Fundamental Research and Applications of Blast Furnace Slag

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Abstract: Blast furnace slag is formed with ore gangue, coke ash and flux during the smelting process of hot metal production. The viscosities of blast furnace slags, including the primary and the intermediate slags (CaO -SiO_2- Al_2O_3 –FeO -MgO), have been systematically investigated. A BF slag viscosity prediction model was established, which provides important parameters for the BF operation. The viscosity and the relationship between viscosity and crystalline behavior of TiO_2-bearing BF slag were also investigated and discussed. The crystallization thermodynamics of TiO_2-bearing BF slag has been studied through phase equilibrium calculation and experimental approaches. The crystal growth and slag viscosity of TiO_2-bearing BF slag have been experimentally examined and discussed, which provides a theoretical support for the extraction of titanium and comprehensive utilization of the blast furnace slag.

On the basis of studying the influence of slag viscosity with its composition, the viscosity of BF slag and its temperature influence can be controlled by suitably adjusting their compositions. The slag fiber fabrication parameters by adding the fly ash to high-temperature molten slag have been achieved. Compared with traditional methods, the heat energy and resources of the slag can be well utilized with this method. This method will provide a new field to fully utilize the energy and resources of BF slag.

Keywords: Blast furnace slag, viscosity prediction model, Ti-bearing slag, slag fiber

1. Introduction

Blast furnace slag is formed with ore gangue, coke ash and flux during the smelting process of hot metal production. The compositions of the primary slag and the intermediate slag of the blast furnace, rich in FeO, change during the process. Its viscosities are also changes with its composition and temperatures. The BF slag viscosity is an important property which influences the BF process. However, the viscosity measurement of the primary slag and the intermediate slag of the blast furnace is very difficult. Aiming at these problems, the viscosity of the CaO-SiO_2-Al_2O_3-FeO-MgO melt is studied along with the influencing rules of each component and temperature to the viscosity. Then a viscosity prediction model is established on the basis of WEB-based neural network-genetic algorithm (ANN-GA) system. The verified result of this model indicates that the error of the model is basically within 16%, which is acceptable.

China is rich in titanium resources, and 95% of them exist as vanadium-titanium magnetite ore in Sichuan province [1]. In the BF process, most of the Ti component is concentrated in the BF slag (22~25%TiO_2) [1-3]. During the process, the viscosity of the slag increases as the slag is in reduction state which will be influencing the separation of slag from liquid iron. In addition, the viscosity of the TiO_2 bearing slag will also influence the utilization of the slag. The viscosity of BF slag has a wide range, depending on the temperature and slag composition. In previous works, the viscosity of Ti bearing slag was measured comparatively lower [4-13]. Based on the experimental and literature data, a model for predicting the viscosity of Ti bearing slag was also proposed. The crystalline behavior of anosovite from the slag has also been experimentally examined and the relationship between the crystal growth rate and the viscosity of the slag has been discussed.

High temperature BF slag also contains large amount of energy. High-temperature molten BF slag contains about 1675MJ/t heat which approximately equals the combustion heat of 57 kg standard coal. In order to take the advantage of this part of sensible heat, this article puts forward the scheme of one-step to produce slag mineral fiber with melting molten blast furnace slag by regulating the composition and the viscosities of the slag as well. The most important factor of producing slag fibers from molten BF slag is that the viscosity of the slag should keep 0.5~2.5 Pa·S during the whole temperature range from the temperature at least 50℃ higher than the liquidus temperature to its liquidus temperature. However, the slag fiber will be too thick if the viscosity is higher or too short if the viscosity is lower. In addition, the slag balls instead of slag fibers will be produced if the slag viscosity is too low at that temperature range. The basicity of BF slag (CaO/SiO_2 or $(CaO+MgO)/(SiO_2+Al_2O_3)$) is the most important factor to influence the slag viscosity during that temperature range. Experimental results reveal that the viscosity of the slag could reach the level for the temperature range by adding SiO_2 and Al_2O_3 to the slag. In this paper, fly ash, a kind of solid waste from Coal-fired power plants with the main composition of SiO_2 and Al_2O_3, is used as the additive to change the composition and the viscosity of the slag. Compared with traditional methods of producing mineral fiber, the heat energy and resources of the slag as well as fly ash can be well utilized with this method.

