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Research Article

The Online Research of B_2O_3 on Crystal Behavior of High Ti-Bearing Blast Furnace Slag

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The existence and phase structures of high Ti-bearing blast furnace slag at a high temperature are the key issue to flow performance and reaction temperature. It is essential to evaluate the physical-chemical properties, such as viscosity and melting point In this work, a new method of online research of B_2O_3 on crystal behavior of high Ti-bearing blast furnace slag is proposed. By ultrahigh-temperature confocal laser scanning microscope and area scanning analysis, it can be concluded that the effect of B_2O_3 additives on the viscosity has a more obvious effect among the low-temperature region of the slag. Compared to the samples without B_2O_3 additives, the liquid phase of Ti-bearing slag with B_2O_3 additives appears earlier at the same experimental temperature, and the solid particles floating on the surface of liquid slag become less. Moreover, the B_2O_3 additives can promote the migration of titanium elements from the high melting point phase to the low melting point phase, and the transferring quantity increases with the addition of the amount of B_2O_3 additives. These results demonstrate that B_2O_3 additives can restrain the appearance of the perovskite phase, decrease the apparent viscosity, and promote the metallurgical properties of Ti-bearing blast furnace slag.

1. Introduction

The lower production cost for iron and steel enterprise becomes one of the most important objectives in the present situation under the premise of ensuring quality. The use of local vanadium titanomagnetite replacing ordinary iron ore could save expensive freight and reduce material cost due to geographical location of Panzhihua Iron and Steel. But the TiO_2 content in slag increased with the improving proportion of vanadium titanomagnetite in blast furnace. The TiO_2 content in blast furnace (BF) slag has a significant effect on the fluidity of slag. The influence degree increases with the fluctuation of TiO2 proportion in blast furnace, thus affecting the slag iron reaction and performance of BF.

At the condition of current technology of BF coal powder injection, the TiO_2 in slag will react with the unburned pulverized coal and produce high melting point phase, such as TiC. The high melting point phase will further increase the slag viscosity and make the slag iron more difficult to separate. Meanwhile, the quality of raw material and fuel into the furnace deteriorates with the continuous exploitation of mineral resources, which results in larger fluctuations of furnace burden composition and makes metallurgical properties of slag deterioration. Therefore, it is essential to improve the flow performance and decrease the effect of component fluctuation [1, 2].

Lin et al. [3] studied the influence of CaF_2 additives on the apparent viscosity of Ti-bearing blast furnace slag and concluded that the CaF_2 additives could reduce the apparent viscosity to a certain extent. Li et al. [4] investigated the variation regularity of B_2O_3 additives replacing SiO_2 for CaO-BaO-SiO_2-Al_2O_3-CaF_2 system and obtained the quantitative relationship between alkalinity and desulfurization rate. Nakamoto et al. [5] studied the evolution regularity of the surface tension of molten silicate with B_2O_3, CaF_2, and Na_2O surfactants. Zhang et al. [6] analyzed the change rules of B_2O_3 and Na_2O in the fluorine-free slag from 1300°C to 1400°C by using a thermogravimetric analyzer.

Tasuku and Fumitaka [7] studied the effect of B_2O_3 additives on desulfurization capacity in FeOx-CaO-MgO_{satd}-SiO_2 slag at the temperature of 1300°C. Shi et al. [8] studied the phase equilibrium law of CaO-SiO_2-5wt.%MgO-20wt.%Al_2O_3-TiO_2 system at 1300°C and 1400°C by SEM-EDS, XRD, and XRF. Li et al. [9] performed some studies about the effect of Al_2O_3 additives on precipitated phase transformation, and the results showed that Al_2O_3 additives could prompt phase change from perovskite to low melting point phase. Bian and Gao [10] investigated the influence of basicity and B_2O_3 on apparent viscosity and microstructure using high-temperature viscosity meter, XRD, etc., and the results showed that the apparent viscosity decreased with the increasing number of B_2O_3 additives and CaO/SiO_2 ratio. Qiu et al. [11] studied the influence of Cr_2O_3 additives on apparent viscosity and microstructure. Above all the researches [12–19], the physical-chemical properties and phase structures of metallurgical slag at high temperature are characterized based on the cooled samples by different cooling rates such as air cooling, water cooling, or nitrogen cooling. However, the actual phase structures of slag melt at high temperature are different from that of solidified slag. The influence mechanism and evolution of the actual structure of Ti-bearing blast furnace slag on the smelting process need to be characterized precisely. Compared with the traditional offline research, the online research can clearly observe the continuous change process of slag melting at high temperature. At the same time, the online research can provide some references for the smelt slag change in the "black box" of blast furnace.

