B. DAI, Y. MA, H. LONG, Y. JI, J. RAO

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PROPERTIES OF MnO ON HIGH Al_2O_3 SLAG AND ITS MECHANISM USED FOR FlUSHING BLAST FURNACE (BF)

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Flushing blast furnace by manganese ore was one of the important methods to recover the hearth inactivity caused by hearth accumulation. In this work, the properties and mechanism of the slag with different MnO content were researched, including the viscosity and critical temperature measured by rotating cylinder method, the mineral phase and microstructure confirmed by X-ray diffraction (XRD), scanning electronic microscopy (SEM) and fourier transform infrared spectrometer (FTIR). The experiment results showed that during the process of flushing blast furnace, the appropriate and optimal MnO in the slag was 1,5 to 2,0 mas .%, the mechanism of flushing by MnO was that the tephroite whose melting point is low forms, the depolymerization of [SiO_4]-tetrahedral structure caused by MnO addition also plays an important role in reducing the viscosity of the slag.

Keywords: blast furnace, high Al_2O_3 slag, MnO, property, structure

INTRODUCTION

A mass of iron ore with high Al_2O_3 which are imported from Australia, India and South Africa [1,2] have to be used in China due to the continuous increase of steel production [3,4]. There are more than 15 mas. % Al_2O_3 in the tapped slag, resulting in the slag viscous, a number of blast furnaces (BF) in China have experienced accumulation of molten slag in the BF hearth, which seriously endangers the production and safety of BFs [5,6].

What's more, when the hearth accumulation happens at the lower part of BF, ironmaking operators often use manganese ores for flushing blast furnace [7]. However, the properties and mechanism of the slag with different MnO content have not been clearly given. Therefore, it is necessary to quantificationally study the mechanism of manganese ores for flushing blast furnace.

In this work, the high Al_2O_3 tapped slag which resulted in hearth accumulation on a 5 500 m^3 large BF in China was as the research object, so the properties of MnO on the high Al_2O_3 slag and its mechanism were researched, including the measurement of viscosity and critical temperature by rotating cylinder method, confirming the mineral phase and microstructure by XRD, SEM and FTIR spectroscopy. Based on the research, the appropriate and optimal content of MnO in the slag and the mechanism were clearly and quantificationally put forward.

EXPERIMENTAL

The chemical composition of the slag samples are shown in Table1.

Table 1 **Chemical composition of the slag samples / mas. %**

No.	MnO	MgO	SiO_2	Al_2O_3	CaO	CaO/SiO_2
1	0	7,35	34,72	16,96	40,97	1,18
2	0,2	7,35	34,63	16,96	40,86	1,18
3	0,5	7,35	34,49	16,96	40,70	1,18
4	0,8	7,35	34,35	16,96	40,54	1,18
5	1,0	7,35	34,26	16,96	40,43	1,18
6	2,0	7,35	33,80	16,96	39,89	1,18
7	3,0	7,35	33,34	16,96	39,35	1,18

Slag samples are prepared using reagent grade chemicals of MnO, MgO, SiO_2, Al_2O_3 and CaO according to the desirable proportions in Table 1. The tested reagents are placed in the oven of 105 °C and baked for 12 hours before weighing, and then the reagents are weighed 140g precisely and mixed with an agate mortar thoroughly. The molybdenum crucible (inner diameter 39 mm, high 60 mm) is used to hold the slag sample.

Based on the rotating cylinder method, the viscosity is measured by a comprehensive analyzer for physical properties of melts (RTW-10 Type). The comprehensive analyzer mainly consists of a computer, viscometer, and high temperature tubular furnace with U-shape $MoSi_2$ heating elements. The crucible containing the slag sample is placed into the constant hot

