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Effect of $\text{MgO}/\text{Al}_2\text{O}_3$ Ratio on Viscosity of Blast Furnace Primary Slag

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Abstract: The effects of MgO , Al_2O_3 , C/S (CaO/SiO_2) and FeO on the viscosity and the liquidus temperature (T_{LQ}) of blast furnace (BF) primary slag were analyzed by using multiphase equilibrium. The results show that the T_{LQ} of primary slag exhibits a minimum value at 12 wt% Al_2O_3 and 14 wt% Al_2O_3 when MgO contents are 8 wt% and 10 wt%, respectively. It can be suggested that the content of MgO in primary slag is prone to be retained at different value when Al_2O_3 is different for smooth operation. The suitable value of $\text{MgO}/\text{Al}_2\text{O}_3$ ratio increases with the increase of Al_2O_3 content from 10 wt% to 18 wt% in the primary slag and the proper $\text{MgO}/\text{Al}_2\text{O}_3$ ratio is 0.4–0.55. The T_{LQ} of the slag increases with the increase of C/S when Al_2O_3 content is lower than 14 wt%, while it decreases with the increase of the C/S when Al_2O_3 is higher than 14 wt%. The slag viscosity decreases with the increase of FeO content. The isoviscosity curves become closer and closer when FeO is in a low level. In the condition of the high Al_2O_3 content, improving the reduction degree of iron ore in the upper area of the BF can achieve a lower T_{LQ} and have a smooth operation.

Keywords: blast furnace, primary slag, $\text{MgO}/\text{Al}_2\text{O}_3$, viscosity, liquidus temperature

Introduction

Considering the environment, resource condition and cost-reducing issues at present, the great efforts to utilize the high-aluminum-content iron ore have been made in ironmaking production in China. The high content of Al_2O_3 in blast furnace (BF) slag with higher T_{LQ} and higher viscosity has a great effect on BF operation, which makes the separation of slag iron difficult and causes the worst permeability of BF gas [1–3]. Increasing MgO content is a good way to ensure the stability and fluidity of molten slag in the actual BF production.

Recently, much of these attention in understanding the MgO effect on the viscosity of slag have been focused mostly on the final slag. Kim et al. [4] studied the effect of MgO on the viscosity of the $\text{CaO}-\text{SiO}_2-20$ wt% Al_2O_3 – MgO slag system with CaO/SiO_2 from 1.0 to 1.2 and MgO content in the range of 5–13 wt% at 1,500°C. Wang et al. [5] revealed the influence of basicity and $\text{MgO}/\text{Al}_2\text{O}_3$ ratio on the viscous behavior of $\text{CaO}-\text{SiO}_2-\text{Al}_2\text{O}_3$ – $\text{MgO}-\text{CaCl}_2$ slags under conditions of $\text{C/S}=0.90$ –1.30 and $\text{MgO}/\text{Al}_2\text{O}_3=0.40$ –0.67. It indicated that the $\text{MgO}/\text{Al}_2\text{O}_3$ ratio almost has no influence on the viscosity of the chlorine-containing slags at higher temperatures. Gao et al. [6] revealed the effect of basicity and MgO content on the viscosity of SiO_2 – CaO – MgO – Al_2O_3 slags, which indicated that increasing the basicity was found to be more effective than increasing the MgO content in decreasing the viscosity of the slag. X.F. Zhang et al. [7] focused on the effect of $\text{MgO}/\text{Al}_2\text{O}_3$ on the viscosity and break point temperature of the BF final slag system under the condition of 14.84–23.84 wt% Al_2O_3 content and relatively high MgO content of 8.87–17.6 wt% as well as a relatively high basicity of 1.14. However, in view of the final slag, the proper $\text{MgO}/\text{Al}_2\text{O}_3$ was recommended in a range of 0.6–0.7 by X.F. Zhang et al. while that was suggested in the range of 0.2–0.5 by F. M. Shen et al. [8] In the actual BF production, $\text{MgO}/\text{Al}_2\text{O}_3$ of final slag was in a wide range in China. More than 700 slag contents in BFs were investigated by the present authors. The results are shown in Figure 1. $\text{MgO}/\text{Al}_2\text{O}_3$ varies in a wide range from 0.35 to 1.0 and the average of $\text{MgO}/\text{Al}_2\text{O}_3$ is 0.6 in China.

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Figure 1: MgO/Al₂O₃ varies with blast furnace effective volume in China.