In this work, a new method of online research of B_2O_3 on crystal behavior of high Ti-bearing blast furnace slag is proposed. The viscosity variation below melting temperature with B_2O_3 additives was detected. The variation law with time of perovskite formation was analyzed by ultrahigh-temperature confocal laser scanning microscope. The crystal behavior of perovskite with B_2O_3 additives was investigated by SEM-EDS. This work provides an exploratory research on the evolvement rule of online high-temperature state.

2. Experimental

2.1. Materials, Apparatus, and Equipment. These materials were synthesized with various analytical grade chemicals according to chemical components of high Ti-bearing blast furnace slag of Panzhihua Steel and Iron Group Corporation, which are listed in Table 1. The synthesized high Ti-bearing blast furnace slag was heated to 1500°C and then kept for 30 minutes to ensure the melt homogenized under Ar atmosphere. After that process, the melt quenched into the water. The quenched samples were ground into powder and sieved with different particle sizes. The grain size of experimental slags was in the range of 50 to 74 micrometer. The B_2O_3 additives were all analytical reagents, which was used in apparent viscosity and confocal laser scanning experiments.

The basic schematic diagram of apparent viscosity experimental apparatus by the rotating cylinder method in the literature [3] and ultrahigh-temperature confocal laser scanning microscope's (VL2000DX-SVF17SP, LASERTEC, Japan) principle is shown in Figure 1. The light beam emitted by the light source was focused on the surface of the experimental sample, and the reflected light to the experimental sample went back along original paths. The reflected light passed through lens, focused again, and imaged onto photoreceptors. Only the reflected light which shined on the surface of experimental samples could be received by the original paths in the confocal laser scan microscope system, and other reflected lights were shielded by pinhole. The maximum temperature of ultrahigh-temperature confocal laser scanning microscope could reach 1700°C, and the error was less than ±2°C. The platinum crucibles instead of graphite crucibles were used in experiment to prevent the TiO_2 reacting with carbon. The chemical components are listed in Table 1. The 0# sample without B_2O_3 was set as a reference slag; the B_2O_3 additives were 1% in 1# sample and 2% in 2# sample.

Table 1: The chemical compositions of samples (%).

	CaO	SiO_2	MgO	Al_2O_3	TiO_2	V_2O_5	C	B_2O_3	R
0#	27.55	26.20	9.19	14.89	21.85	0.10	0.22	0	1.05
1#	27.02	25.73	9.19	14.89	21.85	0.10	0.22	1.0	1.05
2#	26.51	25.24	9.19	14.89	21.85	0.10	0.22	2.0	1.05
3#	26.00	24.75	9.19	14.89	21.85	0.10	0.22	3.0	1.05

2.2. Experimental Procedure. The apparent viscosity of high Ti-bearing blast furnace slag was measured by Brookfield digital viscometer (RTW-10, Northeastern University) by the rotating cylinder method. The molten slag was cooled down by the temperature-controlling program until the viscosity-temperature curve became stationary. The viscosity curves that changed with temperature were recorded by software on computer. Then, the morphologies of samples were analyzed by ultrahigh-temperature confocal laser scanning microscope (VL2000DX-SVF17SP, LASERTEC, Japan).

The platinum crucible which was filled with high Ti-bearing blast furnace slag was put on Al_2O_3 sheets above the sample bracket, and the content of slags was between 50% and 75%. The experimental sample moved slowly until the fixed position by the particular hydraulic system. At this point, high-purity argon was injected into the furnace body, and gas flow rate was kept at about 30 ml/min. The experimental samples were heated up at a rate of 300°C/min. After reaching the set value (1485°C), the experimental samples were kept at a constant temperature for 120 min by adjusting the temperature control system. Then, high-purity argon was switched to helium gas, and the helium flow rate was set to 400 ml/min for cooling the experimental samples down. The huge cooling rate could make the morphologies of products closer to high-temperature state of slags than other cooling methods. After cooling the hot products to room temperature using helium gas, shut the air transporting pipe and collect completely the experimental products for fine-grinding, polishing, composition, and micrograph analysis.

