Wettability between Molten Slag and MgO–C Refractories for the Slag Splashing Process

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Wetting experiments in two cases have been carried out to measure the wettability between molten slag and MgO–C refractories. Especially, the variations of wettability with time are taken into consideration in this paper. The spread diameter increased significantly and the slag height decreased with the increase of the time from 0 to 237 s at 1783 K. While the spread diameter changed slowly, and reached the steady state from 300 to 500 s. More specifically, the fitting formulae for diameter, height, area of the slag as a function of time have been determined. Moreover, the interfacial characteristics of the non-melting slag and MgO–C refractories and of the wetting slag and MgO–C refractories were investigated to further explain the wettability in two cases.

With the help of the wetting experiment, adhesion and protection mechanism was demonstrated. It could optimize the slag splashing process and give guides to the increase of the converter lining life, which can make the contribution to the promotion of technological transformation and innovation of the steel industry.

KEY WORDS: slag splashing; wettability; contact angle; molten slag; MgO–C refractories.

1. Introduction

In the metallurgical process of steelmaking, jet behaviors and metallurgical performance of an innovated double-parameter oxygen lance have already been investigated,¹) which makes great contribution to BOF steelmaking. Moreover, it is promising to understand the multiple jets behavior in a top-blown converter and extrapolate the cavity formation in the LD bath.²) However, the erosion of refractory linings of furnaces is a major cost in high temperature processes. Slag splashing is one method used to produce a freeze lining. Mills et al.³) have made a review of slag splashing technology. In addition, a novel approach to recycle CO₂ separated from converter gas for the green slag splashing technique was firstly proposed, which provides a new energy-saving way for recycling CO₂ and obtaining CO from converter gas.⁴) Therefore, the wettability between the molten slag and MgO–C refractories is a crucial factor to obtain a good understanding of the adhesion and protection mechanism of the slag in the BOF in order to optimize the converter lining life. Some researchers find that the influence of wettability on carbon dissolution into molten slag suggests that the rate of dissolution is significantly affected by the contact area available for the carbon-transfer.⁵) The depth of penetration of molten iron into the refractory and the strength of bonding between the metal and the refractory depend on the wetting behavior of the slag on the refractory.

The study of the wettability between molten slag and MgO–C refractories can not only explain the adhesion mechanism theoretically, but also provide theoretical basis for optimizing the slag splashing technique, adjusting slag composition reasonably and selecting refractory correctly. Although the wettability measurements between the slag and the MgO–C refractories were useful to demonstrate the adhesion and protection mechanism to an extent, yet these researches mainly focused on the theory which is still not clear enough. There is still a lack of wetting experiment using the product material to analyze their essentials in detail, for example the effect of time. Furthermore, the interfacial characteristics of different kind of slag and MgO–C refractories are not enough. Previously, the sessile drop method was employed to determine the surface tension of molten metal in order to study the wettability and its influence on slag splashing.⁶,⁷) In the present work, the wetting behavior and contact angle between molten slag and MgO–C refractories are investigated by using the sessile drop method.

This article proposes wetting experiments in two cases to measure the wettability between the molten slag and MgO–C refractories. First, the effect of time on the contact angle, slag diameter and height were investigated. Thereafter, the interfacial characteristics of the non-melting slag and MgO–C refractories and of the wetting slag and MgO–C refractories. © 2013 ISIJ
refractories were investigated to further explain the wettability in two cases. Finally, the adhesion and protection mechanism of the slag in the BOF were discussed.

2. Experimental

The slag and substrate used in the experiments were the final slag used for slag splashing and the lining MgO–C refractories from the TIANJIN Iron & Steel Group CO., LTD, respectively. The chemical composition of the slag was shown in Table 1. The mineralogical phases of the original slag were shown in Fig. 1, and its density is about 4.1×10³ kg/m³. The physical and chemical properties of MgO–C refractories were shown in Table 2.