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B. Dai, Y. Ma, H. Long, Y. Ji (jiyilongustb@qq.com), Key Laboratory of Multidisciplinary Management and Control of Complex Systems of Anhui Higher Education Institutes, Anhui University of Technology, Maanshan, Anhui, China; Key Laboratory of Metallurgical Emission Reduction & Resources Recycling, Anhui University of Technology, Ministry of Education, Maanshan, Anhui, China;
B. Dai, J. Rao, State Key Laboratory of Vanadium and Titanium Resources Comprehensive Utilization, Panzhihua, Sichuan, China

zone of the analyzer, which is real-time measured by thermocouple and stipulated within ± 2 °C by PID. During the heating process, it was heated to 1 100 °C at a rate of 5 °C/min and then heated to 1 500 °C at 3 °C/min. At the same time, 99,999 % high-purity Ar at a rate of 1L/min is used as protective gas throughout the whole process. The viscometer is calibrated before the experiment. The molybdenum spindle is lowered into the slag and located at 10 mm above the base of the crucible. Then the molybdenum spindle starts to rotate and measure along with continuous cooling at 3 °C/min. The measurement was stopped until the viscosity reached approximately 3,5 Pa. s. After the viscosity measurements, the slag samples are cooled to room temperature and ground for XRD, SEM and FTIR spectroscopy.

RESULTS AND DISCUSSION

It can be seen from Table 1 that the slag belongs to high aluminum slag, for the Al_2O_3 in the slag is more than 16 mas. %. As shown in Figure 1, the viscosity of the slag is above 0,5 Pa. s even at high temperature of 1 480 °C when there is no MnO addition, which is obviously higher than that of ordinary slag. The viscosity of the high aluminum slag increases gradually with the decrease of temperature. Besides that, there is almost no stable area in the cooling process, which indicates that the stability of the slag is not so good. It also can be seen that, all viscosities of MnO addition slags are smaller than that of no MnO addition slag at the same temperature and the curve is almost overlap together in the high temperature area (1 440 - 1 500 °C). It is inferred that the viscosities of slags with MnO addition from 0,2 mas. % to 2,0 mas. % are not big difference at high temperature, but all smaller than that of no MnO addition slag. The critical temperature of slags with different MnO addition are shown in Figure 2. It can be seen that the addition of MnO can significantly reduce the critical temperature of high aluminum slag. When the MnO addition increases from 0 mas. % to 1,5 mas. %, the decreasing rate of critical temperature is nearly the same, but the critical temperature is almost unchanged when the MnO addition increases from 1,5 mas. % to 2,0 mas. %. If only considering the influence of critical temperature on slag, the slag with MnO addition from 1,5 mas. % to 2,0 mas. % is appropriate and optimal, whose critical temperature and viscosity those are about 1 340 °C and 0,3 Pa. s respectively at this time are suitable for flushing blast furnace.

Figure 3 shows the XRD patterns of CaO-MgO-SiO_2-Al_2O_3-MnO system with various MnO contents. When there was no MnO addition, the mineral phase of the slag is just gehlenite. With the addition of 1,0 mas. % MnO, the mineral phases of tephroite is appearing, indicating that MnO have changed the basic mineral