2. Experimental results and discussions

2.1 BF slag viscosity prediction model

Viscosity of BF slag, especially the primary and the intermediate slag, is not enough in the literature for the establishing of the prediction model. Therefore, the viscosity of some intermediate slags was measured as shown in Table 1.

Table 1 Experiment results of viscosity measurements

Number	R	Al2O3/%	MgO/%	FeO/%	1390℃(dPa.s)	1420℃(dPa.s)	1480℃(dPa.s)
1	1	10	4	3	20.29	11.3	4.1
2	1	12	6	6	11.56	5.14	3.43
3	1	14	8	10	8.09	3.91	2.9
4	1	16	10	20	16.19	6.52	2.14
5	1	18	12	30	10.87	5.66	1.67
6	1.1	10	6	10	9.08	4.42	2.37
7	1.1	12	8	20	4.06	2.44	1.8
8	1.1	14	10	30	1.46	0.93	0.78
9	1.1	16	12	3	20.18	10.24	2.83
10	1.1	18	4	6	16.34	6.8	3.9
11	1.2	10	8	30	1.49	1.0	0.93
12	1.2	12	10	3	9.64	4.71	2.05
13	1.2	14	12	6	14.79	5.87	2.17
14	1.2	16	4	10	7.42	4	1.76
15	1.2	18	6	20	8.12	4.8	1.32
16	1.3	10	10	6	3.37	1.66	0.98

17	1.3	12	12	10	6.95	2.46	1.83
18	1.3	14	4	20	3.41	1.98	1.48
19	1.3	16	6	30	2.14	1.05	0.98
20	1.3	18	8	3	17.16	7.43	2.52
21	1.4	10	12	20	2.88	1.78	1.4
22	1.4	12	4	30	1.81	0.63	0.58
23	1.4	14	6	3	14.76	7.23	3.3
24	1.4	16	8	6	7.14	4.23	2.35
25	1.4	18	10	10	12.9	6.44	2.3

The viscosity measurement was performed on the RTW-10 melt physical property comprehensive tester developed by Northeast University (Fig. 1).

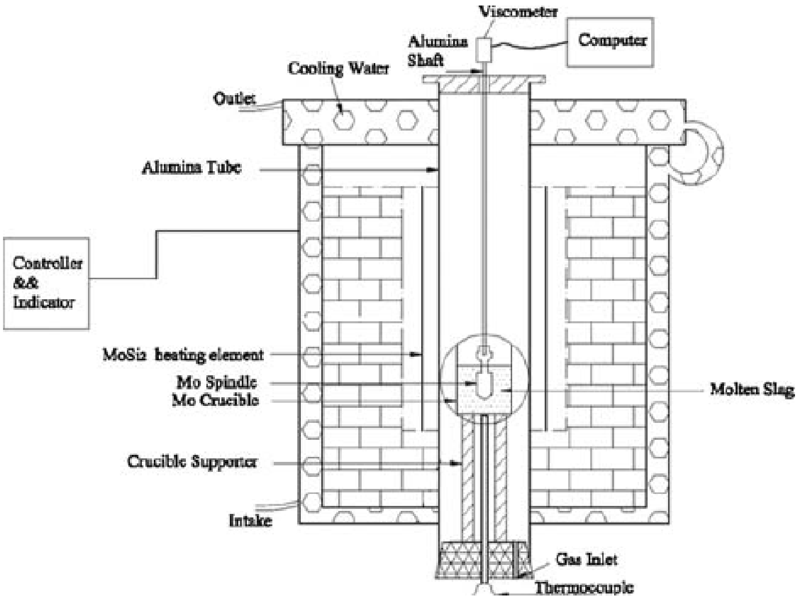


Fig.1 Experimental apparatus for measurement of slag viscosity

Based on the experimental results in the present study and the slag viscosity provided by reference[3-14], a viscosity prediction model is established on the basis of WEB-based neural network-genetic algorithm (ANN-GA) system. In the prediction model, the seven parameters, such as T, slag basicity R, SiO_2 wt.％, CaO wt.％, MgO wt.％, Al_2O_3 wt.％and FeO wt.％ are considered as the main factors influencing slag viscosity. The slag viscosity can be predicted by providing the seven parameters of the slag. The training results are shown in Fig. 2 with a related coefficient 0.992549, which is acceptable.

