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Corrosion behavior of carbon composite brick in high alumina slags

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ABSTRACT

The corrosion behavior of carbon composite brick used in blast furnace hearth by CaO-SiO₂-MgO-Al₂O₃-Cr₂O₃-based slag with and without B₂O₃ at different rotation speeds and temperatures was investigated in this work. The radius decrement of the brick increased with the increase of rotation speed, temperature and content of B₂O₃ in slag. Furthermore, the square of the radius decrement of brick changed linearly with the immersion time, indicating that the dissolution of the brick into slag may be controlled by the mass diffusion step. A slag penetration layer or product layer may be firstly formed during the corrosion process of carbon composite brick in slags, and then the components of brick dissolved into the molten slag by diffusing through this layer. The corrosion of the carbon composite brick by B₂O₃-containing slag is much severer than that by slag without B₂O₃ due to the lower viscosity and melting temperature of B₂O₃-containing slag.

1. Introduction

Long campaign life of blast furnace is an important development trend of the iron-making process. Due to long-term storage of high temperature hot metal and molten slag, as well as the large mechanical abrasion and chemical corrosion at high temperature, the blast furnace hearth life has become a key factor to limit the blast furnace service life [1,2]. The corrosion resistance of refractory used in blast furnace hearth is one of the main factors affecting the hearth life. So it is important to understand the corrosion behavior of refractory in high temperature smelting process. In the case of smelting low-grade ore, such as laterite ore, compositions and properties of the formed slag are complex [3], and the corrosion mechanism of refractory in these kinds of slags is worthy being paid more attention.

Carbon brick is widely used in blast furnace hearth due to its good thermal conductivity and low wettability by slags [4]. However, it is easily to be oxidized and dissolved into hot metal. Accordingly, carbon composite brick is developed and gradually used in blast furnace hearth [5,6]. In order to understand the performance of carbon composite brick, its corrosion behavior in molten slag should be systematically investigated. Hong et al. [7] studied the reaction between Al₂O₃-SiC-SiO₂-C refractory and CaO-SiO₂-Al₂O₃ slag, and found that slag could penetrate into the refractory through pores and low melting point compounds were formed at the surface of refractory, which led to the refractory degradation. Chan et al. [8] investigated the effects of different additives on slag corrosion resistance of Al₂O₃-SiC-SiO₂-C

refractory under reducing atmosphere, and the results showed that Si, Si₃N₄, B₄C and B₂O₃ could reduce the slag penetration resistance, while Al and BN had no significant effect on corrosion resistance of refractory. Wu et al. [9] investigated the effect of B₄C addition (0.5–2.0 wt%) on the property of Al₂O₃-SiC-C based refractory, and found that the refractory with 1.5 wt% B₄C had the best slag corrosion resistance and thermal shock resistance. In order to improve the corrosion resistance of Al₂O₃-SiC-C refractories, Yang et al. [10] studied the influences of β-Sialon and Ti(C,N) additions, and pointed out that these additives could increase the corrosion resistance of the refractory. Zuo et al. [11] investigated the dissolution behavior of carbon composite brick into CaO-SiO₂-MgO-Al₂O₃-based slag by using finger rotation method at different temperatures, however the influences of rotation speed and slag composition were not considered. In our previous study [12], the corrosion mechanism of carbon composite brick by CaO-SiO₂-MgO-Al₂O₃-Cr₂O₃-(MnO) slags has been investigated, while the rate-determining step of brick dissolution is still unclear. Therefore, the dissolution and corrosion behavior of carbon composite brick in slags need to be further investigated. In addition, as a potential lubricant, B₂O₃ could be used instead of CaF₂ to improve the slag fluidity as smelting the low-grade ore such as laterite ore in the blast furnace [3]. In order to make better use of B₂O₃ to maintain stable operation of blast furnace, it is also necessary to clarify the influence of B₂O₃ on refractory corrosion.

In the present work, the influences of rotation speed, temperature and slag composition on the corrosion behavior of carbon composite brick immersed in CaO-SiO₂-MgO-Al₂O₃-Cr₂O₃-(B₂O₃) slags were

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Table 1
Chemical compositions of the slags (wt%).

No.	CaO	SiO ₂	MgO	Al ₂ O ₃	Cr ₂ O ₃	B ₂ O ₃
1	34.0	34.0	8.0	23.0	1.0	0
2	33.0	33.0	8.0	23.0	1.0	2.0

studied, which could provide a reference for improving the refractory quality and eventually extending the campaign life of blast furnace.

2. Experimental

2.1. Materials preparation

The carbon composite brick samples were cut from commercial bricks (Henan Winna Industrial Group Co., Ltd., Gongyi, China) and processed into a cylindrical specimen with the dimensions of 17 mm in height and 17.5 mm in diameter. A through hole of 5 mm in diameter was also drilled in the center of the specimen. The main chemical composition of the brick was 74.05 wt% Al₂O₃, 9.2 wt% C, 6.0 wt% SiC and 8.18 wt% SiO₂. The bulk density and apparent porosity of the brick was 2.98 g/cm³ and 10.9%, respectively.

