Corrosion Behavior of Alumina Containing Refractory in Blast Furnace Hearth by CaO–SiO₂–MgO–Al₂O₃–Cr₂O₃ System Slags

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The corrosion behaviors of corundum brick and carbon composite brick used in blast furnace hearth by CaO–SiO₂–MgO–Al₂O₃–Cr₂O₃(CaF₂) slags were studied in the present work. The degradation of the corundum brick in slag was a result of slag infiltration and brick dissolution, and the corrosion of the brick became more serious with the addition of CaF₂ due to the decrease of slag viscosity. The disintegration of carbon composite brick in CaF₂-containing slag was caused by the combination of slag penetration, brick dissolution and reaction between slag and brick. By comparing the corrosion behavior in CaF₂-containing slag between the corundum brick and carbon composite brick, the corrosion degree of the corundum brick was greater than that of the carbon composite brick. To the blast furnace operation in which a low grade iron ore such as laterite ore and CaF₂ containing slag (about 2 wt%) are used, it was found that the carbon composite brick with better slag corrosion resistance can be selected as a hearth refractory so as to improve the operation performance and ensure the longer campaign life of blast furnace.

KEY WORDS: corundum brick; carbon composite brick; slag; corrosion; CaF₂.

1. Introduction

The life of refractory used in a blast furnace hearth is closely related to the campaign life of the blast furnace, and the refractory with good corrosion resistance is essential and beneficial to ensure the long service life of the blast furnace. Therefore, it is very important to understand the corrosion mechanisms of the refractory in contact with molten slag at iron making temperatures. Alumina refractories and Al₂O₃–C refractories are widely used in blast furnace hearth.1) and the corrosion behaviors of these refractories in slag have been investigated extensively.2–6)

For example, Zuo et al.6) studied the dissolution behaviors of Al₂O₃–SiC–SiO₂–C composite brick and corundum brick in blast furnace slag. It is well known that the slag properties have an important influence on the corrosion or dissolution of refractories into the slag. The blast furnace slag in smelting low-grade iron ore is different from the ordinary blast furnace slag, and there have been few researches on the corrosion behavior of refractory in the blast furnace slag with smelting low-grade ores.

As the main resource of nickel, some high-alumina laterite ores are smelted in blast furnace to produce nickel-containing hot metal. The blast furnace slag with smelting high alumina laterite ores has big difference in composition, properties and performance compared to the ordinary blast furnace slag. For example, the fluidity of this type of slag is very poor.7) In order to maintain the stable operation of the blast furnace, CaF₂ is usually added as a fluxing agent to improve the slag fluidity in the process of practical production, which may lead to more serious corrosion of refractory.8,9) However, the influence and mechanism of CaF₂-containing blast furnace slag on the corrosion of blast furnace hearth refractory has not been well illustrated. Therefore, the corrosion behavior of refractories in such complex slag should be further explored.

In our previous papers10–12) the corrosion mechanisms of refractories, such as carbon composite brick and carbon brick, in CaO–SiO₂–MgO–Al₂O₃–Cr₂O₃-based slag have been systematically investigated. In this work, the corrosion behavior of corundum brick by CaO–SiO₂–MgO–Al₂O₃–Cr₂O₃ slag with or without CaF₂ addition was studied. Furthermore, the corrosion behavior of carbon composite brick in CaF₂-containing slag was also investigated, as a comparison with previous studies.10–12) The aim of this work is to advance the fundamental understanding of the corrosion mechanisms of refractories by blast furnace slags and subsequently provide a guidance to improve the quality of the refractory and prolong the service life of the blast furnace. This will be also helpful so as to increase the use of low-grade ores such as laterite ores in blast furnace.
2. Experimental