The wettability between molten slag and MgO–C refractories was evaluated by the dynamic contact angle. Contact angle was measured by using a sessile drop equipment, which is composed of a heating systems, imaging systems and graphics computing systems.8–12)

The slag specimen was polished to mirror, rinsed in ethanol by an ultrasonic cleaner and dried afterward, while the carbon bricks were prepared by the same steps and then dried in a muffle furnace to remove the gases and impurities. The slag sample was placed on the MgO–C refractories and set into the heating equipment together through a boat. The position of the sample was adjusted by one side of the light source to maintain that the sample and substrate were in the same straight. More than three photographs of droplets were captured at each desired experimental temperature as a function of time. The contact angles were calculated by analyzing these photos with a self-made software. The shape of the droplet is often unable to reach equilibrium after spreading on the solid surface due to various factors such as roughness of the refractory and the type of gas. The contact angle is the average of the left and right ones. The mean value of those data at the same temperature has been considered as the contact angel at this temperature.

Wettability experiments are carried out in two cases at 1 783 K, which is consistent with the temperature of slag before slag splashing process: a) slag was directly contacted with the substrate shown in Fig. 2(a); b) slag was melting on a small alumina crucible to separate it from the substrate and prevent the reduction of the FeO in slag during heating process. After the slag began to melt, it flew over from the alumina crucible by melting and began to spread on the substrate. The experimental time was set to 0 s when the temperature reached 1 783 K.

The interfacial morphology was observed by an optical microscope (Leica DM4000M) and a scanning electron microscope (JSM-6460LV) which is equipped with an energy dispersive spectrometer (EDS) to observe the distribution of elements. The optical microscope was used to observe the microstructure on the interface of the sample.

3. Results and Discussion

3.1. Wetting Behavior between the Slag and MgO–C Refractories

The result is shown in Fig. 2. In the case (a), the converter slag did not melt and the shape did not change either with heating time, and thus the contact angle was constantly 90°.

In the case (b), the molten slag was wettable with the substrate at 1 783 K and the spread area increased with the time while the contact angle decreased. During the spreading process, carbon in the MgO–C refractories was oxidized to CO by FeO in the molten slag, which makes the surface of the spreading molten slag as a foamy slag by evolved CO gas bubbles. Note that Al₂O₃ content of the slag was expected to increase in the case (b), from 1.64 to approximately 2.5 mass% by reported thermodynamic data, though Al₂O₃ content was not analyzed after the experiment. Therefore, it is considered that the increase of Al₂O₃ content did not remarkably affect the melting and wetting behaviors.
Figure 1 shows the XRD spectra of the converter slag in three conditions, which were the original slag, non-melting slag and wetting slag. The mineralogical phases mainly observed in the three kinds of slag were the same. The non-melting slag came from the case (a), and the diffraction peak intensity of the $\alpha$-Fe in the slag increased while that of FeO decreased, which means that chemical reaction occurred. FeO in the slag was reduced to Fe by the carbon in a substrate or CO in the atmosphere, which resulted in the increase of the formation temperature of the initial liquid phase in the slag. It is considered that some other phases observed as small diffraction peaks correspond to the newly created phases by heating or the reaction with refractory materials. The wetting slag came from the case (b), FeO in the slag did not contact directly with the substrate when the slag was on the alumina crucible. The process which the molten slag flew over the crucible and spread on the substrate, however, took little time. Therefore, the diffraction peak intensity of the $\alpha$-Fe and FeO in the slag had little change.

3.2. Effect of Time on the Behavior of the Wettability

The wetting behavior between the molten slag and MgO–C refractories in the case (b) was studied by measuring the dynamic contact angle and the spread diameter. Figure 3 shows the effect of time on the average contact angle ($\theta_{ave}$) between the molten slag and MgO–C refractories at 1783 K. Figure 4 shows the effect of time on the diameter and height of the molten slag at 1783 K. From 0 to 237 s, the spread diameter increased significantly and the slag height decreased as the molten slag spread quickly on the MgO–C refractories with the increase of the time. From 300 to 500 s, the spread diameter changed slowly, and reached the steady state. The relation between the spread diameter and time between 0 and 237 s at 1783 K is expressed as Eq. (1).

$$D = 5.07 + 0.02 \ t \ (t < 237 \ s) \ .................. (1)$$

Where $D$ is the spread diameter of the molten slag (mm) and $t$ means the time (s).