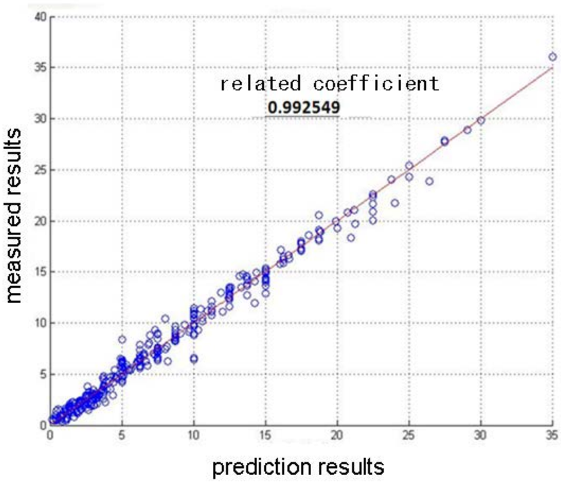


Fig.2 The training results of the prediction model (dPa・s)

In order to confirm the accuracy of the model, we choose several slags with different composition in literature (Table 2) to predict the viscosity of the slags. The predicted and measured results are shown in Table 3. The verification results indicate that the error of this model is basically within 16 % which is acceptable. Then the slag viscosity influencing by the respective factor is obtained with the prediction model as shown in Fig. 3. . Application in Laiwu iron and steel Co. found that this model is a good assistance for BF operation and the raw material option.

Table 2 Compositions of experimental slag for verifying the prediction model

Number	T/℃	SiO2/%	Al2O3/%	CaO/%	MgO/%	FeO/%
1	1500	31.91	10.00	43.09	10	5
2	1500	30.20	14.00	43.80	7	5
3	1390	30.20	14.00	43.80	7	5
4	1430	33.19	10.00	44.81	7	5
5	1340	30.21	14.00	40.79	10	5
6	1450	31.00	10	46.50	5	7.5

Table 3 Comparison between predicted results and measured results

Number	Literature results η/dPa.s	Prediction results η/dPa.s	δ_n %	$\overline{\delta}$ %
1	1.8	1.77	1.51	8.92
2	2.1	1.85	7.32	
3	10.1	9.05	9.51	
4	6.25	5.27	15.71	
5	5.2	5.88	13.1	
6	6.25	5.85	6.36	