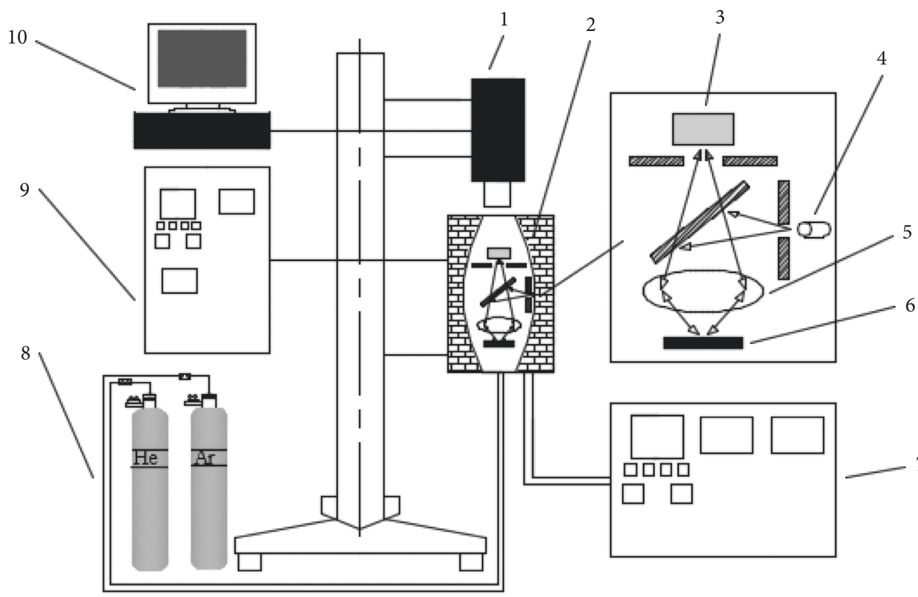


Figure 1: The schematic diagram of the experimental apparatus (1, optical system; 2, furnace; 3, thermal insulation; 4, light source; 5, lens; 6, Al_2O_3 sheets; 7, temperature control system; 8, gas; 9, water cooling system; 10, computer).

3. Results and Discussion

3.1. Effect of B_2O_3 Additives on the Viscosity of Slag. The effect of B_2O_3 additives on the apparent viscosity of slag with temperature variation is shown in Figure 2, the vertical coordinate is the apparent viscosity of high Ti-bearing blast furnace slag, and the horizontal axis is the experimental temperature. The viscosity-temperature curve is a graph drawn by the computer connected with the viscosimeter in the process of measuring viscosity by cooling slag. The 0# sample is the benchmark specimen without B_2O_3, and the B_2O_3 amount of 1#, 2#, and 3# samples is, respectively, 1%, 2%, and 3%.

According to Figure 2, the B_2O_3 additives improve the fluidity and reduce the apparent viscosity of high Ti-bearing blast furnace slag. With increase in the B_2O_3 additives, there are lower apparent viscosity at the same experimental temperature. When the temperature of high Ti-bearing blast furnace slag is above the melting temperature, the apparent viscosity of slag with B_2O_3 additives is lower than that of 0# sample, the difference between the content of B_2O_3 additives is not obvious, and the curves are almost completely coinciding. Compared with the benchmark specimen, the apparent viscosity with B_2O_3 additives is slightly lower than the slag without B_2O_3. Therefore, the B_2O_3 additives can slightly reduce the apparent viscosity of high Ti-bearing blast furnace slag for the temperature above the melting temperature.

When the experimental temperature is lower than the melting temperature, the apparent viscosity of high Ti-bearing blast furnace slag decreases with the addition of B_2O_3. Compared to the benchmark curve, the drop of apparent viscosity is more obvious with the increasing B_2O_3 additives shown in Figure 2. According to Figure 2, making a straight line perpendicular to the ordinate to intersect at four points with four curves, the lower temperature is essential as increasing the amount of B_2O_3 additives to maintain the

