

REACTION MECHANISM ANALYSIS OF THE Al_2O_3 IN BLAST FURNACE (BF) SLAG

Received – Priljeno: 2019-03-22

Accepted – Prihvaćeno: 2019-06-18

Original Scientific Paper – Izvorni znanstveni rad

Al_2O_3 is one of the main component in blast furnace (BF) slag, which the reaction mechanism influence on the metallurgical performance directly in the process of the slag forming. In the paper, ΔG_f^θ was used to analyzed the slag formation reaction process of the Al_2O_3 , at the same time, the phase diagram and activity were calculated by FactSage with CaO - MgO - SiO_2 - Al_2O_3 slag system, it can be found that the complete liquid phase region temperature is about 1 500 °C and the content of the Al_2O_3 is 11 %. Activity of CaO is stronger than the others, from which the liquid phase can be formed easily in the high temperature, meantime the reaction energy barrier between CaO and SiO_2 is lower and stabilization of the product is better. By the high temperature experiment, a lot of $Ca_2Al_2SiO_7$ was separated out with the high content of Al_2O_3 and slag basicity, as a result, the transformation of the solid phase to the liquid phase was effected by the constantly increasing the content of Al_2O_3 .

Keywords: blast furnace, Al_2O_3 content, slag formation reaction, crystallization, melting temperature

INTRODUCTION

The CaO - MgO - SiO_2 - Al_2O_3 is the basic slag system of the BF besides the hot metal, which the metallurgy performance play an important role in the BF smelting, fusion, fluidity and hot stability influenced directly on the reaction velocity, breathability of the stock, heat exchange, desulfuration, BF refractory material life and so on [1]. The forming process, component and the high temperature reconstruction mechanism is the key research on the metallurgical performance of the slag, from which the physicochemical property can be revealed in the process of the smelting [2].

Iron ore supply of international market was fluctuated strongly recent years, the application amount of the Al_2O_3 ore was increased when the economics ore blending was considered [3], as a result, the content of Al_2O_3 was increased to more than 15 %, meantime the viscosity of the slag was increased, which the stock breathability was affected seriously below the cohesive zone [4,5], the void fraction of the coke skeletal, coal gas resistance was increased, meantime the diffusion of the sulphur was effected when the viscosity is increased, so the desulfuration ability was decreased, the slag can't be removed easily, in this way, the research of the Al_2O_3 reaction mechanism is very important [6,7].

In the paper, thermodynamic calculation was used to analyze liquid phase product with the different content of Al_2O_3 in CaO - MgO - SiO_2 - Al_2O_3 basic slag system,

meantime the BF slag was compound by the chemical analytical purity, the interrupt experiment was carried out by water quenching method at the temperature of 1500 °C, then the samples were detected by X - Ray Diffraction (XRD), as a result, the fusion and fluidity of the slag analyzed from the reaction energy barrier, activity and acton mechanism.

THERMODYNAMIC CALULATION ΔG_f^θ analysis of the slag reaction process

As Figure 1 showed, standard gibbs free energy of the compound (ΔG_f^θ) is less than 0 from the main BF slag, the decompose and formation reaction can be proceeded spontaneously, but the reaction energy barrier of CaO and SiO_2 is less than the other, so it can be react earlier under the same conditions and the production is very stabilization, which is the liquid phase basis of the BF slag. The intersection point between CaO and Al_2O_3 , Al_2O_3 and MgO are at the temperature of 1 050 K, but the reac-

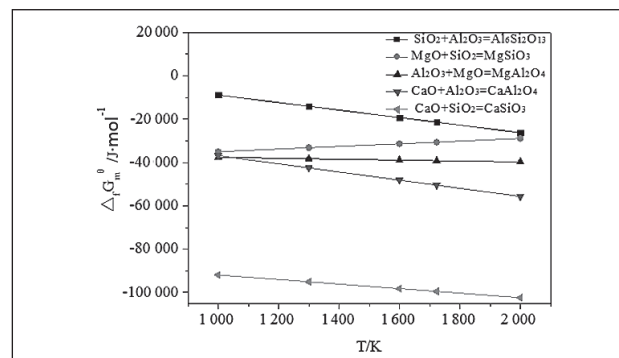


Figure 1 The main compound ΔG_f^θ of the BF slag

tion energy barrier is lower of the reaction between CaO and Al_2O_3 , and the reaction is easier with the increasing of the temperature, at the same time, the stability is more high than others, therefore the activity of the CaO is strongest, from which the liquid phase can be formed easily, In contrast, the reaction energy barrier of $Al_2O_3 - MgO$, $MgO - SiO_2$, $Al_2O_3 - SiO_2$ are more high and the reaction is difficult to carry out, so the more physics heat should be absorbed to smelt and form the slag during smelting process, even the hot metal and slag can not be separated easily with the too much Al_2O_3 . Then the fluidity of the BF slag should be controlled by adding the MgO when the high content of Al_2O_3 was used.