2.1. Materials Preparation

The corundum brick and carbon composite brick samples were cut from commercial refractories which were produced by Henan Winna Industrial Group Co., Ltd. The main compositions of corundum brick were 83.0 wt% Al₂O₃, 3.6 wt% C, 3.6 wt% SiC, and 9.7 wt% SiO₂, and the bulk density and apparent porosity of the brick were 3.0 g/cm³ and 15.0%, respectively. The main compositions of carbon composite brick were 74.05 wt% Al₂O₃, 9.2 wt% C, 6.0 wt% SiC, and 8.18 wt% SiO₂, and its bulk density and apparent porosity were 2.98 g/cm³ and 10.9%, respectively. All these bricks were processed into cylindrical specimens (height = 17 mm, diameter = 17.5 mm) with a through hole of 5 mm in diameter. All the brick samples were dried in a desiccator for 12 h at 105°C to remove the moisture before conducting corrosion experiments.

The slag samples were synthesized by using reagent grade oxides of CaO, SiO₂, MgO, Al₂O₃, Cr₂O₃ and CaF₂, which were dried at 105°C in a desiccator for 12 h at 105°C before use. According to the compositions shown in Table 1, reagent powders were weighed 125 g precisely and then mixed thoroughly in the agate mortar.

2.2. Experimental Procedure

In order to reflect the real flow state of molten slag in the blast furnace hearth, the corrosion experiments of the refractories in CaO–SiO₂–MgO–Al₂O₃–Cr₂O₃–CaF₂ slags were studied by using finger rotating method, which has been employed in our previous studies and by many other researchers. Since the detail of experimental apparatus has already been described in our previous study, it is not mentioned in this paper. The corrosion behavior of corundum brick in slag No.1 (without CaF₂) and No. 2 (with CaF₂) and the corrosion behavior of carbon composite brick in slag No 2 were investigated. The prepared slag sample was immersed into the molybdenum crucible and heated to 1550°C in a muffle furnace, then maintained at this temperature for about 2 h to homogenize the molten slag. Subsequently, the refractory sample, which was mounted on a molybdenum rod with the diameter of 5 mm, was immersed into the slag about 10 mm above the crucible bottom and rotated at a speed of 200 rpm for 120 min under Ar atmosphere. After the experiment, the refractory sample was raised to the upper position of the crucible and rotated again to remove the attached slag on the refractory surface. Then the refractory sample was pulled out of the furnace and cooled in air. In order to characterize the corrosion degree of the refractory, the diameter of the reacted brick sample was measured at different heights using a vernier caliper and the average value could be employed as the final diameter. The relative average deviation (Δ, %) was calculated by using the Eq. (1), and the relative average deviation of diameter of all bricks was smaller than 0.28%. Thus the diameter decrement which was the difference of the original and final diameter could be obtained.

\[
\Delta = \frac{1}{N} \sum_{i=1}^{N} \frac{|d_i - d_{ave}|}{d_{ave}} \times 100\% \quad \text{(1)}
\]

where \(d_i\) and \(d_{ave}\) are the measured original diameter and the final diameter (i.e. the calculated average diameter) of the corroded refractory sample, respectively; \(N\) represents the number of measurement.

The morphology and elemental distribution of the refractory in the vicinity of refractory-slag interface after experiment was investigated by using scanning electron microscope (SEM; FEI MLA250, USA) with energy dispersive spectroscopy (EDS). The surface phase characterization of the corroded refractory was identified by X-ray diffraction (XRD; Ultima IV, Japan) over the 2θ range of 10°–90° (Cu Kα radiation, \(\lambda = 1.5406 \text{ Å}\)).

3. Results and Discussion

3.1. Diameter Decrement of Refractory Samples

In the present study, the diameter decrement was used to compare the corrosion degree between the corundum brick and carbon composite brick samples, and the effect of CaF₂ addition on the corrosion degree of bricks was also evaluated by this method. The comparison of the diameter decrement of corundum brick and carbon composite brick by corrosion was shown in Fig. 1. As can be seen from Fig. 1, the diameter decrement of the corundum brick sample corroded was 0.44 mm by CaO–SiO₂–MgO–Al₂O₃–Cr₂O₃–CaF₂ slag and 0.79 mm by CaO–SiO₂–MgO–Al₂O₃–Cr₂O₃–CaF₂ slag, respectively. It can be concluded that the corrosion degree of the corundum brick sample by molten slags increased with the addition of CaF₂. As a comparison, the diameter decrement of the carbon composite brick sample after corrosion by CaF₂-containing slag was only 0.38 mm, much lower than that of the corundum brick sample (0.79 mm), indicating that the carbon composite brick had better corrosion resistance to the CaO–SiO₂–MgO–Al₂O₃–Cr₂O₃–CaF₂ slag than that of corundum brick.

