Influence of Al$_2$O$_3$ and MgO on the Viscosity and Stability of CaO–MgO–SiO$_2$–Al$_2$O$_3$ Slags with CaO/SiO$_2$ = 1.0

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The viscosity of CaO–SiO$_2$–MgO–Al$_2$O$_3$ slags (CaO/SiO$_2$=1.0, 14–17 mass% Al$_2$O$_3$, 5–15 mass% MgO) was measured to analyze the effect of MgO and Al$_2$O$_3$. The infrared spectra was employed to analyze the ionic structure of the slag. The viscosity of CaO–SiO$_2$–MgO–17% Al$_2$O$_3$ slags decreases with the increase of MgO content which is in the range of 5–10 mass%. However, the dependence relationship is reversed when MgO content is over 10 mass%. The viscosity of CaO–SiO$_2$–10 mass% MgO–Al$_2$O$_3$ slags and CaO–SiO$_2$–11% MgO–Al$_2$O$_3$ slags exhibits the minimum value at 16 mass% Al$_2$O$_3$, which may contribute to the amphiprotic properties of Al$_2$O$_3$. The above phenomenon can also be verified by the infrared spectra. Simultaneously, in order to make the blast furnace working smoothly, the viscosity value of the slag is below 1.0 Pa·s commonly. Thus, we define the temperature of the slag with a viscosity value of 1.0 Pa·s as “Critical Temperature (CT)”. And, the effect of MgO and Al$_2$O$_3$ content on CT is also studied by the phase diagram. We can conclude that the fall of the CT can be owe to the simplified network structure at the MgO content from 5 mass% to 10 mass%, while the rise may be because of the appearance of solid phase at the MgO content from 10 mass% to 15 mass%.

KEY WORDS: slag viscosity; Al$_2$O$_3$; MgO; infrared spectra; critical temperature.

1. Introduction

Slag viscosity is one of the most important physico-chemical properties governing gas permeability, slag/metal separation and desulfuration in the blast furnace. So viscous behavior of the slag plays a critical role in determining the stability and productivity in the blast furnace operation. Thus, it is necessary to understand the slag viscosity and the influence factors for improving the stability and productivity.

Recently, iron ore containing high Al$_2$O$_3$ content has been largely used as the raw material in the blast furnace. Thus, the Al$_2$O$_3$ content in the slag will be certainly increased, and then the viscous behavior of the slag will be variation. It is well known that Al$_2$O$_3$ is an amphoteric oxide. Al$_2$O$_3$ behave as either a basic oxide or an acidic oxide depending on the slag composition. In order to improve the properties of slag containing high Al$_2$O$_3$ content, some researchers have investigated the effect of MgO addition on the viscosity. In CaO–MgO–SiO$_2$–Al$_2$O$_3$ slag system, the viscosity decreases firstly and then increases with increasing MgO content. In CaO–MgO–SiO$_2$–20 mass% Al$_2$O$_3$ slag system, the viscosity decreased significantly with the MgO content from 5 to 10 mass%, while it decreased slightly with the MgO content from 10 to 13 mass%. Therefore, the effect of MgO content on the viscosity in different slag system does not reach an agreement. Thus, the influencing factor on the viscosity should be researched further.

In addition, the temperature of the slag with a viscosity value of 1.0 Pa·s is defined as “Critical Temperature (CT)” in this paper. It is necessary to obtain the CT value of different CaO–MgO–SiO$_2$–Al$_2$O$_3$ slag system for understanding the stability of the slag.

Therefore, the effect of Al$_2$O$_3$ and MgO on the viscosity of CaO–MgO–SiO$_2$–Al$_2$O$_3$ slags (CaO/SiO$_2$=1.0) containing MgO content from 5 to 15 mass% and Al$_2$O$_3$ content from 14 to 17 mass% was investigated in this paper. The CT of the slags containing different Al$_2$O$_3$ and MgO content was analyzed. In addition, fourier transform infrared (FT-IR) spectroscopy of the slag was measured to understand the structural rule of the slags. The relation between the slag viscosity and structure will also be discussed.