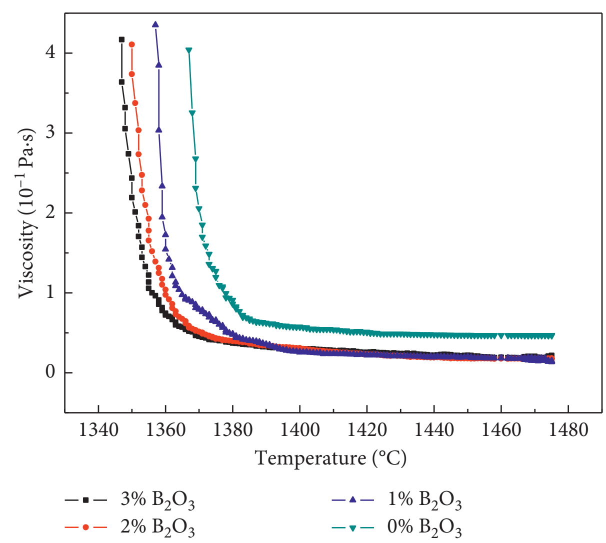


Figure 2: The relationship between apparent viscosity and the amount of B_2O_3 additives.

same apparent viscosity of high Ti-bearing blast furnace slag; that is, the slag has lower apparent viscosity at the same experimental temperature as the amount of B_2O_3 additives increases. When the experimental temperature is equal to the melting temperature, it decreases with the increasing amount of B_2O_3 additives. Therefore, the B_2O_3 additive has an obvious effect on low temperature area of high Ti-bearing blast furnace slag, influences the area above the hearth of BF, and promotes the stability of blast furnace.

3.2. The Evolution of Perovskite Phase at Different Temperatures. Figures 3–5 show the evolution morphologies of high Ti-bearing blast furnace slags within B_2O_3 additives with the variation of the temperature. The temperature of slag

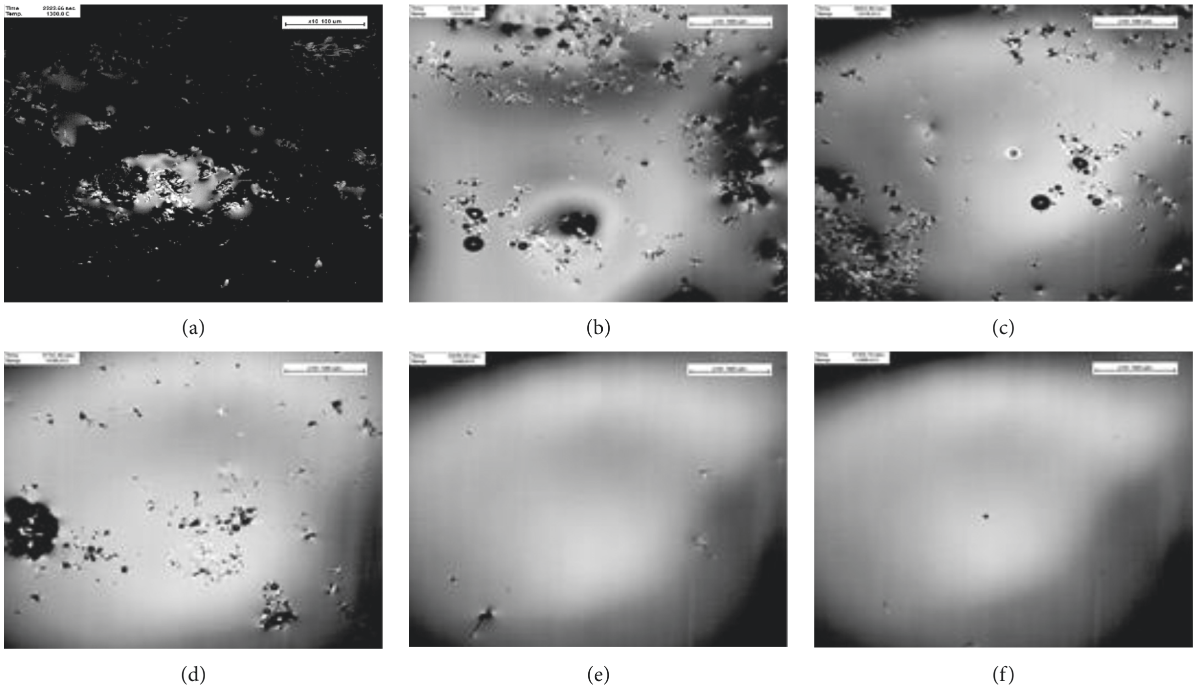


Figure 3: The evolution rules of morphology without B_2O_3: (a) 1300°C; (b) 1310°C; (c) 1320°C; (d) 1340°C; (e) 1350°C; (f) 1360°C.