![Fig. 1. Diameter decrement of corundum brick and carbon composite brick samples after corrosion by molten slags.](Online version in color.)

<table>
<thead>
<tr>
<th>Table 1. Chemical compositions of the slags (wt%).</th>
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3.2. Corrosion Behavior of Corundum Brick in Slags

In order to understand the corrosion mechanism of the corundum brick in contact with slag, the morphology of the corroded brick sample was analyzed by using SEM-EDS. Figure 2 presents the SEM micrographs and the EDS results of the corundum brick sample after corrosion experiment by CaO–SiO₂–MgO–Al₂O₃–Cr₂O₃ slag. As can be seen from Fig. 2(a), a thin layer of slag was formed on the surface of corundum brick sample, which can be confirmed from the EDS results in Figs. 2(b) and 2(c). The calcium oxide was not contained in the brick sample, therefore the presence of calcium element inside the brick sample means that the slag penetrated into the corundum brick sample during the interaction process of the slag and brick sample. Figure 2(d) shows another corrosion zone of the corundum brick sample. From Fig. 2(d) and EDS mapping results in Figs. 2(e)–2(i), a clear boundary can be seen between the undissolved corundum particle and the corroded refractory, which may be formed due to the slag infiltration. Comparing the element distribution of Ca, Al and Si as shown in Figs. 2(g)-2(i), it was found that Ca element could further penetrate into the brick interior due to the higher mobility of Ca^{2+} cations. This phenomenon may indicate that the slag penetration is an important factor which affects the refractory degradation. From Fig. 2(d), some pores were also observed in the slag layer. The pores may be formed due to the escape of gases generated by the oxidation reaction of carbon in the corundum brick sample with the slag oxides such as Cr₂O₃ according to the reactions (2) and (3). Hong et al. investigated the in-situ reactions of Al₂O₃–SiC–SiO₂–C refractory, indicating that the reaction between SiO₂ and C could occur according to the reactions (4) and (5). Therefore, besides the Cr₂O₃, the SiO₂ in slag or in the refractory might also act as an oxidant, contributing to the generation of the gas pores.

\[
\text{Cr}_2\text{O}_3 (l) + C (s) = 2\text{CrO} (l) + \text{CO} (g) \quad (2)
\]

\[
\text{CrO} (l) + C (s) = \text{Cr} (s) + \text{CO} (g) \quad (3)
\]

\[
\text{SiO}_2 (s or l) + 3\text{C} (s) = \text{SiC} (s) + \text{CO} (g) \quad (4)
\]

\[
\text{SiO}_2 (s or l) + \text{C} (s) = \text{SiO} (g) + \text{CO} (g) \quad (5)
\]

The corrosion mechanism of the corundum brick in the slags studied can be discussed as below. The corundum refractory, mainly consisting of Al₂O₃ and SiO₂, has good wettability with molten slag. Therefore the slag could easily dissolve and react with the corundum brick sample when the corundum brick sample was immersed into the molten slag. Meanwhile, the slag could infiltrate into