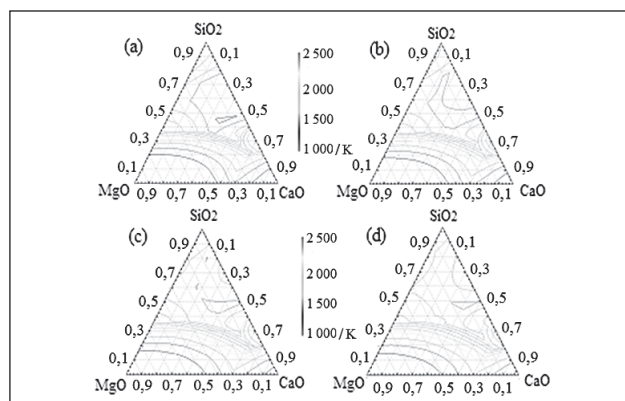
Phase diagram analysis of the slag reaction

Liquid phase projection drawing of the $SiO_2 - CaO - MgO - Al_2O_3$ slag system were calculated with the different content Al_2O_3 . When the temperature of furnace was increased to $1300\text{ }^\circ C$, the reaction between CaO and SiO_2 can be carried out with the low basicity, then the others component can be participated the reaction with increasing of the temperature, and the liquid phase region can be extended continuously, so the liquid re-

gion is maximum when the content of Al_2O_3 is 11 % at the temperature of $1500\text{ }^\circ C$ in Figure 2 (a), the melting temperature region would be decreased and the shape is changed when the content of Al_2O_3 is 13 % in Figure 2 (b), the liquid phase region would be shrinked and the two tiny liquid phase region was formed when the Al_2O_3 is 15 % in Figure 2 (c), the liquid phase region is minimum at the content of Al_2O_3 is 17 % in Figure 2 (d).

Activity calculation of the different content of Al_2O_3 in BF slag

The activity of the number 1 to number 4 samples from Table 1 were calculated by FactSage, the different component activity variation were analyzed when the content of Al_2O_3 was changed in the $CaO - MgO - SiO_2 - Al_2O_3$ slag system in the Figure 3. The activity of Al_2O_3 increased constantly with adding itself, the activity of MgO didn't be changed much by the content variation of the Al_2O_3 , but the CaO activity was fluctuated with the increasing content of Al_2O_3 , which is opposite trend curve with the SiO_2 . The main reason of the above phenomenon is that Al_2O_3 is the indissolvable matter, the low melting point matter was formed by the reaction between CaO and Al_2O_3 when the content of Al_2O_3 is lower than 13 %, meantime the activity of CaO was in-



(a) Al_2O_3 content is 11 % (b) Al_2O_3 content is 13 %
(c) Al_2O_3 content is 15 % (d) Al_2O_3 content is 17 %

Figure 2 The $SiO_2 - CaO - MgO - Al_2O_3$ slag system phase diagram

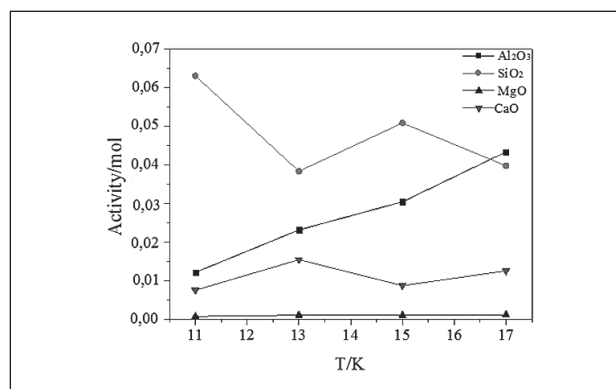


Figure 3 The different component activity variation with the Al_2O_3 of the $CaO - MgO - SiO_2 - Al_2O_3$ slag system