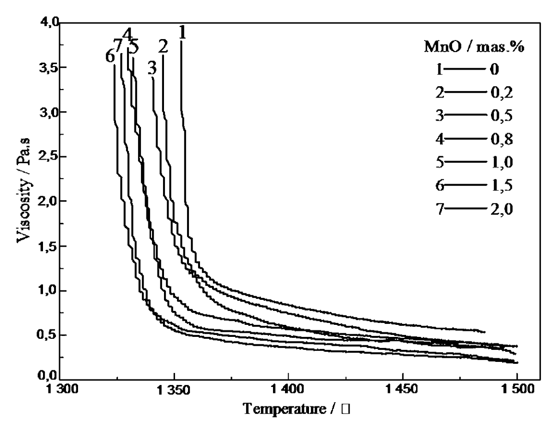

Figure 1 Effect of MnO on viscosity

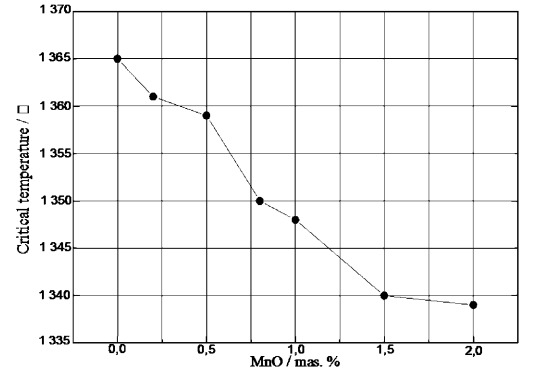

Figure 2 Effect of MnO on critical tem- perature

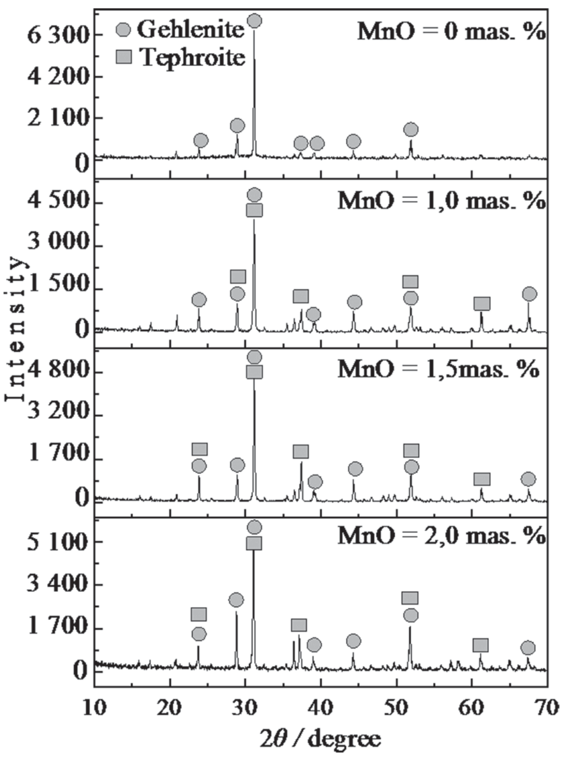

Figure 3 XRD patterns of the high Al2O3 slags with various MnO

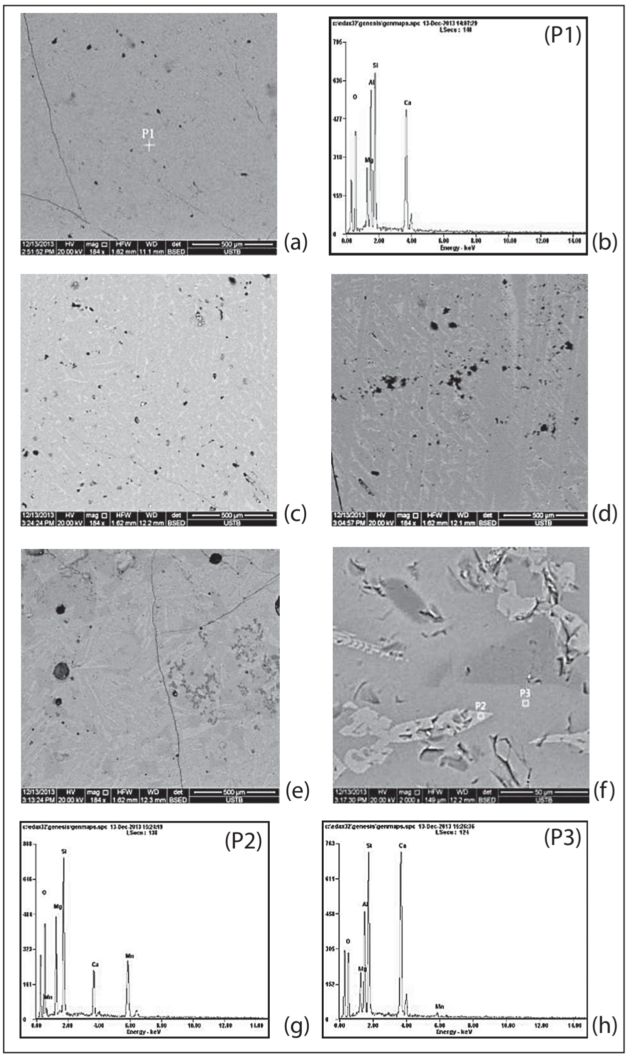

Figure 4 SEM and Energy Dispersive Spectroscopy of slags with different MnO contents, (a) MnO = 0 mas .% ,(c)MnO = 1,0 mas .%,(d)MnO = 1,5 mas .%,(e)MnO = 2,0 mas .%