Furthermore, as can be seen from the statistics data in Figure 1, the larger the volume of BFs, the lower the MgO/Al₂O₃ of the slags. So the BFs can have a smooth operation in a wide MgO/Al₂O₃ of final slag. Besides, the increase of the viscosity of BF final slag with the decrease of MgO content in the high temperature is negligible. The sulfur removal capacity and the fluidity of final slag have not significantly been affected by lowering the MgO content as binary basicity is the most important factor. Moreover, as well known, the performance of the primary slag is important for the BF operation. Thus, it is necessary to study the fluidity and the stability of BF primary slag with the change of MgO/Al₂O₃ for maintaining stable BF operations.

In terms of the reduction of iron ore in the BF, the viscosities of CaO–SiO₂–Al₂O₃–MgO–FeO system slags were measured for slag compositions at C/S=1.15–1.6, 10–13 mass% Al₂O₃, 5–10 mass% MgO and 0–20 mass% FeO by Lee et al. [9]. Kim et al. [10] studied the viscosities of CaO–SiO₂–Al₂O₃–MgO–FeO slag which were measured under conditions of C/S=1.35–1.45, 10–18 mass% Al₂O₃, 3.5–10 mass% MgO and 5 mass% FeO. However, few study on the influence of MgO/Al₂O₃ on the viscosity and T_{LQ} of CaO–SiO₂–Al₂O₃–MgO–FeO slag system. Thus, in this paper, CaO–SiO₂–Al₂O₃–MgO–FeO slag systems were investigated in the conditions of C/S=1.25–1.40, 5–15 wt% FeO, 10–18 wt% Al₂O₃ and 4–10 wt% MgO to have a better understanding of MgO/Al₂O₃ on the BF slag and the preferential slag compositions for optimal BF operation.

Research method

The cell model was adopted and further developed by the CSIRO group in the past few decades. In addition, the available experimental data as well as the modeling studies results of the viscosity of iron-containing silicate slags in the CaO–MgO–FeO–Fe₂O₃–SiO₂–Al₂O₃ system has been reviewed. Based on the analysis, a new model and database that includes a substantial list of oxide species commonly found in ferrous smelting was developed, which is incorporated in a computational package, multiphase equilibrium (MPE) software [11, 12].

The scope and capability of the MPE software covers a great number of elements in various condensed phases that are commonly found in processes such as ironmaking and steelmaking, copper smelting etc. The previous published work has provided some details of the assessment carried out as well as application of the model to predict the viscosities of the melts [13, 14]. Figure 2 shows a comparison of the modeling results with the measured viscosity of BF slags. Very close agreement is observed over several orders of magnitude between model predictions and experimental measurements. The MPE software has been applied by researchers and plant metallurgists for the prediction of the multiphase equilibria of the slag as well as the viscosity. In this paper, the effect of the C/S, MgO, Al₂O₃ and FeO on the viscosity and the liquidus temperature of the BF primary slags were analyzed by using MPE, and all of the data were from the MPE software.

Figure 2: Comparison between the calculated and experimental viscosity.

Results and discussion

Effect of Al₂O₃ and MgO on viscosity

The effect of Al₂O₃ contents on the viscosity of the SiO₂–CaO–MgO–Al₂O₃–FeO slag system at a fixed basicity of 1.3 as a function of temperature is shown in Figure 3. With the temperature increasing, the viscosity decreases smoothly in the fully liquid region. And, the slag viscosity increases rapidly as the temperature increases to a specific value. Thermodynamically, the liquid and solid phase can coexist in equilibrium at that temperature, which should be the liquidus temperature of the slag, T_{LQ} .

Similar to formerly published work [15], the additions of Al₂O₃ in the molten slag can increase the slag viscosity, as shown in Figure 3(a). Regardless of the Al₂O₃ concentration in the slag, a lower temperature of the slag corresponds to a higher viscosity, which clarifies that the effect of temperature is predominant compared to the Al₂O₃ additions and that the effect of temperature is much more influential at high Al₂O₃ content. With the increase of MgO (from Figure 3 (a) to Figure 3(d)), the influence of Al₂O₃ on the slag viscosity becomes weaker as the temperature range becomes smaller.

The influence of Al₂O₃ on the slag viscosity in different MgO content is too complex to distinguish easily. For example, from the calculation curve which is on behalf of the result at 4 wt% MgO, the slag viscosity increases with the increase of Al₂O₃ both in the high slag temperature range and in the low-temperature range. The viscosity increases with the increase of Al₂O₃ in the high slag temperature

range but varies differently in the low-temperature range for the result of 10 wt% MgO. Thus, for a clearer view of the viscosity stability, the liquidus temperatures of different MgO content and different Al₂O₃ content are calculated and shown in Figure 4.