Two slag samples were prepared by using reagent grade oxides of CaO, MgO, Al₂O₃, SiO₂, Cr₂O₃ and B₂O₃, all of which were dried in a desiccator at 105 °C for 12 h before use. The compositions of the slags were shown in Table 1. Then 125 g of reagent powders were weighed precisely according to the composition shown in Table 1 and mixed thoroughly in the agate mortar.

2.2. Experimental procedure

The experimental apparatus used to study the corrosion behavior of carbon composite brick can be seen in our previous paper [12]. The experimental conditions were presented in Table 2. During each experimental run, the slag sample contained in a molybdenum crucible (height 60 mm, diameter 39 mm) was heated to 1550 °C in the electrical furnace under an argon gas (99.999%, 2.0 L/min) atmosphere, and then held at 1550 °C for about 2 h to ensure the homogeneity of slag. Then the temperature was maintained at 1550 °C or decreased at a rate of 5 °C/min to the desired experimental temperature (1520 or 1480 °C). When the slag temperature reached the set value, the brick specimen mounted on a molybdenum rod with 5 mm in diameter was fully immersed into the melts and rotated at a desired speed (200, 150 or 50 rpm) for 30–120 min. After that, the specimen was lifted to the top of the crucible and rotated again to remove the slags attached to the brick surface. Then the brick specimen was taken out of the furnace and cooled down to room temperature in air. The diameter of the brick was measured by using a vernier caliper at different heights and the mean value was adopted as the final diameter. Then, the diameter decrement of the brick could be calculated by the difference between the original and final diameters.

The carbon composite brick after the experiment was cut longitudinally using a diamond saw, and then its cross section was molded, ground and polished for the analysis of scanning electron microscopy

Table 2
Experimental conditions.

Slag	Temperature (°C)	Rotation speed (rpm)	Immersion time (min)
No. 1	1550	200	120, 90, 60, 30
No. 1	1550	150	120, 90, 60, 30
No. 1	1550	50	120, 90, 60, 30
No. 1	1520	200	120, 90, 60, 30
No. 1	1480	200	120, 90, 60, 30
No.2	1550	200	120, 90, 60, 30

(SEM; FEI Quanta 250, USA) with energy dispersive spectroscopy (EDS). The surface phase composition of the brick after experiment was analyzed using X-ray diffraction (XRD; Ultima IV, Japan) in 2θ range from 10° to 90° (Cu Kα radiation, λ = 1.5406 Å).

3. Results and discussion

3.1. Kinetics analysis

The corrosion behavior of refractory by molten slag is very complicated. It could be controlled by the chemical reaction at the interface between slag and refractory or the diffusion through the slag boundary layer or the solid phase layer [13]. At high temperatures, the reaction rate is generally considered to be high. Therefore, the mass diffusion or transport maybe the rate controlling step [14,15]. In the case of mass diffusion controlling, the relationship between the radius decrement of cylindrical refractory and corrosion time was deduced as follows.

The radius decrement, which was expressed by x , was adopted to represent the corrosion degree of refractory. When x was enough small, area of different cylindrical surface in product layer could be considered as a constant. Then the dissolution weight of refractory into the slag per minute could be expressed as follows:

$$\frac{dG}{dt} = \frac{d(\rho Ax)}{dt} = \rho A \frac{dx}{dt} \quad (1)$$

where G is the dissolution weight of refractory (g), ρ is the bulk density of refractory (g/cm³), A is the surface area between refractory and slag (cm²), x is the radius decrement of refractory (cm) and t is the immersion time (min), respectively.

Assuming that mass diffusion in the product layer is the rate controlling step for the dissolution of refractory, the following equation could be established based on the mass balance of the refractory.

$$\rho A \frac{dx}{dt} = AD_{\text{eff}} \frac{C_s - C_n}{x} \quad (2)$$

where D_{eff} is the effective diffusion coefficient (cm²/s), C_s is the concentration of solute in the refractory (g/cm³) and C_n is the concentration of solute at the interface between slag and product layer (g/cm³), respectively.

Eq. (2) could be integrated to obtain Eq. (3):

$$x^2 = \frac{2D_{\text{eff}}(C_s - C_n)}{\rho} t \quad (3)$$

If defining

$$k_d = \frac{2D_{\text{eff}}(C_s - C_n)}{\rho} \quad (4)$$

Then, Eq. (3) could be expressed as follows:

$$x^2 = k_d t \quad (5)$$

Therefore, the square of the radius decrement of refractory changed linearly with the immersion time when the mass diffusion is the rate controlling step.

3.2. Influence of rotation speed on the corrosion of brick by slags

The square of radius decrement of the carbon composite brick by slag No.1 at 1550 °C as a function of immersion time at different rotation speeds was presented in Fig. 1. It can be found that the square of the radius decrement increased linearly with increasing the immersion time. Therefore, combining with the above theoretical analyses, it can be considered that the dissolution of the brick into slag may be controlled by the mass diffusion in the product layer which was formed due to the slag infiltration or reaction between slag and refractory. The calculated diffusion rate constant k_d at different rotation speeds was $2.438 \times 10^{-4} \text{ mm}^2/\text{min}$ (200 rpm), $1.851 \times 10^{-4} \text{ mm}^2/\text{min}$

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