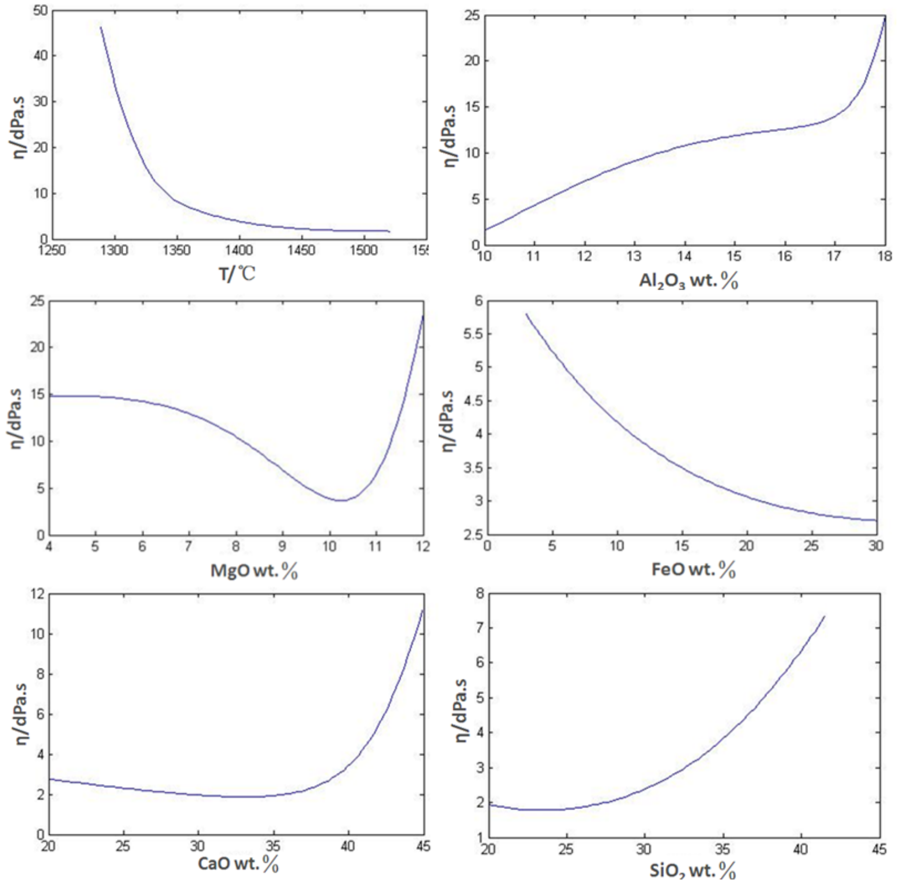


Fig.3 The slag viscosity Influencing with respective factor

(T＝1400℃, R＝1.2, Al_2O_3 wt.％＝10%, MgO wt.％＝10%, FeO wt.％＝10%）

2.2 Viscosity of Ti-bearing BF slag and crystallization experiment

Li et.al [15] proposed that the selective precipitation was the most potential method to recover Ti component from the Ti-bearing slag. In this method, Ti-bearing BF slags were modified and cooled down in a controllable cooling rate to enrich the Ti component into anosovite or rutile. The viscosity of molten slag has a decisive effect on the precipitation event. However, to the knowledge of present authors, the viscosity containing high TiO_2 content has not been systematic studied. Thus, the measurements in viscosity for Ti-bearing slag are strongly required for the better performance of selective precipitation process of Ti-bearing BF slag. In the present study, Ti-bearing BF slag with varying basiciy and TiO_2 content were designed based on the industrial BF slags from Panzhihua Iron & Steel Corporation. The viscosities of these slags were then measured, as Fig. 4 shows.

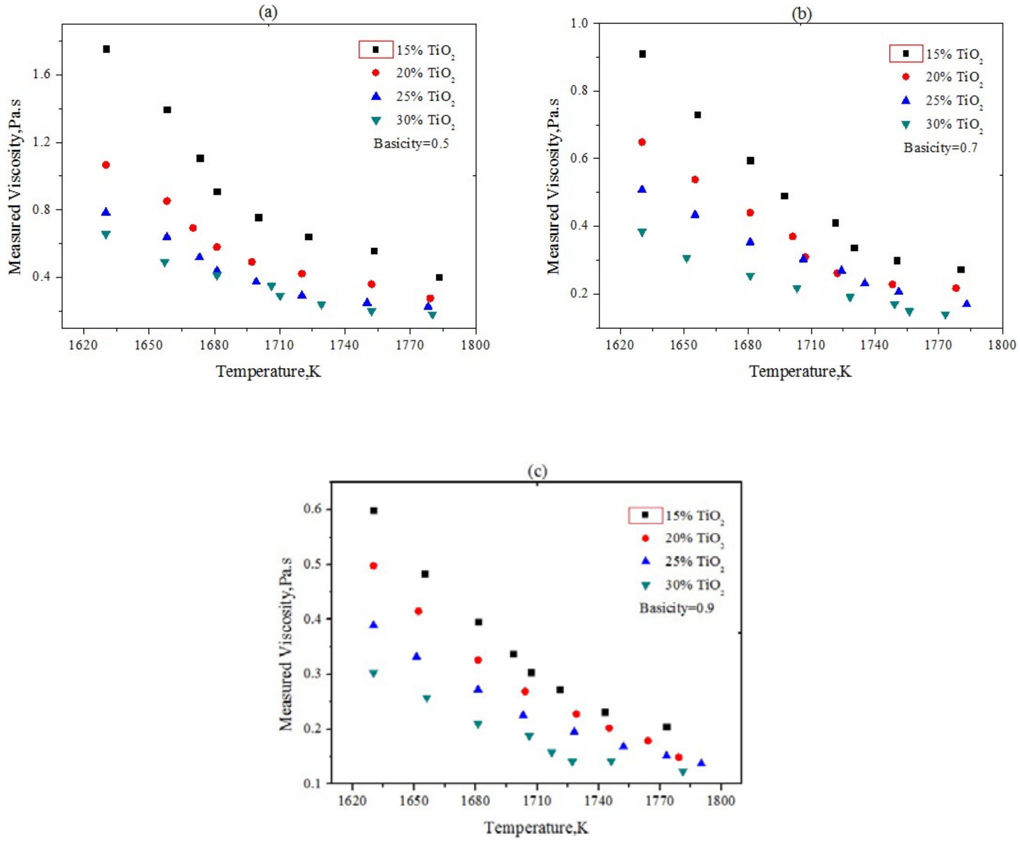
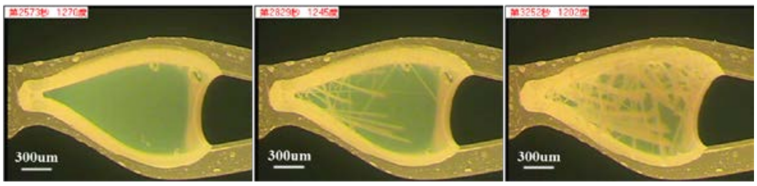
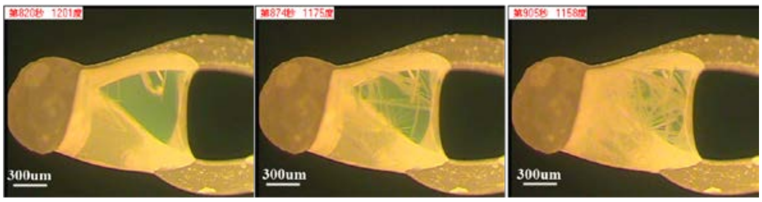