![Fig. 2. SEM images and EDS results of the corundum brick sample after corrosion by CaO–SiO₂–MgO–Al₂O₃–Cr₂O₃ slag. (a) and (d): morphology of the brick; (b) and (c): EDS results of P1 and P2 regions; (e)–(i): EDS mapping results of image (d). (Online version in color.)](image-url)
the corundum brick sample through the pores, cracks and grain boundaries of the brick, and consequently the grains of Al$_2$O$_3$ or SiO$_2$ in the refractory would be detached from the bulk of the corundum brick sample. It would make the penetration of the slag into the brick sample and the dissolution of the detached Al$_2$O$_3$/SiO$_2$ grains into the slag promoted further. As a result, the microstructure and densification of the brick sample was changed and degraded.$^{17,18}$ Furthermore, the oxides of Al$_2$O$_3$ and SiO$_2$ could be dissolved into the slag by thermodynamic driving force, which was expressed as the concentration difference of Al$_2$O$_3$ and SiO$_2$ between the brick sample and the molten slag.$^{19}$ The dissolution process of the components would change the microstructure of corundum brick and lead to the brick being corroded directly. A similar corrosion mechanism was also demonstrated by our previous investigation on the corrosion behavior of carbon brick,$^{12}$ that the corrosion of the carbon brick in the region with Al$_2$O$_3$ as the main component primarily caused by the slag penetration and brick dissolution. Consequently, the combined effects such as refractory dissolution and slag infiltration resulted in the disintegration of the corundum brick.

The phase characterization of the hot surface of the corroded corundum brick was conducted by XRD and the XRD patterns were presented in Fig. 3. It can be seen from Fig. 3 that the phases on the hot surface of the corroded corundum brick sample were corundum (Al$_2$O$_3$), SiC, spinel (MgAl$_2$O$_4$) and gehlenite (Ca$_2$Al$_2$SiO$_7$). The phases of Al$_2$O$_3$ and SiC were from the original corundum brick, which was not dissolved into the slag yet. The new phases (spinel and gehlenite) may be formed by the reactions between the oxides in corundum brick sample with the oxides in slag during the corrosion process or crystallized out of the slag then adhering to the brick surface at lower temperature. Such phases of the spinel and gehlenite were also found in the surface of the carbon brick or carbon composite brick after corrosion by slag.$^{10,12}$ The presence of spinel with high volumetric stability may prevent the penetration of slag into corundum brick. However, if the temperature at the hot face of the corundum brick was higher than the melting temperature of the phases such as gehlenite (which were formed at the hot face by the reactions between slag and refractory) under the smelting conditions, it would not be conducive to the formation of protective slag crust on the brick surface. These low-melting products will fall down from the hot surface of the brick and result in the deterioration and corrosion of the brick.

The SEM and EDS mapping images of the corundum brick sample corroded by the CaO–SiO$_2$–MgO–Al$_2$O$_3$–Cr$_2$O$_3$–CaF$_2$ slag were shown in Fig. 4. It can be seen that calcium element was mainly enriched in the hot face of the corundum brick sample, indicating that a slag layer was formed on the brick sample surface due to the slag penetration into the brick and interaction between the slag and brick sample. The metal chromium was observed in the slag layer, which may be explained by the reaction between carbon in the brick sample and the Cr$_2$O$_3$ in the slag. As both the carbon content in the corundum brick sample and the Cr$_2$O$_3$ content in the slag were very low, only a small amount of chromium was formed. As shown in Fig. 4, magnesium was observed in the slag layer and in particular concentrated at
the interface of brick sample and slag layer, which indicates that magnesia reacted with the alumina inside the corundum brick sample to form spinel (MgO-Al2O3).11)

The degradation of corundum brick in CaF2-containing slag was also caused by the dissolution of the corundum brick and the penetration of slag into the brick. The slag properties have a significant effect on the corrosion of the refractory. This means that the slag performance could be changed with the addition of CaF2, which will further affect the corrosion process of the refractory in contact with the slag. According to earlier studies, the infiltration rate of slag into refractory increased with the decreasing of slag viscosity. The slag viscosity decreased with the addition of CaF2, which could improve the slag fluidity and promote the penetration of slag into the corundum brick sample. Furthermore, it accelerated the mass transfer rate of the reactants at the reaction interface and provided more opportunity to make components of the refractory in contact with the slag, then resulted in the formation of compound such as MgO-Al2O3 and aggravated the brick disintegration. When the CaF2-containing slag infiltrated into the brick, the binder in the brick may be also dissolved by the penetrated slag, and then weaken the connectivity of the Al2O3 particles. On the other hand, CaF2 may also increase the solubility of Al2O3 in the slag and facilitate the direct dissolution of corundum brick.24) Therefore, the degradation degree of the corundum brick by slag increased with the addition of CaF2.