2. Experimental

The slags are prepared by mixing pure oxides (MgO, SiO$_2$, Al$_2$O$_3$), and pure CaCO$_3$ as source of CaO respectively. The chemical compositions of slags are shown in Table 1. The 200 g powders are pre-melted for 1 h at 1773°C.
K in order to obtain the quenched slag as the sample for the experiments. The slag sample of 10 g is used to measure the FT-IR spectra of the slags and the other slag sample is used to measure the viscosity.

The rotating-cylinder method\(^8,10\) is employed to measure the slag viscosity in this work. The schematic diagram of the experiment apparatus is shown in Fig. 1. An electric resistance furnace with U-shape MoSi\(_2\) heating elements is used for system heating. 140 g sample is placed in the graphite crucible (height, 80 mm; inner diameter, 40 mm), and then the sample is heated up to 1773 K at a rate of 5 K/min with constant Ar gas (500 mL/min). The viscosity measurement is carried out at every 10 K interval on cooling. The equilibration time is 20 min at each temperature.

### Table 1. The chemical compositions of slags.

| Sample Number | Chemical composition/mass% | CaO/SiO\(_2\) (Mass/Mass) |
|---------------|---------------------------|----------------------------|
| 01            | 39.0 39.0 5.0 17.0        | 1.0                        |
| 02            | 38.0 38.0 7.0 17.0        |                            |
| 03            | 37.0 37.0 9.0 17.0        |                            |
| 04            | 38.0 38.0 10.0 14.0       |                            |
| 05            | 37.5 37.5 15.0           |                            |
| 06            | 37.0 37.0 16.0           |                            |
| 07            | 36.5 36.5 17.0           |                            |
| 08            | 37.5 37.5 11.0 14.0      |                            |
| 09            | 37.0 37.0 15.0           |                            |
| 10            | 36.5 36.5 16.0           |                            |
| 11            | 36.0 36.0 17.0           |                            |
| 12            | 35.5 35.5 12.0 17.0      |                            |
| 13            | 35.0 35.0 13.0 17.0      |                            |
| 14            | 34.5 34.5 14.0 17.0      |                            |
| 15            | 34.0 34.0 15.0 17.0      |                            |

The rotating-cylinder method\(^9,19\) is employed to measure the slag viscosity in this work. The schematic diagram of the experiment apparatus is shown in Fig. 1. An electric resistance furnace with U-shape MoSi\(_2\) heating elements is used for system heating. 140 g sample is placed in the graphite crucible (height, 80 mm; inner diameter, 40 mm), and then the sample is heated up to 1773 K at a rate of 5 K/min with constant Ar gas (500 mL/min). The viscosity measurement is carried out at every 10 K interval on cooling. The equilibration time is 20 min at each temperature.

### 3. Results and Discussion

#### 3.1. The Effect of MgO on the Viscosity

The dependence of viscosity of the CaO-SiO\(_2\)-17 mass% Al\(_2\)O\(_3\)-MgO slag (CaO/SiO\(_2\) = 1.0) on temperature at different MgO content is shown in Fig. 2(a). Viscosity of slag with MgO content more than 12 mass% increases rapidly with decrease of the temperature. Conversely, the viscosity curve of slag with MgO content less than 11 mass% is relatively smooth. The steep rise phenomenon may be due to generate solid phase with high melting point in the slag.

Figure 2(b) shows the effect of MgO content on viscosity of the CaO-SiO\(_2\)-17 mass% Al\(_2\)O\(_3\)-MgO slag at 1673 K, 1723 K and 1773 K. In present studies, the viscosity decreases with increasing MgO content from 5 to 10 mass%. This is because of that MgO could provide oxygen ions for the slag and then depolymerized network structure in the slag into simple polymer type units. When the MgO content is about 10 mass%, the network structure could has become the relatively simple units in the slag. The further depolymerization is rarely with increasing the MgO content. But the MgO in excess of 10 mass% could be embedded into the simple units, which will result in the increase of the viscosity. At the same time, the increase of the viscosity is more obvious at 1673 K is contribute to the appearance of the solid phase in the slag.\(^17\)