Fig. 4 Viscosity of the CaO-SiO_2-7wt%MgO-TiO_2-12wt%Al_2O_3 system as a function of TiO_2 concentration from 1793K to 1623K with varying basicity for (a) basicity=0.5, (b) basicity=0.7 and (c) basicity=0.9.

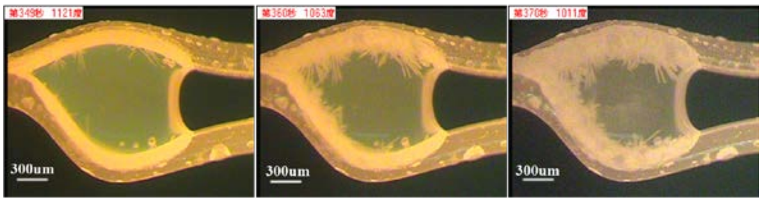
In Fig. 4, it can be noted that slag viscosity decreases with increasing TiO_2 content at different basicity. This is consistent with the previous works [8,14,16], although the chemical compositions are a little different. Saito et al. [8] have investigated the effect of TiO_2 on the viscosity of 40CaO-40SiO_2-20Al_2O_3 (wt.%) slags. The viscosity of these quaternary slags decreased with the increase in the content of additive TiO_2. A. Shankar et al.[14)] studied the viscosities of CaO-SiO_2-MgO-Al_2O_3 and CaO-SiO_2-MgO-Al_2O_3-TiO_2 slag systems. They found that at high basicity (~0.8), the slag viscosity decreased with a small amount of TiO_2 (~2 wt.%) addition in the slag. Consequently, the variation of viscosity will influence the crystallization of Ti-bearing BF slag. First, the crystallization temperature of the molten slag increases with its viscosity decreasing. Liu[17)] investigated the relationship between the crystallization temperature and viscosity of the CaO-SiO_2-Na_2O-CaF_2-Al_2O_3-MgO slag. The crystallization temperature increased (decreased) and viscosity decreased (increased) with the increasing of CaF_2 (Al_2O_3) content. In the present study, the authors found that viscosity of these Ti-bearing BF slags decreased with an increase in the content of additive TiO_2, i.e., it can be concluded the crystallization temperature of Ti-bearing BF slags would increase with the increasing TiO_2 content. In the process of selective precipitation, the cost of the production will increase, due to the high heat treatment temperature that depended on the crystallization temperature of Ti-bearing slags. Secondly, the average size of crystal increases with its viscosity decreasing. It is a consensus that the atomic diffusion coefficient increasing with the decease of viscosity of slags. Consequently, promote the growth of crystal. Li [18] investigated the effect of steel slag on the viscosity and crystallization behavior of Ti-bearing, and found that the viscosity increased and the average size of crystal decreased with an increase in the content of steel slag. In the present study, the present authors found that viscosity of these Ti-bearing BF slags decreased with an increase in the content of additive TiO_2, i.e., it can be concluded the average size of crystal of Ti-bearing BF slags would increase with the increasing of TiO_2 content. Experimental results show that, during the cooling process of molten Ti-bearing BF slags, the average size of crystal anosovite is bigger as the cooling rate is lower, which results in the viscosity of the slag increasing slowly. The results are shown in Fig.5.