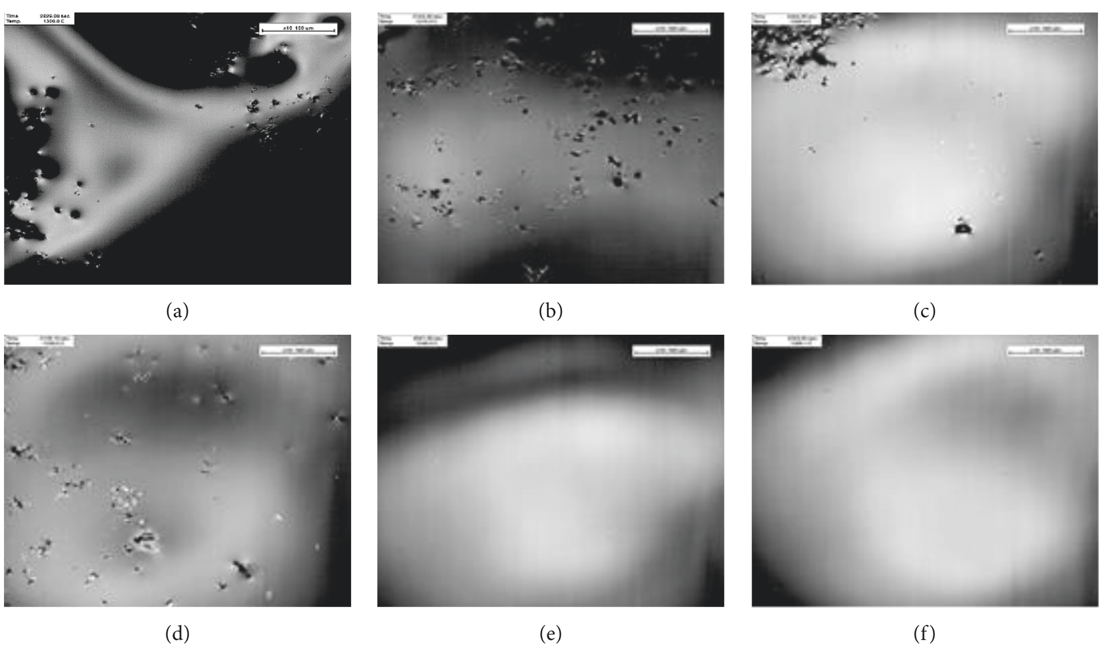


Figure 4: The evolution rules of morphology with 1% B_2O_3: (a) 1300°C; (b) 1310°C; (c) 1320°C; (d) 1340°C; (e) 1350°C; (f) 1360°C.

in the picture is 1300°C (Figures 3(a), 4(a), and 5(a)) and 1360°C (Figures 3(f), 4(f), and 5(f)), and the temperature interval of two adjoining pictures is 10°C. Compared with the traditional offline research, the online research can clearly observe the continuous change process of slag melting at high temperature. At the same time, the online research can provide some references for the smelt slag change in the "black box" of blast furnace.

According to Figure 3(a), the liquid phase of high Ti-bearing blast furnace slag starts to appear at the temperature of 1300°C, as shown in the white area, and the black area is the solid materials. As the temperature of high Ti-bearing blast furnace slag continuously increases, the liquid slag steadily becomes more as shown in the white area of Figure 3(b), and the other solid materials floats on the surface of the liquid slag. When the temperature of slag