In general, the rate determining step of the dissolution of refractory into slag under high temperature was the mass diffusion or transport.12) Li et al.19) investigated that the dissolution process of alumina rod into CaO–Al2O3–CaF2 slag and found that the diffusion of Al2O3 in the slag boundary layer was the rate determining step. While the results of Li et al.20) indicated that the dissolution of Al2O3 into CaO–BaO–MgO–Al2O3–SiO2–B2O3–CaF2–Li2O–Na2O flux was controlled by the diffusion of Al2O3 in the product layer. Thus, the dissolution of the corundum brick sample into molten slag may be controlled by the diffusion of Al2O3 in the slag boundary layer or product layer. However, based on the present results, it is insufficient to determine the rate controlling step of the dissolution of corundum brick, and which should be further investigated.

3.3. Comparison of Corrosion Behaviors between Corundum Brick and Carbon Composite Brick in CaF2-containing Slag

In order to compare the corrosion behavior of corundum brick and carbon composite brick in CaF2-containing slag, the morphology of carbon composite brick eroded by CaF2-containing slag was also investigated, which was shown in Fig. 5. It can be seen from the EDS line scanning results in Figs. 5(a)–5(b) that the Al concentration decreased while the concentrations of Ca, Mg, Si and Cr elements increased from the interior to the exterior of the brick sample. The line scanning results indicated that the slag penetrated into the carbon composite brick sample and a slag layer was formed on the hot face of the brick sample. From the EDS results in Figs. 5(c) and 5(d) and mapping results in Figs. 5(e)–5(k), some metallic Cr were also present in the slag layer, which indicates the occurrence of the reaction between the carbon in refractory and the Cr2O3 in slag. Furthermore, Cr-carbide or Cr-silicide may be also formed due to the coexistence of C, Si and Cr in the region of P1, and the formation of carbide or silicide has been proved by our previous studies. Figure 5(a) shows that some unreacted carbon existed near the surface of the slag layer or Cr layer. The carbon has poor wettability with the slag and the carbon present in the carbon composite brick could hinder the infiltration of molten slag into the carbon composite brick, which could decrease the corrosion degree of the refractory by slag.

The surface phase of the corroded carbon composite brick sample was analyzed by using XRD, which can be seen from Fig. 6. As shown in Fig. 6, the phases detected at the brick sample surface after corrosion experiment were carbon, Al2O3 (Al1.96Cr0.02O3), SiC, Cr3Si, melilite (Ca3Al2MgSi2O8), anorthite (CaAl2Si2O6) and spinel (MgAl2O4). The existence of Cr3Si could further prove the formation of silicide, which was consistent with the EDS results in Fig. 5(c). In our previous paper,21) anorthite and spinel phases as the intermediate compounds were found in the product layer. Therefore, the mixture of anorthite, spinel and melilite can be considered as the reaction products of the molten slag with the refractory during the corrosion process.