(a): Cooling rate at 0.1K/second



(b): Cooling rate at 0.5K/second



(c): Cooling rate of 5K/second

Fig. 5 The crystal process of anosovite from the Ti-bearing BF slags with different colling rates.

2.3 Slag fiber production experiment

Controlling the composition and the viscosity of BF slag, the slag fiber can be experimentally produced. The BF slag used in this experiment is from Capital Iron & Steel Corporation. Fly ash from Shanxi Province was kept 1000 ℃ for 12 hours to remove the residual carbon. The composition of blast furnace slag and coal ash is shown in Table 4. The slag modified with fly ash was produced into slag fiber by air injecting shown in Fig. 6.

Table 4 Composition of blast furnace slag and coal ash

	CaO	SiO_2	Al_2O_3	MgO	Na_2O	K_2O	Fe_2O_3	TiO_2	Mk
Blast furnace slag	39.19	32.51	16.18	8.96	0.33	0.46	0.43	1.19	1.01
Fly ash	3.69	46.46	41.93	0.59	0.47	1.07	3.36	1.81	20.65

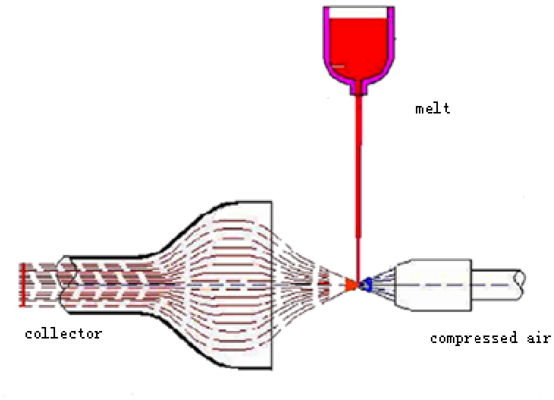


Fig. 6 Schematic diagram of producing slag fiber with air injection method

In this experiment of slag fiber producing, 10kg antivacuum induction furnace was used to melt the mixed slag and fly ash. Graphite crucible in the furnace was used as the inductive heating element while platinum rhodium thermocouple was inserted into the furnace to control the temperature. In this process, BF slag and fly ash were mechanical mixed and put into a corundum crucible. Then placed the crucible into induction furnace, started the heating until the temperature reached 1600℃. Maintained this temperature for 10 minutes, then slowly cooled the temperature to 1450℃ in 20 minutes. Finally the molten slag could be blown into fibers by high-velocity air. The blow pressure in this experiment was 0.85MPa. During the experiment, infrared thermo-detector was used to monitor the temperature of the molten slag.

Different ratios of the BF slag and the fly ash have been experimentally studied. The results are shown in Fig. 7. BF slag ratio on the impact of slag fiber diameter is shown in Fig.8. According to the standard < GB/T 11835-2004 >, a fiber whose diameter is smaller than 7μm is qualified. So when BF slag ratio is 60%~80%, the qualified slag fibers could be produced.