#### 3.2. The Effect of Al\(_2\)O\(_3\) on the Viscosity

The dependence of viscosity of the CaO-SiO\(_2\)-Al\(_2\)O\(_3\)-10, 11 mass% MgO slag (CaO/SiO\(_2\) = 1.0) on temperature at different Al\(_2\)O\(_3\) content is shown in Fig. 3(a). The minimum

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\(^9\) But the MgO in excess of 10 mass% could be embedded into the simple units, which will result in the increase of the viscosity. At the same time, the increase of the viscosity is more obvious at 1673 K is contribute to the appearance of the solid phase in the slag.\(^17\)
viscosity of the slag containing 10 mass% MgO appear at 16 mass% Al₂O₃, which has the similar regularity with the slag containing 11 mass% MgO. Figure 3(b) shows the effect of Al₂O₃ content on viscosity of the CaO-SiO₂-Al₂O₃-10 mass% MgO slag at 1673 K, 1723 K and 1773 K. The viscosity is approximate agreement with the previous work, but the viscosity is fluctuant with increasing Al₂O₃ content in present work. It is well known that Al₂O₃ is an amphoteric oxide. When Al₂O₃ behave as a basic oxide, it can depolymerize the slag structure and decrease the viscosity. However, when Al₂O₃ behave as an acid oxide, it can increase the viscosity. Therefore, Al₂O₃ should exist in two forms that are Al³⁺ and [AlO₄]³⁻. When the Al₂O₃ content ranged from 14 to 15 mass%, more [AlO₄]³⁻ structure will been generated in the slag, and the viscosity of the slag will be increased. The amount of Al³⁺ increases more dominant than [AlO₄]³⁻ with increasing the Al₂O₃ content to 16 mass%, and the viscosity is decreased.

3.3. FT-IR Spectra of the Slags

To understand the effect of the slag structure on the viscosity, FT-IR spectra of the quenched slag at 1773 K is measured. The FT-IR spectra of CaO-SiO₂-Al₂O₃-MgO slag (CaO/SiO₂ = 1.0) at different MgO content is shown in Fig. 4. The trough of the Si–O symmetric stretching bands are found between 1200 and 760 cm⁻¹ when the slag contains 5 mass% MgO. However, they are found between 1200 and 730 cm⁻¹ when the slag contains 10 mass% MgO. The results indicates that the degree of polymerization of silicate units decreases with increasing MgO content from 5 mass% to 10 mass%. The trough of the bands of 10 mass% MgO is similar with that of 15 mass% MgO. At the same time, the prominent peak that caused by the simple [SiO₄]⁴⁻ tetrahedra appears at about 860 cm⁻¹. It may be cause that the most of the silicate units have already been depolymerized to the relatively simple units at the 10 mass% MgO. The silicate units will seldom change with the MgO content up to 15 mass%. However, the depth of the transmittance bands becomes deeper at 15 mass% MgO than that at 10 mass% MgO. This suggests that the silicate units may behave more distinct in the slag containing 15 mass% MgO. Therefore, the structure of the slag containing 10 mass% MgO may be the most simple, which corresponds well with the result of the viscosity in Fig. 3(b).
at 15 and 17 mass% $\text{Al}_2\text{O}_3$ but relatively inapparent at 16 mass% $\text{Al}_2\text{O}_3$. In addition, the depth of the transmittance bands for the $\text{Si}–\text{O}–\text{Al}$ rocking near 480 cm$^{-1}$ becomes shallower at 16 mass% $\text{Al}_2\text{O}_3$. Therefore, the viscosity of the slag containing 16 mass% $\text{Al}_2\text{O}_3$ behave the most lowest.