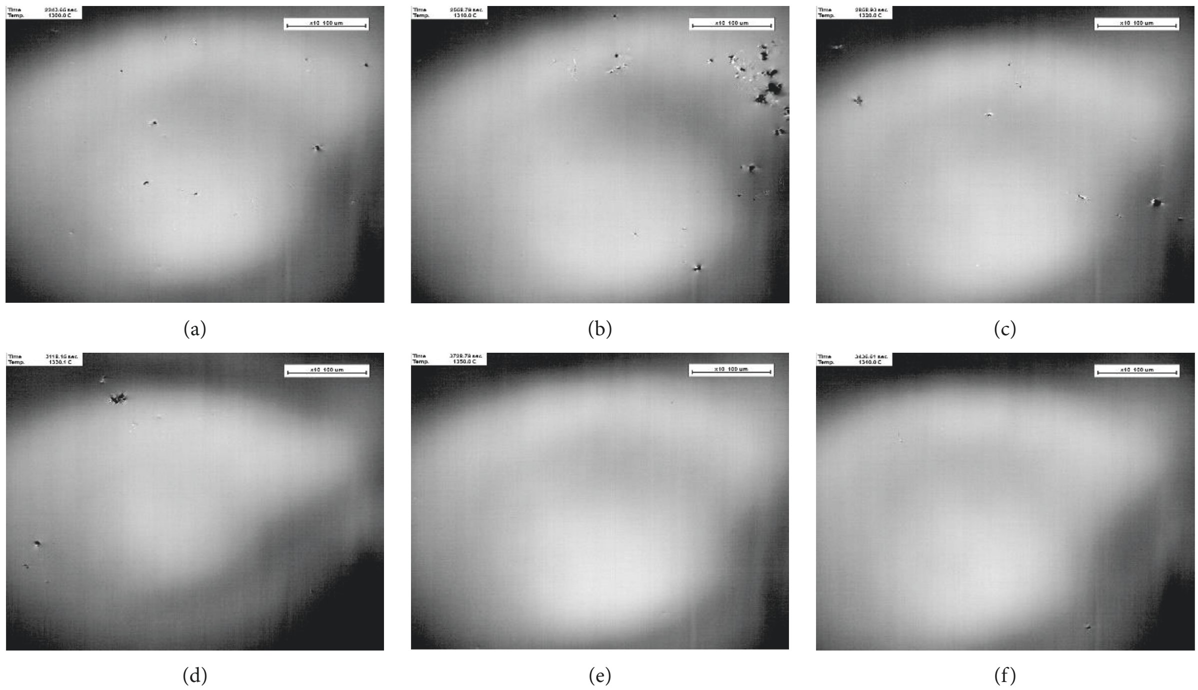


Figure 5: The evolution rules of morphology with 2% B_2O_3: (a) 1300°C; (b) 1310°C; (c) 1320°C; (d) 1340°C; (e) 1350°C; (f) 1360°C.

continues to rise (Figures 3(c) and 3(d)), the suspended phase on the surface of liquid slag gradually disappears, and the suspended phase is hardly visible in Figures 3(e) and 3(f). This phenomenon is inconsistent with the ultrahigh melting point of perovskite phase. Therefore, it can be concluded that the perovskite phase is distributed in liquid slag with fine dispersion particles and influences the viscosity of slag.

According to Figures 3–5, the amount of suspended phase appears smaller at the same temperature with addition of the B_2O_3, the degrees of decline increase with the increasing amount of B_2O_3 additives. When the amounts of B_2O_3 additives are added to 2%, there have no obvious suspended phase on the surface of the slag at the temperature of 1300°C. The phenomenon shows that the B_2O_3 addition can decrease the melting temperature of Ti-bearing slag and lead to downward movement of viscosity-temperature curves. Compared with offline research [3], the online research of Ti-bearing blast furnace slag could reflect the constant changes in "black box" rather than a frozen moment.

Therefore, the B_2O_3 addition can not only make the slag become the liquid phase earlier but also can translate the high melting point of Ti-bearing slag into other low melting point phase, showing better flowing properties.

3.3. The Crystal Behavior of Perovskite on Adding B_2O_3. In order to investigate the effect of B_2O_3 additives on the Ti-bearing phase below high-temperature condition, the samples in ultrahigh-temperature confocal laser scanning microscope were cooled by helium at the temperature of 1485°C, in which the B_2O_3 amount was 0%, 1%, and 2%, respectively. The quench products kept the morphology of slag in a great degree below high-temperature condition. Figures 6–8 represent the results of area scanning mapping of Ca, Si, Mg, Al, O, and Ti in different additions of B_2O_3.

Lots of cruciform phases disperse in blast furnace slag without B_2O_3 addition at the temperature of 1485°C, as shown in Figure 6. It can be concluded that the crossed phase is perovskite by the analysis of the area scanning mapping and energy spectrum. The perovskite phase still exists in liquid slag in the form of solid particles and forms solid-liquid mixtures at the temperature of 1485°C.

When the amount of B_2O_3 additives is equal to 1%, the existential state of slag is shown in Figure 7 at the temperature of 1485°C. According to Figure 7, the crossed phase is perovskite which exists in the form of solid particles under the experimental temperature. Compared with the samples without B_2O_3 additives, a certain amount of perovskite phase disappears in liquid slag.