The corrosion mechanism of carbon composite brick in CaF2-containing slag was influenced by factors of slag infiltration, refractory dissolution and slag-refractory reaction. When the brick was in contact with the slag, the slag would infiltrate into the brick matrix and form a slag layer on the brick hot face, and then degrade the brick structure. Meanwhile, the oxidation of carbon in the brick by the oxide of Cr2O3 or SiO2 in the slag may lead to more holes or channels inside the brick and further facilitate the penetration of molten slag. In addition, the brick component such as Al2O3 could dissolve into the slag and lead to direct erosion of the brick.10,11,27) The combination of slag penetration, brick dissolution and reaction between slag and brick finally resulted in the brick disintegration. Due to the little oxides of Cr2O3 in the slag, the influence of reaction between Cr2O3 and carbon on the corrosion of carbon composite brick may be small. Therefore, the factors of refractory dissolution and slag infiltration may be more important. The presence of CaF2 in slag could decrease the slag viscosity and promote the infiltration of slag into the brick or accelerate the dissolution of brick component into the slag by increasing the thermodynamics driving force,25) therefore increasing the corrosion degree of the carbon composite brick. According to our previous study,10) the rate determining step of dissolution of the carbon composite brick into CaO–SiO2–MgO–Al2O3–Cr2O3–B2O3 slag was the solute (Al2O3) diffusion through the product layer. It can be concluded that CaF2, like B2O3, would not change the rate-controlling step but increase the diffusion rate of the solute. Therefore, the dissolution of carbon composite brick into the CaF2-containing slag in this study was also controlled by the solute diffusion step.

By comparing the corrosion behaviors of corundum brick and carbon composite brick in CaF2-containing slag, it can be found that the corundum brick was corroded much more severe than the carbon composite brick, indicating the exis-
The content of carbon in the refractory has a positive effect on the slag corrosion resistance of refractory. In the present experiment, the Cr₂O₃ content in slag was only 1.0 wt%, which could not completely oxidize the carbon in brick, and then the unoxidized carbon could restrain the penetration of slag. However, the corundum brick was easier to be penetrated by slag due to much less carbon content present in the corundum brick. On the other hand, the dissolution of the main component of the refractory such as Al₂O₃ was also the reason of the refractory degradation. The content of Al₂O₃ and SiO₂ in the corundum brick was higher than that in the carbon composite brick, enabling faster dissolution of the corundum brick into molten slag. Consequently, the corrosion degree of the corundum brick was greater than that of the carbon composite brick. The similar conclusion was also obtained by the study of the corrosion behavior of

**Fig. 5.** SEM images and EDS results of the carbon composite brick sample after corrosion by CaO–SiO₂–MgO–Al₂O₃–Cr₂O₃–CaF₂ slag. (a): morphology of the brick; (b): EDS line scanning results; (c) and (d): EDS results of P1 and P2 regions; (e)–(k): EDS mapping results of image (a). (Online version in color.)
carbon composite brick and corundum brick in CaO–SiO2–MgO–Al2O3-based slag. It can also be concluded from Fig. 1 that the corrosion degree of carbon composite brick by CaO–SiO2–MgO–Al2O3–Cr2O3 slag was lower than that of corundum brick by CaO–SiO2–MgO–Al2O3–Cr2O3 slag. Therefore, when 2 wt% CaF2 was added in slag as a fluxing agent to improve the operation of the blast furnace when smelting the low-grade iron ores such as laterite ores, the carbon composite brick, instead of corundum brick, with good corrosion resistance could be selected as the hearth refractory to ensure the longer campaign life of blast furnace.

4. Conclusions

The corrosion behaviors of corundum brick and carbon composite brick in CaO–SiO2–MgO–Al2O3–Cr2O3-based slags with or without CaF2 have been systematically investigated in this study. The main conclusions are summarized as follows:

(1) The degradation of corundum brick in slag was caused by the comprehensive effects of brick dissolution and slag infiltration. The presence of CaF2 could improve the slag fluidity and increase the solubility of Al2O3 in slag, which promoted the penetration of slag into the refractory and facilitated the direct dissolution of corundum brick, consequently aggravating the brick disintegration.

(2) The corrosion of carbon composite brick by CaF2-containing slag was a result of slag infiltration, brick dissolution and reaction between slag and brick. By comparing the corrosion behavior in CaF2-containing slag between corundum brick and carbon composite brick, the corundum brick was corroded much more severe than the carbon composite brick.

(3) For the blast furnace smelting low grade iron ores such as laterite ore and adding 2 wt% CaF2 in slag to improve the operation of the blast furnace, the carbon composite brick is superior to corundum brick in terms of corrosion resistance and could be selected as the hearth refractory to ensure the longer campaign life of blast furnace.

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