### 3.4. The Critical Temperature (CT) of the Slags

In order to receive the critical temperature (CT), An Arrhenius-type relationship was adopted. The Arrhenius-type is expressed as

$$\ln \eta = \ln A + E_\eta / (RT)$$

Where $\eta$ is viscosity, $A$ is Arrhenius constant, $R$ is gas constant, $T$ is temperature, $E_\eta$ is activation energy. The viscosity value less than 1.0 Pa·s in Figs. 2 and 4 is used to calculate A and E to ensure the linear relation. The results of the calculation are provided in Table 2 and Fig. 6. The Figs. 6(a) and 6(b) shows the dependence of natural logarithm of viscosity of the CaO–SiO$_2$–Al$_2$O$_3$–MgO slag (CaO/SiO$_2$=1.0) on reciprocal of temperature at different MgO and Al$_2$O$_3$, respectively. The slag containing 10 mass% MgO has the lowest activation energy in the CaO-SiO$_2$-17 mass% Al$_2$O$_3$-MgO slag system. Meanwhile, in the CaO-SiO$_2$-Al$_2$O$_3$-10 mass% and 11 mass% MgO slag system, both the activation energy of the slag containing 16 mass% Al$_2$O$_3$ has the lowest value.

The CT can be calculated according to Table 2 and Fig. 6. Sometimes, The CT will be also revised by Figs. 2(a) and 3(a) for reducing errors. The CT in CaO–SiO$_2$–Al$_2$O$_3$–MgO (C/S = 1.0) slag containing Al$_2$O$_3$ content from 14 mass% to 17 mass% as a function of MgO content is showed in Fig. 7. The CT firstly decreased and then increased with increasing MgO content when the Al$_2$O$_3$ content is 17 mass%. Figures 8(a) and 8(b) shows the phase diagrams of CaO–SiO$_2$–Al$_2$O$_3$–MgO slag containing 15 mass% and 20 mass% Al$_2$O$_3$. $^{23}$ It can be seen that the liquidus temperature is close to 1673 K at MgO content from 5 mass% to 10 mass%. However, the liquidus temperature rises obviously when the MgO content is 15 mass%. This indicates that the fall of the CT can be owe to the simplified network structure at the MgO content less than 10 mass% while the rise is because of the appearance of solid phase in the slag containing more than 10 mass% MgO. The CT has a minimum value at 16 mass% Al$_2$O$_3$ and a maximum value at 15 mass% Al$_2$O$_3$ when the slag contains 10 mass% and

### Table 2. The viscosity activation energy of slags.

| CaO/SiO$_2$ (Mass/Mass) | MgO (Mass%) | Al$_2$O$_3$ (Mass%) | $E_\eta$ (kJ/mol) |
|-------------------------|-------------|---------------------|------------------|
| 1.0                     | 5           | 17                  | 216              |
| 7                       | 17          |                      | 212              |
| 9                       | 17          |                      | 224              |
| 10                      | 14          | 223                 |
| 15                      | 222         |
| 16                      | 215         |
| 17                      | 200         |
| 11                      | 14          | 208                 |
| 15                      | 229         |
| 16                      | 204         |
| 17                      | 206         |
| 12                      | 17          | 206                 |
| 13                      | 17          | 210                 |
| 14                      | 17          | 188                 |
| 15                      | 17          | 161                 |

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11 mass% MgO. The existence form of Al₂O₃ in the slag play a major role in the CT.

4. Conclusion

In this study, the viscosity of CaO–SiO₂–Al₂O₃–MgO quaternary slag (CaO/SiO₂=1.0) containing different Al₂O₃ and MgO content is measured. The viscosity of the slag containing 17 mass% Al₂O₃ decreases with the increase of MgO content from 5 to 10 mass%, and then the viscosity increases with MgO content from 10 up to 15 mass%. The FI-TR spectra also shows that the silicate units have already been depolymerized to the most simple units at the 10 mass% MgO. The viscosity of the slag containing 10 and 11 mass% MgO is fluctuant with the increase of Al₂O₃ content from 14 to 17 mass%. It shows a minimum when the slag contains 16 mass% Al₂O₃, which can be confirmed by the FI-TR spectra. The fall of the CT can be owe to the simplified network structure at the MgO content less than 10 mass% while the rise is because of the appearance of solid phase in the slag containing more than 10 mass% MgO.

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