Research Article

Influence of Al\textsubscript{2}O\textsubscript{3} Content on the Melting and Fluidity of Blast Furnace Type Slag with Low TiO\textsubscript{2} Content

Hao Liu, Yuelin Qin, Yanhua Yang, Qianying Zhang, and Nengyun Deng

1 School of Metallurgy and Materials Engineering, Chongqing University of Science and Technology, Chongqing 401331, China
2 Value-Added Process and Clean Extraction of Complex Metal Mineral Resources, Chongqing Municipal Key Laboratory of Institutions of Higher Education, Chongqing 401331, China

Correspondence should be addressed to Yuelin Qin; qinyuelin710@163.com

Received 11 September 2017; Revised 1 December 2017; Accepted 26 February 2018; Published 4 April 2018

The increasing usage of iron ores with high Al\textsubscript{2}O\textsubscript{3} content significantly increases the amount of Al\textsubscript{2}O\textsubscript{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\textsubscript{2}O\textsubscript{3} content on the fluidity of the CaO–SiO\textsubscript{2}–Al\textsubscript{2}O\textsubscript{3}–MgO–TiO\textsubscript{2} slag system that is characterized by high Al\textsubscript{2}O\textsubscript{3} and low TiO\textsubscript{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\textsubscript{2}O\textsubscript{3} content, and Al\textsubscript{2}O\textsubscript{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\textsubscript{2}O\textsubscript{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\textsubscript{2}O\textsubscript{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\textsubscript{2}O\textsubscript{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\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3}, which eventually causes the Al\textsubscript{2}O\textsubscript{3} content of blast furnace slag to increase constantly.

As the Al\textsubscript{2}O\textsubscript{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 MgO/Al\textsubscript{2}O\textsubscript{3} in blast furnace feedstock by regulating the proportion of MgO during sintering and accordingly inhibiting the negative effect of increased Al\textsubscript{2}O\textsubscript{3} content on smelting. Park et al. [11, 12] demonstrated that Al\textsubscript{2}O\textsubscript{3} exhibited an amphoteric character in the CaO–SiO\textsubscript{2}–Al\textsubscript{2}O\textsubscript{3}–MgO slag system. When the Al\textsubscript{2}O\textsubscript{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\textsubscript{2}O\textsubscript{3} content. Kim et al. [13] reported that Al\textsubscript{2}O\textsubscript{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...
contains a small amount of TiO$_2$, the effect of Al$_2$O$_3$ on the CaO–SiO$_2$–Al$_2$O$_3$–MgO–TiO$_2$ slag system remains unclear. To address this issue, the current study mainly explores the effects of increased Al$_2$O$_3$ 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 under a decreasing temperature, and temperature reduction was controlled at 2°C/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 1,500°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 1,450°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$_2$O$_3$ Content on Viscosity

Figure 3 shows the viscosity-temperature curve of blast furnace slag under...
different Al$_2$O$_3$ 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$_2$O$_3$ contents. These results indicate that the low TiO$_2$–CaO–SiO$_2$–Al$_2$O$_3$–MgO–TiO$_2$ slag is acidic. Blast furnace viscosity demonstrates a rising trend with an increase in Al$_2$O$_3$ content. This rising trend is apparent when temperature is lower than 1,400°C mainly because Al$_2$O$_3$ becomes acidic with the gradual decrease in MgO/Al$_2$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$_2$O$_3$ 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°C 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$_2$O$_3$ 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$_2$O$_3$ 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, SiO$_2$ becomes the main viscous flow unit in molten slag. The change in slag composition leads to the disintegration or aggregation of SiO$_2$. 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:

$$\eta = A_w e^{E/RT},$$

where $\eta$ 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:

$$\eta = A_w T \cdot e^{E/RT}.$$  

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

$$\ln \eta = \ln A_w + \ln T + \frac{E}{RT}.$$

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$_2$O$_3$ content when the binary basicity is $R = 1.18$ in the CaO–SiO$_2$–Al$_2$O$_3$–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$_2$O$_3$ content of slag changes from 15% to 24%. This finding indicates that activation energy exhibits a rising trend with a decline in MgO/Al$_2$O$_3$ content mainly because the quantity of MgO is
of the experimentalslag system is $2\text{CaO\cdotAl}_2\text{O}_3$ shown in Figure 7. It can be seen that the phases in the crystallization amount of the melilitite phase 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 $\text{Al}_2\text{O}_3$ 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 $\text{Al}_2\text{O}_3$ 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 $\text{Al}_2\text{O}_3$ content if temperature remains unchanged.

### 3.3. Effect of $\text{Al}_2\text{O}_3$ 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 F'Toxide, 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–SiO$_2$–Al$_2$O$_3$–MgO–TiO$_2$ slag system under different $\text{Al}_2\text{O}_3$ 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 $[dt(fraction\ solid)/dT]$ 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 $2\text{CaO\cdotAl}_2\text{O}_3\cdot\text{SiO}_2$.

Figure 8 illustrates the changes in major phase crystallization temperature with $\text{Al}_2\text{O}_3$ content in the CaO–SiO$_2$–$\text{Al}_2\text{O}_3$–MgO–TiO$_2$ 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 $\text{Al}_2\text{O}_3$-rich spinel phase with an increase in $\text{Al}_2\text{O}_3$ content.

### Figure 5: Effect of $\text{Al}_2\text{O}_3$ content on apparent activation energy.

![Graph](image)

According to the thermodynamic calculation, it can be found that the major precipitated phase is melilitite during the cooling crystallization process of the CaO–SiO$_2$–$\text{Al}_2\text{O}_3$–MgO–TiO$_2$ slag system. Figure 9 shows the changes in the crystallization amount of the melilitite phase along with temperature under different $\text{Al}_2\text{O}_3$ 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 $\text{Al}_2\text{O}_3$ 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 $\text{Al}_2\text{O}_3$ 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 $\text{Al}_2\text{O}_3$ content if temperature remains unchanged.

### 4. Conclusions

This study applies the rotational viscometer method to measure the viscosity of the CaO–SiO$_2$–$\text{Al}_2\text{O}_3$–MgO–TiO$_2$ blast furnace slag system and investigates the effects of changes in $\text{Al}_2\text{O}_3$ 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/SiO$_2$ = 1.18, wt(TiO$_2$) < 4%, and wt($\text{Al}_2\text{O}_3$) > 15%, slag viscosity exhibits a rising trend with an increase in $\text{Al}_2\text{O}_3$ 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 $\text{Al}_2\text{O}_3$ 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 $\text{Al}_2\text{O}_3$ 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.

### Table 2: Solid fraction at break point temperature.

<table>
<thead>
<tr>
<th>$\text{Al}_2\text{O}_3$ content/%</th>
<th>15</th>
<th>18</th>
<th>21</th>
<th>24</th>
</tr>
</thead>
<tbody>
<tr>
<td>Break point temperature/°C</td>
<td>1358</td>
<td>1370</td>
<td>1378</td>
<td>1386</td>
</tr>
<tr>
<td>Solid fraction/%</td>
<td>53</td>
<td>45</td>
<td>42</td>
<td>39</td>
</tr>
</tbody>
</table>

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.
Acknowledgments

The authors would like to acknowledge the National Natural Science Foundation of China (no. 51604054), Scientific and Technological Research Program of Chongqing Municipal Education Commission (no. KJ1601331), and Research Foundation of Chongqing University of Science & Technology (nos. CK2015B08, CK2016Z04).

References