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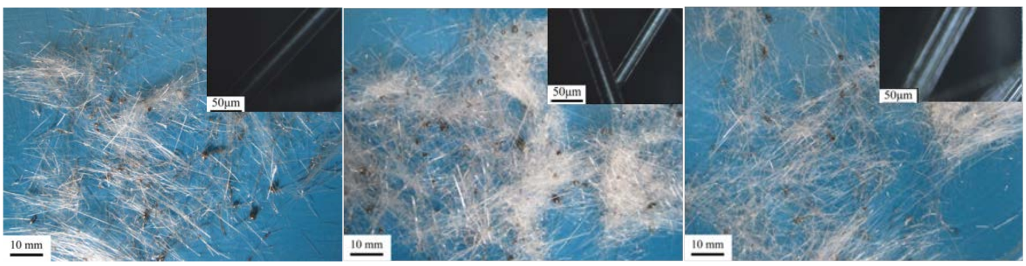
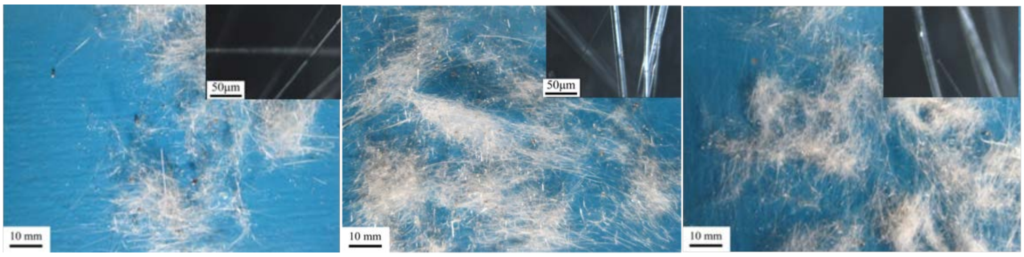
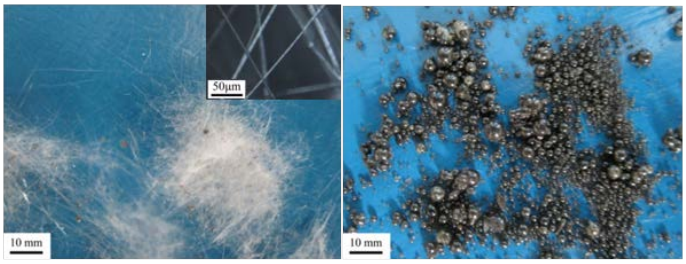


(a) Slag ratio=20% (b) Slag ratio =30% (c) Slag ratio =40%



(d) Slag ratio =50% (e) Slag ratio =60% (f) Slag ratio =70%



(g) Slag ratio =80% (h) Slag ratio =90%

Fig. 7 Morphology of slag fibers at different **ratio of** the BF slag and the fly ash produced at 1450 ℃

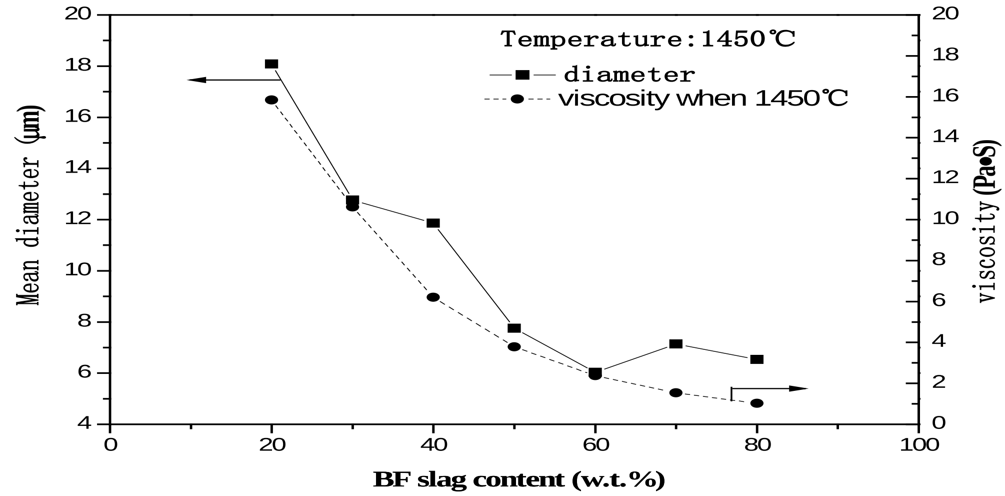


Fig. 8 The average diameter of slag fiber

With a fixed the slag ratio of 60%, the injection temperature on the impact of slag fiber diameter was experimentally examined and shown in Fig. 9. From Fig.9, we can see that when the injection temperature increases from 1400℃ to 1500℃, the change on diameter of the fiber is slight (6.31~5.56μm). The viscosity changes from 4.03 Pa·s to 1.44 Pa·s.