Table 1 The chemical composition of BF slag /wt, %

| Number | Basicity | CaO | SiO_2 | MgO | Al_2O_3 | FeO | MnO_2 | S |
|--------|----------|-------|---------|-----|-----------|-----|---------|------|
| 1 | 1 | 40,73 | 40,73 | 6 | 11 | 0,6 | 0,3 | 0,64 |
| 2 | 1,1 | 40,58 | 36,88 | 8 | 13 | 0,6 | 0,3 | 0,64 |
| 3 | 1,2 | 40,1 | 33,36 | 10 | 15 | 0,6 | 0,3 | 0,64 |
| 4 | 1,3 | 39,3 | 30,16 | 12 | 17 | 0,6 | 0,3 | 0,64 |
| 5 | 1,2 | 43,35 | 36,11 | 6 | 13 | 0,6 | 0,3 | 0,64 |
| 6 | 1,3 | 44,95 | 34,51 | 8 | 11 | 0,6 | 0,3 | 0,64 |
| 7 | 1 | 35,73 | 35,73 | 10 | 17 | 0,6 | 0,3 | 0,64 |
| 8 | 1,1 | 37,5 | 33,96 | 12 | 15 | 0,6 | 0,3 | 0,64 |
| 9 | 1,3 | 43,8 | 33,66 | 6 | 15 | 0,6 | 0,3 | 0,64 |
| 10 | 1,2 | 40,1 | 33,36 | 8 | 17 | 0,6 | 0,3 | 0,64 |
| 11 | 1,1 | 40,6 | 36,86 | 10 | 11 | 0,6 | 0,3 | 0,64 |
| 12 | 1 | 36,73 | 36,73 | 12 | 13 | 0,6 | 0,3 | 0,64 |
| 13 | 1,1 | 39,55 | 35,91 | 6 | 17 | 0,6 | 0,3 | 0,64 |
| 14 | 1 | 37,73 | 37,73 | 8 | 15 | 0,6 | 0,3 | 0,64 |
| 15 | 1,3 | 42,7 | 32,76 | 10 | 13 | 0,6 | 0,3 | 0,64 |
| 16 | 1,2 | 41,2 | 34,26 | 12 | 11 | 0,6 | 0,3 | 0,64 |

creased, but the activity of SiO_2 was decreased because of the participating reaction, when the content of Al_2O_3 is more than 13 %, the activity of SiO_2 was increased, but it was decreased when the basicity was increased, meanwhile the activity of Al_2O_3 is increased when itself was added, and the activity of MgO was enhanced little, in this way, the infusible problem of can be solved partly, and the fluxion can be improved.

EXPERIMENT

Experiment raw material

The sample were prepared by chemical analytical pure and one of the sample is 30 g, the compound of the raw material is in Table 1, then it was smelted by high temperature muffle furnace, the samples were kept at 800 °C half an hour, then the interrupt experiment was carried out at the temperature of the 1 500 °C, the sample was handle with water immediately when the furnace was opened. The XRD detection was used when the samples were milled to below 200 mesh, in this way, how the slag performances were influenced by basicity variation was analyzed by Highscore Plus software, from which microstructure was studied by the changing of the content and component of the slag, as a result, the slag formation process were analyzed in BF.

RESULTS AND DISCUSSION

The $Ca_2Al_2SiO_7$ was detected in the Figure 4, peak value of number 4, number 5, number 10, number 15 sample are more high by XRD in Figure 4 (c) and Figure 4 (d), peak value are lower in Figure 4 (a) and Figure 4 (b), so the crystallization phenomenon was happened when the basicity is high to the 1,2 or 1,3, meantime the glass phase of the slag was effected by the content of the Al_2O_3 , the precipitated phase wasn't influenced by basicity when the content of Al_2O_3 is 15 %,and the precipitated phase is little, as a result, the existence of the $Ca_2Al_2SiO_7$ was effected by basicity and content of Al_2O_3 , especially the transformation from the solid phase to the glass phase.

The iron and steel enterprise BF slag was detected by XRD in Figure 5, there is also a big envelope peak, which is identical with the laboratory test, as a result, the slag formation and the final slag performance are effected by Al_2O_3 ,and the glass phase was existed in final slag with the lower basicity, but the precipitated phase is existed possibly when the basicity is high.

CONCLUSIONS

The reaction energy barrier between CaO and Al_2O_3 is lower, and the production is very stabilization, meantime, the activity of the CaO is strongest, from which the liquid phase can be formed easily, the liquid phase region is maximum when the content of Al_2O_3 is 11 % at the temperature of 1 500 °C.

