Erosion of Carbon Brick by Zinc in Hearth of Blast Furnace

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The service life of a blast furnace (BF) is affected by the accumulation of zinc. To clarify the erosion mechanism of the carbon bricks, due to the zinc action, a dissection investigation of a commercial BF was carried out. The results show that the zinc content reaches up to 10.59% in the tuyere coke. The carbon bricks were sampled in a region characterized by high erosion levels and molten iron was detected. More interestingly, zinc was detected between the molten iron and the carbon bricks: the high zinc content of the bosh gas of the BF induces the zinc vapor to penetrate into the molten iron surface. The zinc vapor and the molten iron mix together, and zinc migrates from the molten iron into the carbon bricks. The thermodynamic behavior of zinc was analyzed and the volume expansion rate (56.94%) was calculated when Zn oxidizes into ZnO. The oxidation process may be the main reason behind the carbon brick erosion. The results show that molten zinc flows to the brittle layer of the carbon bricks, and finally solidifies, the carbon bricks become easy to break at the brittle layer. Countermeasures to reduce the harm of zinc have been suggested based on the zinc balance calculation.

KEY WORDS: blast furnace; hearth; zinc; carbon brick; erosion mechanism.

1. Introduction

Zinc usually exists in raw materials in the form of oxide (ZnO), ferrate ($\text{ZnO} \cdot \text{Fe}_2\text{O}_3$ in sinter), silicate ($2\text{ZnO} \cdot \text{SiO}_2$), or sulfide (ZnS). The boiling point of zinc is 1 180 K, and for this reason zinc-based raw materials are easy to be reduced into zinc vapor rising in the blast furnace (BF) gas. The cyclic accumulation of zinc in a BF occurs due to the oxidation of the zinc vapors at low temperatures and their transformation into raw materials.^{1–3)} Zinc vapor condenses into fine particles in the pores of the raw materials and this causes hanging in the BF. Willemite (Zn_2SiO_4) and zinc aluminate ($\text{ZnO} \cdot \text{Al}_2\text{O}_3$), which are considered as furnace accretions, are formed when zinc oxidizes on the surface of the lining.^{4–6)} Zinc atoms have a large particle weight and a small particle radius, which allow them to enter into the lining of the furnace at high temperatures and oxidize, resulting in the expansion of the lining. The zinc circulation induces heat transfer from high temperature zones to low temperature zones.⁷⁾

In recent years, molten zinc has been found between the small sleeve and the middle sleeve of the tuyere after its blowing-down. Moreover, the zinc expansion inside the tuyere's bricks leads to the upward-warp of the tuyere itself.^{8,9)} Molten zinc flows out from the grouting hole of

the BF hearth when the operator opens it, indicating that zinc is present there.^{10,11)} Moreover, the effect of zinc was observed in the hearth's carbon bricks in several dissection investigations.¹²⁾ Zinc vapors are expelled from the main trench of the molten iron and are accompanied by flames when tapping.¹³⁾ This process increases the fuel ratio and accelerates the erosion of the carbon bricks.^{14,15)} The effects of zinc contained in the BF hearth on the erosion mechanism of the carbon bricks should be investigated more systematically and countermeasures to reduce this process should be defined.

2. Dissection Investigation of the Blast Furnace

2.1. Heat Flux Intensity before the Shut Down Procedure

A commercial BF with an inner volume of 1 050 m³, 20 tuyeres, and two tapholes located in its south and north sides, was investigated. The BF was started in 2006 and shut down in 2017. The structure of its hearth is presented in **Fig. 1**. Its bottom part was lined with semi-graphite carbon bricks, microporous carbon bricks, and ceramic pads. The sidewall was lined with microporous carbon bricks and ceramic cups.

In October 2017, the BF blew-down due to its fluctuating conditions. The heat flux intensity of the cooling staves before the shut down procedure is presented in **Fig. 2**: the heat flux intensity increased rapidly during the blow-down

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Fig. 1. The structure of the commercial BF hearth. (Online version in color.)

Table 1. The sampling position and height.

Samples	Position	Height, m
Skull	14 section cooling stave	21.53
Skull	12 section cooling stave	20.24
Skull	Belly cooling stave	17.00
Skull	Bosh cooling stave	14.40
Coke	Tuyere	11.60
Slag-iron-coke	12 layer carbon brick	9.80
Slag-iron-coke	10 layer carbon brick	9.20
Slag-iron-coke	9 layer carbon brick	8.80
Slag-iron-coke	8 layer carbon brick	8.30
Slag-iron-coke	7 layer carbon brick	8.00
Slag-iron-coke	6 layer carbon brick	7.80

Fig. 2. The heat flux intensity of the cooling staves before shut down.

Fig. 3. The distribution of zinc in BF along the height. (Online version in color.)

process and the heat flux intensity of the cooling stave No. 12, No. 13, and No. 17 was close to 40 000 kJ/(m²·h) despite the furnace shell was sprinkled with water. The BF was shut down due to its high heat flux intensity. The dissection investigation was carried out after the shut-down procedure and its skulls, cokes, and carbon bricks were sampled.