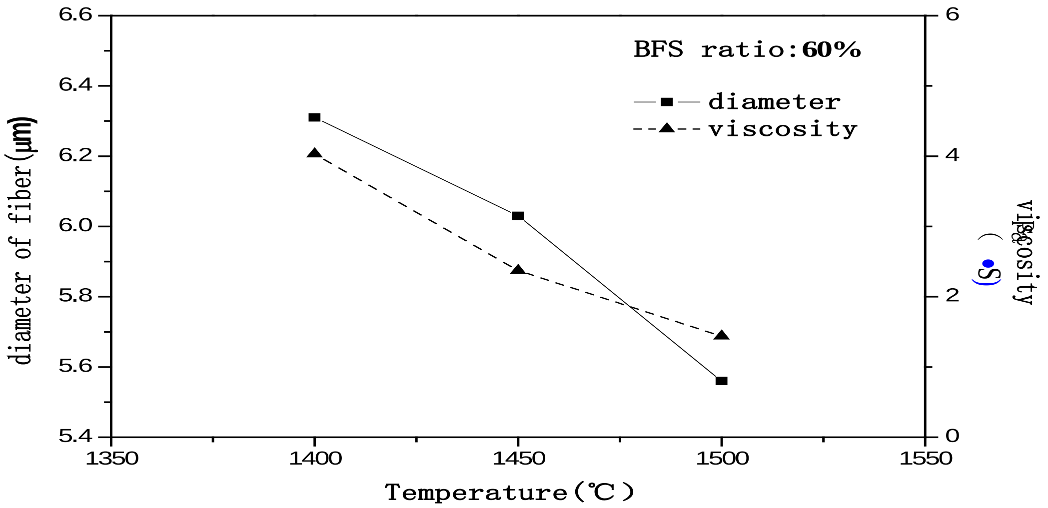


Fig. 9 The average diameter of slag fiber dependence of the injection temperature

With a fixed the slag ratio of 60% and an injection temperature of 1450 ℃, the injection pressure on the impact of mineral wool fiber diameter is shown in Fig.10. While injection pressure changes from 0.65MPa to 0.85MPa, mean diameter is decreased from 7.71μm to 6.03μm. The injection pressure is higher, the air velocity is greater, and results in the fiber diameter smaller.

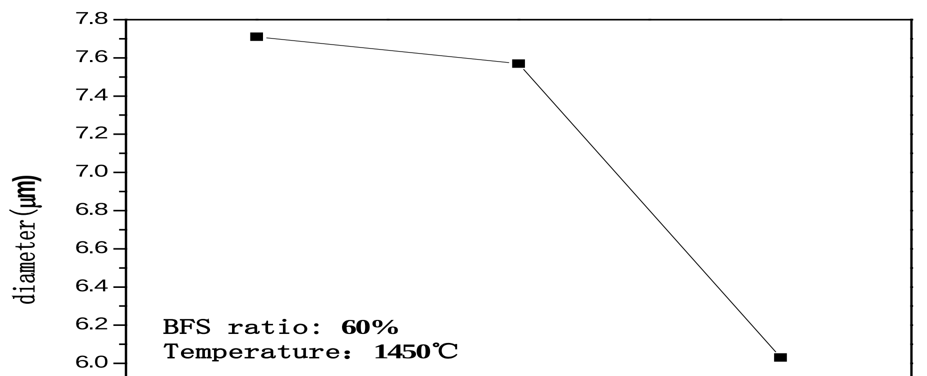


Fig. 10 The average diameter of slag fiber dependence of the injection pressure

3. Conclusions

A viscosity prediction model, with the error within 16%, of the CaO-SiO_2-Al_2O_3-FeO-MgO melt is established, which provides an important parameter for BF operation and the raw material option.

The crystallization behavior of the anosovite from the slag has also experimentally examined and the relationship between the crystal growth rate and the viscosity of the slag has been discussed, which provides a theoretical support for the extraction of titanium and comprehensive utilization of the blast furnace slag.

On the basis of studying the relation of BF slag viscosity with its composition, a method to produce slag fiber with molten BF slag modified with fly ash has been experimentally studied. Qualified slag fiber has been produced with suitable ratio of BF slag and fly ash at proper temperature and air pressure. Compared with traditional methods of producing mineral fiber, the heat energy and resources of the slag as well as fly ash can be well utilized with this method.

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