In Figure 4, T_{LQ} of slag with 10 wt% FeO and C/S = 1.3 exhibits a minimum value at about 4 wt% MgO when Al₂O₃ is 10 wt% and T_{LQ} increases with the increase of MgO. In the case of 12 wt% Al₂O₃, the T_{LQ} of slag achieves a minimum value at approximately 8 wt% MgO followed by 6 wt% MgO. When Al₂O₃ is over 14 wt%, T_{LQ} decreases with the increase of MgO. In addition, the T_{LQ} of slag with 4 wt% MgO and 6 wt% MgO increases from about 1,320 to 1,440 °C by increasing Al₂O₃ content from 10 wt% to 18 wt%, while that of slag with 8 wt% MgO and 10 wt% MgO first decreases and then increases with the increase of Al₂O₃. The T_{LQ} of slag has a minimum value at about 12 wt% Al₂O₃ and 14 wt% Al₂O₃ when MgO contents are 8 wt% and 10 wt %, respectively. Thus, it can be indicated in terms of T_{LQ} of slag that MgO content in primary slag is prone to be maintained at a different value when Al₂O₃ is different for the stable BF operation. Furthermore, the melting temperature and the viscosity of primary slag play a significant role for BF operation because the temperature of cohesive region, at which slag formation proceeds, is less than 1,500 °C. In addition, compared to the final slag, Al₂O₃ content in primary slag is not assimilated sufficiently with ash as part of SiO₂ and Al₂O₃ are from coke and/or coal. So Al₂O₃ in the primary slag is much lower than that of the final slag.

The isoviscosity curves of the slag are shown in Figure 5 at different MgO/Al₂O₃ and the fixed Al₂O₃ content as a function of temperature. The contents of Al₂O₃ in Figure 5 (a)–5(e) are 10 wt%, 12 wt%, 14 wt%, 16 wt%, and 18 wt%, respectively. With the temperature decreasing and the Al₂O₃ content increasing, the isoviscosity variations become closer and closer, which clarifies that the thermal stability of primary slag starts to deteriorate. Al₂O₃ plays much more influence on the slag viscosity at high Al₂O₃ concentration with the Al₂O₃ content increasing and the temperature decreasing. It can be seen that the viscosities at constant MgO/Al₂O₃ ratio increase with the decrease of temperature in particular at a lower MgO/Al₂O₃ ratio and the value rises abruptly as the decrease of temperature.

In addition, it is found from Figure 5 that the MgO/Al₂O₃ ratio of the slag presents obvious effect on the slag viscosity. For example, in the area where the MgO/Al₂O₃ ratio is low in Figure 5(b), with the increase of the MgO/Al₂O₃ ratio, the isoviscosity curves become scarce gradually, which declares that the MgO/Al₂O₃ ratio can reduce the effect of the temperature on the slag viscosity gradually and that the MgO/Al₂O₃ ratio can improve the

Figure 3: Viscosities of CaO-SiO₂-Al₂O₃-MgO-10 wt% FeO systems by varying Al₂O₃ content as a function of temperature at C/S=1.3: (a) 4 wt% MgO; (b) 6 wt% MgO; (c) 8 wt% MgO; (d) 10 wt% MgO.

Figure 4: T_{LQ} of CaO-SiO₂-Al₂O₃-MgO-10 wt% FeO slags as a function of Al₂O₃.

slag stability. However, it has an opposite effect in the area where the MgO/Al₂O₃ ratio of the slag is high. Therefore, the MgO/Al₂O₃ ratio of the slag cannot remain too much deviated, and the stability and the fluidity of the slag can be obviously improved by a suitable MgO/Al₂O₃ ratio. In addition, comparing Figure 5(a)–5(e), it indicates that the proper value of the MgO/Al₂O₃ ratio increases with the increase of Al₂O₃ content from 10 wt% to 18 wt% in the slag and the proper MgO/Al₂O₃ ratios are 0.4, 0.5, 0.55, 0.55 and more than 0.55, respectively.

The dependence of slag viscosity on the binary basicity (C/S) of the slag from 1.25 to 1.4 is shown in Figure 6. Al₂O₃ in Figure 6(a) is 10 wt% while that in Figure 6(b) is 16 wt%. As shown in Figure 6, the slag viscosity increases with C/S in the lower temperature when Al₂O₃ is 10 wt% while the slag viscosity decreases with C/S when Al₂O₃ is

Figure 5: Influence of MgO/Al₂O₃ ratio and temperature on viscosity for different Al₂O₃. (a) 10 wt%, (b) 12 wt%, (c) 14 wt%, (d) 16 wt% and (e) 18 wt%.

Figure 6: Effect of the slag basicity from 1.25 to 1.4 on the slag viscosity. (a. Al₂O₃ = 10 wt%, b. Al₂O₃ = 16 wt%).

Figure 7: Influence of MgO/Al₂O₃ ratio and temperature on viscosity for Al₂O₃ = 10 wt% (a) and Al₂O₃ = 16 wt% (b).