2.2. Distribution of Zinc in the Blast Furnace

The skulls on the hot face of the cooling stave, the slag-iron-coke on the hot face of the carbon bricks, and the tuyere coke were sampled along the height of the BF. The locations of these samples are listed in Table 1. The chemical composition of the samples and the zinc distribution along the entire height of the BF were analyzed.

As shown in Fig. 3, a high zinc content in the skulls of the cooling stave was measured, due to the solidification process of the zinc vapors on the hot face of the cooling

stave and their gradual accumulation. The highest zinc content, which reached 10.59%, was found in the tuyere coke together with a large amount of zinc oxides found in previous studies.⁹⁾ Such high zinc content in the bosh gas seems to be responsible for the zinc vapor migration into the coke pores. In addition, the zinc accumulation in the coke would cause an increase in the CRI (Coke Reactivity Index) and a decrease of the CSR (Coke Strength after Reaction).^{16–18)} Zinc was also detected in the slag-iron-coke on the hot face of the carbon bricks, showing that the properties of the carbon bricks were modified.

2.3. Carbon Brick Sample in the Serious Erosion Region

A series of carbon bricks located in the 7th layer was sampled in the serious erosion region, as shown in Fig. 1. Their circumferential position corresponds to No. 13 cooling

stave, where the maximum heat flux intensity was measured before the shut-down. The residual thickness of the carbon bricks was lower than 100 mm (Fig. 4).

The hot face of the carbon bricks was observed via SEM (Scanning Electron Microscopy) and EDS (Energy Dispersive Spectrometry) (Fig. 5). The results show that molten iron was detected together with zinc located between the

Fig. 4. The carbon brick at serious erosion region. (Online version in color.)

molten iron and the carbon bricks. These observations may be explained via the mixing of the zinc vapor with the molten iron (Fig. 5(a)) and the migration of the zinc vapor from the molten iron into the carbon bricks. The interior of a carbon brick was observed via SEM and EDS (Fig. 6): the zinc vapor diffused along the pores into the interior of the carbon brick and then, migrated from the molten iron to the hot face of the carbon brick when the iron came into direct contact with it. The analysis of the EDS results shows that the iron content in zinc measured 6.26%, and that the zinc vapor diffused along the pores of the carbon brick under the effect of the pressure. The liquefaction of the zinc vapor occurred at a temperature lower than 1 180 K,¹⁹⁾ which induced the molten zinc to continue its migration into the inner part of the carbon brick. The compressive strength of the carbon brick decreased, due to the oxidation expansion of the molten zinc, which solidified in the interior of carbon brick when the temperature lowered to 692.5 K.²⁰⁾

3. Analysis of the Erosion Mechanism

3.1. Thermodynamic Behavior of Zinc

The reduction and the oxidation reactions of zinc include the reduction reactions of ZnO by CO, ZnO by C, ZnO by Fe, and the oxidation reaction of Zn by CO in the BF hearth.

These reduction and oxidation reactions inside the BF can be described respectively via the following expressions:

Fig. 5. The hot face of carbon brick observed by SEM and EDS. (Online version in color.)

Fig. 6. The interior of carbon brick observed by SEM and EDS. (Online version in color.)

In the actual hearth:

$$\Delta G = -238\,490 + 204.71T - 8.314T \ln a_{\text{Zn}} \frac{P_{\text{CO}}}{P^0} \text{ J/mol} \dots (5)$$

According to Eq. (5), when the partial pressures of Zn and CO measure 0.1 atm and 1 atm, respectively, the oxidation may occur below 1 119 K.

The Zn and ZnO crystal cell parameters were obtained by using Findit, which is a crystal structure database software. From the reaction (4), one can see that Zn transforms into ZnO after the reaction. Moreover, the Zn and ZnO crystal cell volumes are $30.42 \text{ \AA}^3$ and $47.74 \text{ \AA}^3$. The volume expansion rate of the oxidation of Zn into ZnO can be calculated via the following expression:

$$\frac{V_{\text{ZnO}} - V_{\text{Zn}}}{V_{\text{Zn}}} \times 100\% = 56.94\% \quad \text{..... (6)}$$

This value may be the cause behind erosion of the carbon bricks under the Zn action.