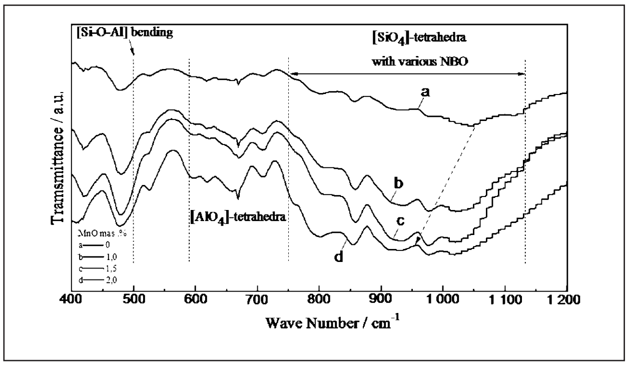

Figure 5 FTIR of slags with different MnO content

phase in the slag after the doping process. With the increasing of MnO, the diffraction peak intensity of gehlenite is weakened, on the other hand, the diffraction peak intensity of tephroite is strengthened. The XRD results indicate that the tephroite whose melting point is low forms in the slag. With the tephroite continuously and massively forming, the critical temperature of the slag decreases as well, which is also consistent with the previous viscosity and critical temperature experiment.

The SEM results of the slag with various MnO addition are presented in Figure 4. As seen in Figure 4(a), the slag surface is smooth and uniqueness when there is no MnO addition, the slag structure is almost entirely equiaxed crystal, which tends to lose the fluidity easier during the continuous cooling process. Figure 4(b) is the EDS (Energy Dispersive Spectroscopy) analysis diagram of point P1, so there are no other elements except of Ca, Mg, Si, Al and O, it is a typical blast furnace slag.

It can be seen from Figure 4(c)(d)(e) that the microstructure of slags have changed obviously, the gray-white speckles in slag have appeared and increased gradually with the increase of MnO content. The slag is almost occupied by gray-white speckles when MnO reached 2,0 mas. %. In Figure 4(g)(h), EDS of point P2 shows that the gray-white speckle contained a certain amount of Mn, on the other hand, point P3 is little Mn. Therefore, we affirm that the tephroite ($2MnO·SiO_2$) is formed in the slag while MnO is added, which is consistent with the previous research of XRD.

The FTIR results of the slag with different MnO additions are shown in Figure 5. The characteristic vibration around 500 cm^{-1} corresponds to the [Si-O-Al]-bending trough, while the wave number region within 590 - 750 cm^{-1} is related to the asymmetric $[AlO_4]$-tetrahedral stretching vibration, the vibration bands for $[SiO_4]$-tetrahedra are typically focused within the band group between 750 and 1 030 cm^{-1}, which corresponds to the NBO/Si (non-bridging oxygen per silicon)= 4, 3, 2 and 1 (850, 940, 980 and 1 030 cm^{-1} bands, respectively [8] .The broadening of the width of the $[SiO_4]$-tetrahedral bands can be observed with the addition of MnO, which suggests the increase of the distance between Si and O. Besides, with the increase of MnO content, the trough of $[SiO_4]$-tetrahedra dampens and the center of its gravity also shifts towards low frequency near 940 cm^{-1}, implying the depolymerization of slag structures. On the other hand, the trough of the [Si-O-Al] bending vibration band and the trough of the $[AlO_4]$-tetrahedral asymmetric stretching band became somewhat pronounced with higher MnO content, which indicates that MnO depolymerize the network structures of the slag by modifying the $[SiO_4]$-tetrahedral structure but slightly enhances the linkage between $[SiO_4]$-tetrahedral and $[AlO_4]$-tetrahedral structure of the aluminosilicate melts and the $[AlO_4]$-tetrahedral structure. Obviously, the depolymerization of $[SiO_4]$-tetrahedral structure caused by MnO addition plays a more important role in reducing the viscosity of the slag.

CONCLUSION

The properties and mechanism of the slag with different MnO content were researched in this work, including the viscosity and critical temperature measured by rotating cylinder method, the mineral phase and microstructure confirmed by X-ray diffraction, scanning electronic microscopy and fourier transform infrared spectrometer. The experiment results showed that during the process of flushing blast furnace, the slag with MnO addition from 1,5 mas. % to 2,0 mas. % whose critical temperature and the viscosity are about 1 340 °C and 0,3 Pa. s respectively is appropriate and optimal for flushing blast furnace. The mechanism of flushing blast furnace by MnO was that the tephroite whose melting point is low formed in the slag, at the same time, the depolymerization of $[SiO_4]$-tetrahedral structure caused by MnO addition also plays an important role in reducing the viscosity of the slag.

Acknowledgement

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Note: Y. MA is responsible for English language, Anhui, China