The relation between the height and time between 0 to 237 s at 1783 K is expressed by Eq. (2).

$$H = 5.20 - 0.01 \ t \ (t < 237 \ s) \ .................. (2)$$

Where $H$ is the height of the molten slag (mm).

If the molten slag spread evenly on the MgO–C refractories, the relation between area and time is calculated as follows from the relation $S = \pi D^2/4$:

$$S = 3.80 \times 10^{-4} \ t^2 + 0.18 \ t + 20.17 \ .................. (3)$$

Where $S$ is the spread area of the molten slag (mm$^2$).

3.3. Interfacial Characteristics of the Non-melting Slag and MgO–C Refractories

Figure 5(a) shows the optical micrographs of the interface between the non-melting converter slag and the substrate, which is area (a) shown in Fig. 1. The slag did not melt even with the increase of temperature and time, while the distribution of metallic iron on the interface was observed. This is because the reduction of iron oxide in the slag is the main reaction which affects the wettability in slag and carbonaceous materials system. On the one hand, oxide reduction is bound to occur in the area where slag directly contacts with the substrate, especially the reduction of FeO in slag. On the other hand, thanks to the CO generated by Boudouard reaction, the surface of the slag is exposed to the reducing atmosphere, where iron oxide reacts with CO by indirect reduction.

$$\text{FeO (l)} + \text{C (s)} = \text{Fe (l)} + \text{CO (g)} \ .................. (4)$$

$$\text{FeO (l)} + \text{CO (g)} = \text{Fe (l)} + \text{CO}_2 (g) \ ............. (5)$$

$$\text{CO}_2 (g) + \text{C (s)} = 2\text{CO (g)} \ .................... (6)$$

FeO is one of the main factors that affects the slag melting temperature (which is the temperature when the slag becomes the hemi-spherical shape in this paper). On one hand, FeO has lower melting point than other oxides which can provide O$^-$ ion. On the other hand, FeO can react with CaO and SiO$_2$ to form low melting point compounds, solid solution or composite compounds such as pseudowollastonite and fayalite whose melting point is in the range from 1473 to 1723 K.

When FeO content is lower than 5 mass%, it has the small effect on the melting temperature of the slag, while the effect becomes bigger at FeO content larger than 5 mass%. In the wetting experiments with 17.24 mass% FeO in slag.

Fig. 3. Contact angle between molten slag and MgO–C refractories as a function of time at 1783 K.

Fig. 4. Diameter and height of the molten slag on MgO–C refractories as a function of time at 1783 K.
and 18 mass% carbon in MgO–C refractories, the melting temperature of the slag increases significantly as FeO content decreases with the reduction reaction, and thus the slag kept the initial columnar shape.

EDS line scanning graph of the solidified non-melting sample in area (a) is shown in Fig. 6(a). Line AB in the upper figure corresponds to the position for EDS line scanning, which results are shown in the lower figure. Iron has the highest intensity on the interface, which means that reduction occurred on the interface. It implies the decrease of FeO content in the slag, which is consistent with the previous discussion.

3.4. Interfacial Characteristics of the Wetting Slag and MgO–C Refractories

Figure 5(b) shows the optical micrograph of the interface between the molten converter slag and the substrate, which is area (b) shown in Fig. 1. Slag spread on the MgO–C refractories with good wettability, and at the same time the foamy slag was formed by CO which was produced by the reduction reaction between FeO in the slag and carbon in the MgO–C refractories. Some slag penetrated into the gap which was made after carbon consumption by FeO reduction on the surface and contacted with the MgO particles to form high melting point protection layer. It should be pointed out that the above process occurred within a short time.