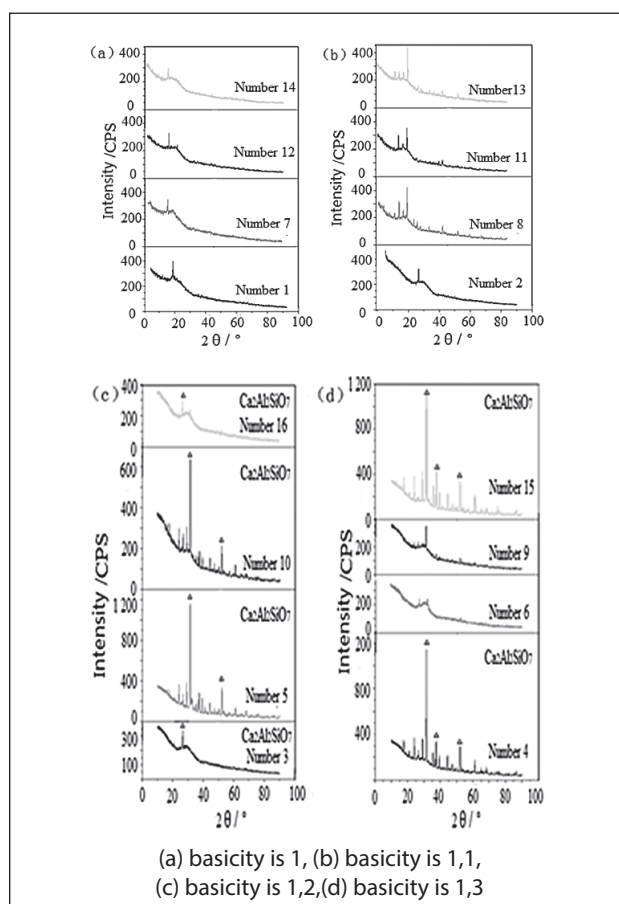


Figure 4 XRD atlas of the different basicity slag samples

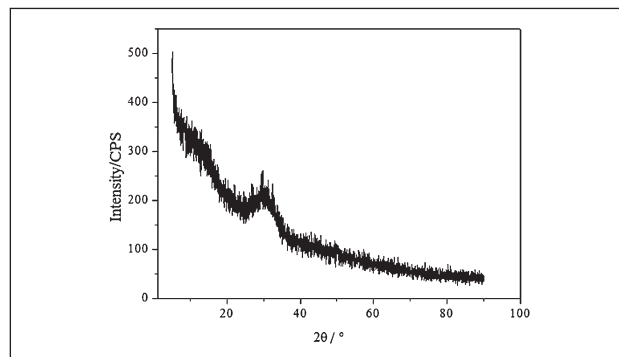


Figure 5 XRD atlas of the iron and steel enterprise BF slag

The activity of Al_2O_3 increased constantly with adding itself, the activity of MgO didn't be changed by the content variation of the Al_2O_3 ,but the low melting point matter can be formed when the reaction was happened between MgO and Al_2O_3 ,then the fluidity of slag can be improved.

A mass of $Ca_2Al_2SiO_7$ can be appeared when the both content of Al_2O_3 and the basicity are high, the process of the slag formation and the performance of eventually slag can be effected directly, so the translation of BF slag from the solid phase to liquid phase was influenced.

Acknowledgements

This work is financially Supported by the National Science and Foundation of China. (No. 2018010784 - 301 & No. 51504132 & No. 51874717)

REFERENCES

- [1] Guo J., Cheng S. S., Zhao H. B. Modeling research for estimating viscosity of SiO_2 - CaO - MgO - Al_2O_3 system molten slag based on slag structure theory [J], *Journal of Iron and Steel Research* 25 (2013) 8, 6 - 12.
- [2] Zhang K. H., Zhang Y. L., Wu K. Kinetics of hot metal desulfurization using CaO - SiO_2 - Al_2O_3 - Na_2O - TiO_2 slag [J], *Iron and Steel* 55 (2018) 11, 22 - 28.
- [3] Zhang Y. P., Zhang J. L., Mao R., Liu Z. J., Yuan X. Thermodynamic analysis on fusion temperature and melting characteristics of BF Slag [J], *Journal of Iron and Steel Research* 26 (2014) 11, 11 - 15.
- [4] Kondratieva A., Jak E., Hayes P. C. Predicting slag viscosities in metallurgical systems [J], *JOM* 54 (2002) 11, 41 - 45.
- [5] Ma X., Wang G., Wu S., et al. Phase equilibria in the CaO - SiO_2 - Al_2O_3 - MgO system with CaO/SiO_2 ratio of 1.3 relevant to iron blast furnace slags [J], *ISIJ International* 55 (2015) 11, 2310 - 2317.
- [6] Hyunsoo K., Gyu K. J. The role of molten slag in iron melting process for the direct contact carburization: wetting and separation [J], *ISIJ International* 50 (2010) 8, 1099 - 1106.
- [7] Shen F. M., Wen Q. L., Jiang X., Zheng H. Y., Wei G., Han H. S. Comparison of blast furnace slag (MgO)/(Al_2O_3) home and abroad [J], *Ironmaking* 34 (2015) 2, 1 - 3.

Note: The responsible translator for language English is associate professor Y. Wu - University of Science and Technology Liaoning, China