization process. The major conclusions are presented as follows:

(1) In case of CaO/SiO₂ = 1.18, wt(TiO₂) < 4%, and wt(Al₂O₃) > 15%, slag viscosity exhibits a rising trend with an increase in Al₂O₃ content, and melting temperature rises from 1357°C to 1385°C, thereby showing a linear rising trend.

(2) The Wayman–Frankel relation is adopted to analyze the viscous flow activation energy of molten slag. The viscous flow activation energy of molten slag rises from 157 kJ/mol to 172 kJ/mol with an increase in Al₂O₃ content. The viscous flow units also become large and complicated.

(3) The thermodynamic calculation software Factsage is used for the thermodynamic calculation of cooling crystallization laws. The major phase precipitated during the slag cooling process is melilitite. Spinel, perovskite, and olivine are also observed. Changes in Al₂O₃ content significantly affect the crystallization behavior of melilitite.

Conflicts of Interest

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

FIGURE 6: Crystallization of CaO-SiO₂-Al₂O₃-MgO-TiO₂.

FIGURE 7: XRD results of experimental slag system.

FIGURE 8: Crystallization temperature with different Al₂O₃ contents.

FIGURE 9: Crystallization amount of the melilitite phase.

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