Three layers, namely the slag layer, penetration layer and MgO–C layer (i.e. refractories) can be observed at the interface between the molten slag and the substrate after the molten slag spread on the MgO–C refractories. Slag layer consists of the residual slag after spreading and slag penetrating layer. Penetration layer is the protection layer composed of the high melting point oxide phases formed after wetting between the slag and the MgO particles. MgO–C layer is the unreacted refractory layer.

EDS line scanning graph of the solidified sample in area (b) of Fig. 5 is shown in Fig. 6(b). Line CD in the upper fig-
ure corresponds to the position for EDS line scanning, which results are shown in the lower figure. The metallic Fe layer at the interface between slag and the refractory material is thinner compared with the case (a). It means that the degree of FeO reduction at the interface is lower and the change of FeO content in the slag is relatively small, which provides evidence to the discussion of Fig. 2.

3.5. Adhesion and Protection Mechanism

According to the analyses on the wetting behavior and the interfacial properties between the slag and the MgO-C refractories described previously, the pores or cracks are formed as the graphite in the MgO-C refractories contacts with the oxygen in the gas phase or FeO in the slag phase. The liquid slag spreads and penetrates into the MgO-C refractories through the pores and cracks on the surface during the process of slag splashing. The strength of the refractory lining is reduced and it is vulnerable to the erosion of the slag if the decarburized layer is formed on the surface. The strength of the refractories through the pores and cracks on the surface during the process of slag splashing. The strength of the refractory lining is reduced and it is vulnerable to the erosion of the slag if the decarburized layer is formed on the surface of the MgO-C refractories.

Based on the phase diagram for the FeO–MgO–Fe₂O₃ system, magnesioferrite MgO·Fe₂O₃ is formed by MgO and Fe₂O₃, and it can further react with FeO to form the solid solution. Both magnesioferrite and the solid solution is high melting point refractory. The slag has good wettability with the coarse magnesia particles which are bare in the MgO-C refractories. Therefore, after the slag penetration layer is formed, Fe₂O₃ and FeO in the slag easily react with MgO in the MgO-C refractories to form a yellow permeable layer filling the pores between the large magnesia particles. Permeable layer is denser than the decarburized layer on the surface of the lining. With relatively high melting point, it can effectively inhibit the high temperature oxidative slag residue or furnace gas from diffusing or penetrating into the internal brick, and avoid further oxidation of carbon in the MgO-C refractories, resulting in the protection of the lining protection.

4. Conclusions

The wetting behaviors between the slag and MgO-C refractories in two cases were investigated. The interfacial characteristics between two kinds of slag and MgO-C refractories were also studied. The conclusions of the present study were summarized as follows.

(1) The slag was non-melting in the case that the slag contacted directly with the substrate while the slag melted and it was wettable in the case that slag was separated with the substrate before complete melting at 1 783 K.

(2) From 0 to 237 s, the spread diameter increased significantly and the slag height decreased as the slag spread quickly on the MgO-C refractories with the increase of the time at 1 783 K. From 300 to 500 s, the spread diameter changed slowly, and reached a steady state.

(3) Thicker metallic Fe layer on the interface between the non-melting slag and the substrate was observed. This is because the reduction of iron oxide in the slag by carbon in the MgO-C refractory occurred, which affects the wettability of the slag and carbonaceous materials system.

(4) Slag melted at 1 783 K on the alumina crucible and spread better on the substrate. Foamy slag was formed by CO gas bubbles which were produced by the reduction reaction between FeO in the slag and carbon in of the MgO-C refractories. Then the slag penetrated into the gap made in the MgO-C refractories after decarburization on the surface and the penetrated slag contacted with MgO particles to form a high melting point protection layer.

(5) Permeable layer can effectively inhibit the high temperature oxidative slag residue or furnace gas from diffusing or penetrating into the internal brick, and avoid further oxidation of the carbon in the MgO–C refractories, resulting in the lining protection.

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