When the amount of B_2O_3 additives further increases to 2%, there is a significant area of nonperovskite phase in samples, as shown in Figure 8(a). Compared with 0# sample and 1# sample, the amounts of perovskite phase decrease significantly. The product is cooled to room temperature from 1485°C by helium, and the scanning mapping and energy spectrum analysis results are shown in Figure 8(b). According to Figure 8(b), the titanium element not only concentrates in the perovskite phase but also distributes largely in the nonperovskite area. Finally, based on the results, it can be concluded that the B_2O_3 addition can translate perovskite phase of high melting point into the other Ti-bearing materials of low melting point. It is one of the important reasons that B_2O_3 additives cause the decrease of slag's viscosity.

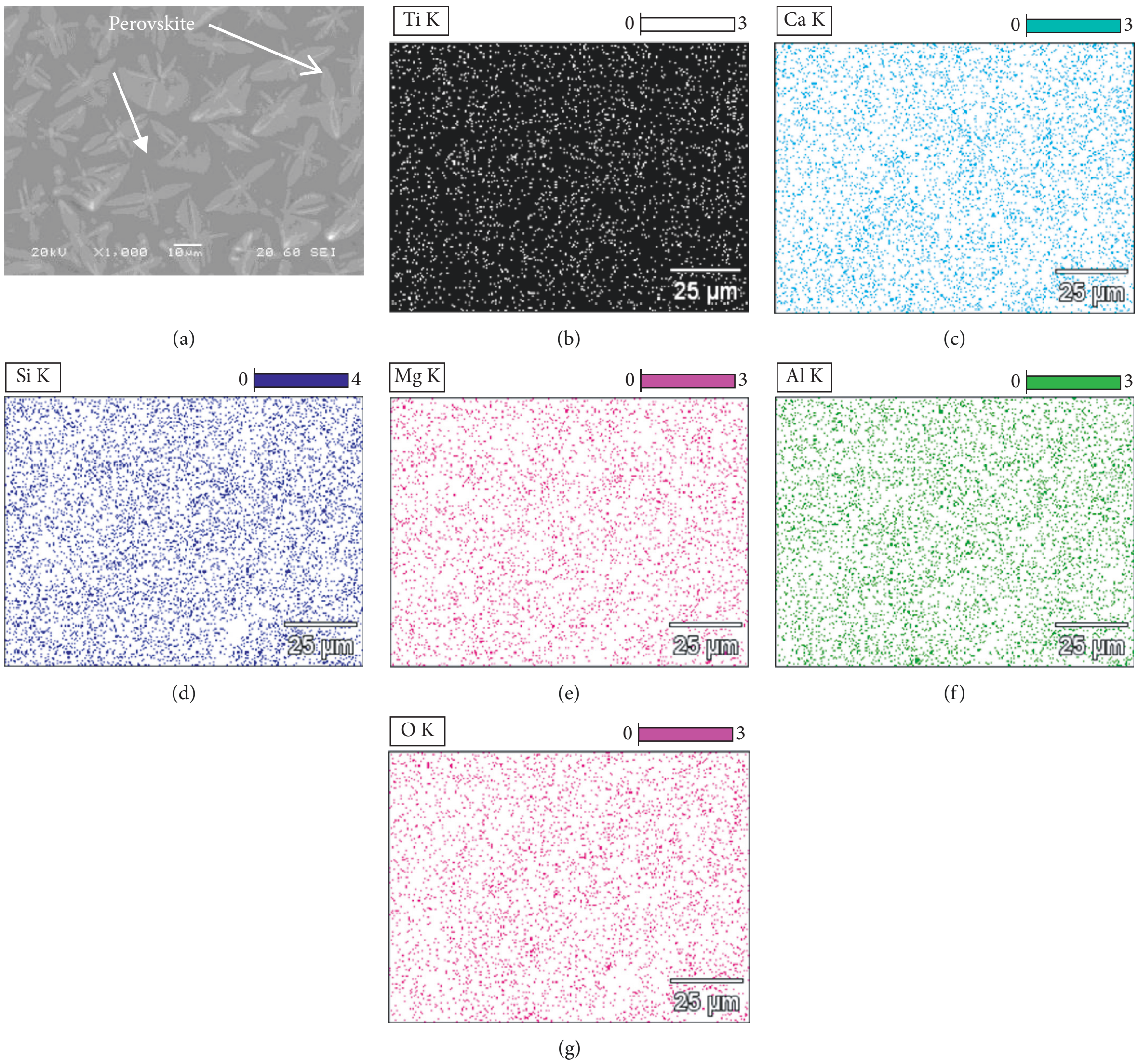


Figure 6: Area scanning mapping of Ti, Ca, Si, Mg, Al, O, and EDS in 0# sample without B_2O_3 at 1485°C.