16 wt%. Therefore, C/S has an important effect on the slag viscosity. The isoviscosity curves of 10 wt% Al₂O₃ and 16 wt% Al₂O₃ are indicated in Figure 7. It can be seen that when Al₂O₃ is in a low level, increasing C/S can reduce the slag viscosity. It is a good way to reduce the slag viscosity by decreasing C/S if Al₂O₃ is in a high level. Figure 8 exhibits the dependence of slag T_{LQ} on the slag C/S from 1.25 to 1.4. The slag T_{LQ} decreases with the increase of C/S and then increases at higher C/S. Besides, the T_{LQ} at C/S = 1.25 and 1.3 exhibits minimum values at about 12 wt% Al₂O₃, while the T_{LQ} at C/S = 1.35 and 1.4 exhibits minimum values at about 14 wt% Al₂O₃. The T_{LQ} of the slag increases with the increase of the C/S when Al₂O₃ is lower than 14 wt%, while the T_{LQ} of the slag decreases with the increase of the C/S when Al₂O₃ is higher than 14 wt%. In general, the viscosity of slags decreases with the increase of C/S because the structure

Figure 8: Effect of the basicity on the T_{LQ} of CaO-SiO₂-Al₂O₃-MgO-FeO system at 8 wt% MgO and 10 wt% FeO.

of the silicate network in the melt will be destroyed, producing a simple structure with the increase in basic oxides [14, 16]. Theoretical analysis of silicate polymerization degree can be used to explain the result of slag viscosity in the composition of Al₂O₃ lower than 14 wt%. It is well known that Al₂O₃ is amphoteric oxide and its behavior depends on the composition of the slag [17]. In the condition of high Al₂O₃ content slag in the study, Al₂O₃ would behave as acid oxide and the increasing of viscosity with the increase of Al₂O₃ can be understood based on the increase of the polymerization degree by the incorporation of the [AlO₄]-tetrahedral into the [SiO₄]-tetrahedral units, as explained in the reference [18].

Figure 9 exhibits the dependence of primary slag viscosity on the FeO content from 5 wt% to 15 wt%. It indicates that the slag viscosity decreases with the increase of FeO. It is also demonstrated by the isoviscosity curves in Figure 10. It can be seen that the isoviscosity curves become closer and closer when FeO is low. Dependence of T_{LQ} on FeO content and Al₂O₃ content at C/S = 1.3 and 8 wt% MgO is shown in Figure 11. The T_{LQ} of the slags increase first and then decrease as Al₂O₃ content increases from 10 wt% to 18 wt%. It can be seen from Figure 11 that the typical slags containing Al₂O₃ content which is more than 14 wt% exhibit relatively high T_{LQ} . The T_{LQ} decreases with the increase of FeO content in the slag. Thus, the slag fluidity in BF cohesive zone could be affected by the reduction rate of iron ore and the content of the slag. Toop and Samis found that in CaO–FeO–SiO₂ melts, FeO does not associate with the silicate groups in the low basicity region but supplies free Fe²⁺ and O²⁻ ions to the silicate melts and causes the mixing entropy of silicate melt to increase [19]. FeO in the slag can lower the melting

Figure 9: Effect of FeO content from 5 wt% to 15 wt% on the slag viscosity.

Figure 10: Influence of FeO and temperature on viscosity for MgO/Al₂O₃ = 0.67.

Figure 11: T_{LQ} of CaO–SiO₂–Al₂O₃–MgO–FeO system as a function of the FeO and Al₂O₃ at 8 wt% MgO and C/S at 1.3.

temperature of slags [20]. It indicates that improving the reduction rate of iron ore can achieve a lower T_{LQ} and have a smooth operation in high Al₂O₃ content slag.

Conclusions

- (1) The T_{LQ} of slag exhibits a minimum value at about 12 wt% Al₂O₃ and 14 wt% Al₂O₃ when MgO contents are 8 wt% and 10 wt%, respectively. The MgO content in primary slag is prone to be maintained at different values when Al₂O₃ is different for the stable BF operation.

- (2) The suitable value of the MgO/Al₂O₃ ratio increases with the increase of Al₂O₃ content from 10 wt% to 18 wt% in the slag and the proper MgO/Al₂O₃ ratios are 0.4–0.55.
- (3) The T_{LQ} of the slag increases with the increase of C/S when Al₂O₃ is lower than 14 wt% while that decreases with the increase of the C/S when Al₂O₃ is higher than 14 wt%.
- (4) The slag viscosity decreases with the increase of FeO. The isoviscosity curves become closer and closer when FeO is low. Improving the reduction rate of iron ore can achieve a lower T_{LQ} and have a smooth operation in the high Al₂O₃ content.

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