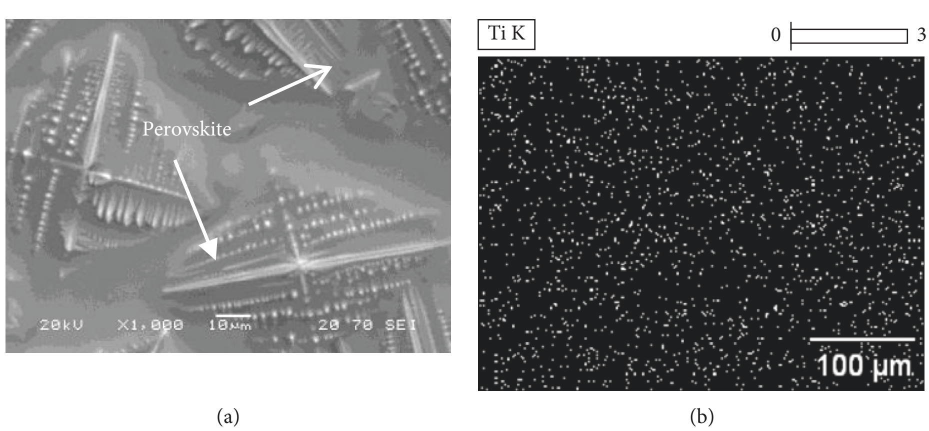
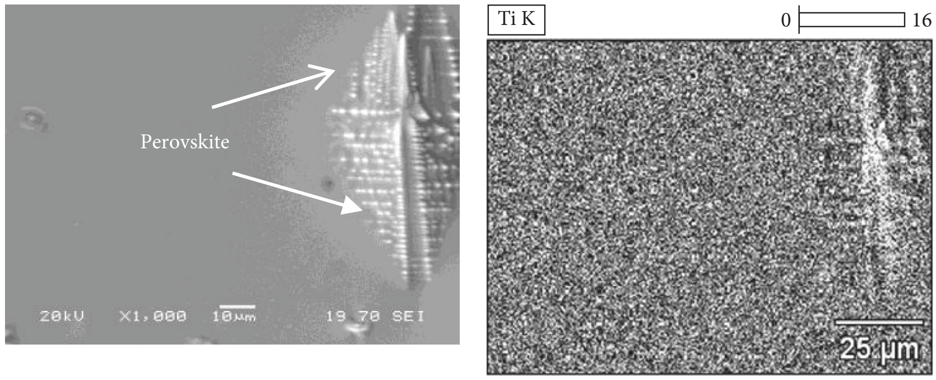


Figure 7: Area scanning mapping of Ti and EDS in 1# sample with 1% B_2O_3.



(a) (b)

Figure 8: Area scanning mapping of Ti and EDS in 2# sample with 2% B_2O_3.

4. Conclusions

The effect of B_2O_3 additives on the crystallization behavior of high Ti-bearing blast furnace slag was investigated online by ultrahigh-temperature confocal laser scanning microscope under inert atmosphere. The results show that the B_2O_3 additives can have a significant impact on the melting temperature and Ti element distribution of slag, and some important conclusions are as follows:

When the temperature of high Ti-bearing blast furnace slag is higher than the melting temperature, the apparent viscosity of slag slightly decreases with the increasing amount of B_2O_3 additives. However, the apparent viscosity of slag appears largely to change with the increasing amount of B_2O_3 additives as the temperature of slag is lower than the melting temperature. Therefore, the B_2O_3 additives have more obvious influence on the low temperature region of slag.

The B_2O_3 additives can induce the earlier appearance of liquid phase and decrease the amounts of solid particles which float on the surface of liquid slag at the same experimental temperature by online observation. Combined with the area scanning analysis, the B_2O_3 additives can make the titanium elements migrate from the high melting point phase to the low melting point phase, which result in a loss of the perovskite phase and titanium distribution more diffuse. The B_2O_3 additives could not only restrain the appearance of perovskite production but also provide the higher metallurgical properties of Ti-bearing blast furnace slag. Therefore, the rational content of B_2O_3 additives provides a feasible and convenient method to reduce the melting temperature and increase the liquidity of Ti-bearing blast furnace slag.

Data Availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also form part of an ongoing study.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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