3.2. Theoretical Analysis of the Existence of Zinc in the Hearth

A relative high amount of zinc was found in the BF hearth: after the raw materials containing zinc are loaded into the BF through the throat and the reduction of ZnO into Zn takes place, Zn is transferred into zinc vapors in the bosh gas. The zinc vapor dissolves then into the molten iron. **Figure 7** shows the measured vapor-liquid equilibrium and the vapor pressure. In this work, a theoretical analysis to explain the presence of zinc in the BF hearth is provided. The bosh gas, which is generated by the reaction in the BF hearth is an important parameter to describe many phenomena that take place during the BF smelting process.^{21,22)} The bosh gas index of the BF is employed to replace the smelting intensity and to evaluate the production capacity of the BF itself.²³⁾ A high utilization coefficient inevitably leads to a high bosh gas volume. However, the zinc content in the gas is at its maximum level, due to the accumulation process. The zinc content index in the bosh gas was defined by Jiao *et al.* as follows:²⁴⁾

$$R = \frac{m_{bosh}}{m_{total}} \dots\dots\dots (7)$$

where R is the zinc content index of the bosh gas of BF; m_{bosh} is the zinc content in the bosh gas of BF, kg/t; m_{total} is the zinc load in the furnace expressed in kg/t.

The calculated value of the zinc content index of the bosh gas is 6.85, which indicates that the zinc content in the bosh gas is 6.85 times higher than the zinc load in the furnace. The zinc load of the BF dissection is 0.67 kg/t, implying that the zinc content measures 4.59 kg/t: this value is high enough to destroy the carbon bricks.

Zinc can be dissolved into molten iron, and this was confirmed by the small quantities of zinc detected in the molten iron in previous studies.^{25,26)} Henry's law explains the presence of zinc in the molten iron:²⁷⁾ the solubility of the zinc vapor is directly proportional to its equilibrium pressure on the molten iron surface. This can be expressed mathematically by the formula:

$$p_{(Zn)} = k_{\%Zn} [\%Zn] \dots\dots\dots (8)$$

where $p_{(Zn)}$ is the zinc vapor pressure in the bosh gas of the BF; $k_{\%Zn}$ is Henry's constant; $[\%Zn]$ is the mass percent of zinc in the molten iron.

As Eq. (8) shows, the zinc content in the molten iron increases upon the increase of the zinc vapor pressure.

Fig. 7. Zinc vapor in BF bosh dissolves into molten iron.

Moreover, the phase diagram of the Fe–Zn alloy shows that zinc is fully dissolved in the molten iron.

The Clausius-Clapeyron relation is employed to describe the trend of the saturated vapor pressure of zinc as a function of the temperature.

$$\lg P = -\frac{\Delta H}{RT} + C \dots\dots\dots (9)$$

Here, P is the saturated vapor pressure of zinc expressed in Pa, ΔH corresponds to the enthalpy change during the evaporation process, which is measured in kJ/mol, T is the phase equilibrium temperature measured in K, and C is a constant.

As shown in Eq. (9), the saturated vapor pressure of zinc increases with the increase of temperature. The higher the saturated vapor pressure is, the easier it is for zinc to volatilize from molten iron and contact with carbon bricks in BF hearth.

While, as shown in Fig. 6(b), the concentration of zinc is 93.74%. When the pressure decreases, zinc vapor forms via the evaporation of zinc from the molten iron. The vapor then migrates along the pores in the carbon bricks and when it reaches the end of the pores, it condenses into liquid and comes in contact with the carbon bricks, due to the decrease in temperature.

3.3. The Erosion Process of the Carbon Bricks by Zinc

The erosion process of carbon bricks due to the zinc presence is presented in Figs. 8(a)–8(h). Initially, due to the high blast pressure and the high zinc content in the bosh gas of the BF, the zinc vapor dissolves into molten iron on the liquid surface (Fig. 8(a)). Successively, zinc migrates continuously from the liquid surface into the molten iron below the central line of the taphole under the action of a concentration gradient (Fig. 8(b)). In the regions which present a high erosion level, the molten iron comes into contact with the carbon bricks directly (Fig. 8(c)), and its temperature decreases, due to the cooling effect of the cooling surface. The zinc saturation vapor pressure in the tuyere area is high under the action of high blast pressures and high temperatures. When the zinc saturation vapor pressure decreases rapidly, due to the temperature gradient inside the carbon bricks, zinc evaporates from the molten iron onto the hot face of the carbon bricks forming zinc vapors (Fig.

Fig. 8. The erosion process of carbon brick by zinc. (Online version in color.)

8(d)). Then, the zinc vapors migrate towards the interior of the carbon bricks along the pores (Fig. 8(e)) and their temperature decreases, due to the temperature gradient inside the carbon bricks. When the zinc vapors reach the end of the pores, they condense into liquid and come in contact with the carbon bricks, due to their decrease in temperature (Fig. 8(f)). As shown in Fig. 8(g), the zinc vapor liquefies and oxidizes in the pores and the cracks, while a volume expansion occurs, due to the oxidation reaction. The calculated volume expansion rate measures 56.94%, which implies that the pores of the carbon bricks increased in size and that the strength of the carbon bricks was reduced. The molten iron penetrates inside the pores of the carbon bricks after their expansion, the dissolution of the carbon bricks occurs, and then the erosion of the carbon brick accelerates due to the presence of undersaturated carbon in the molten iron.^{28,29)} The molten zinc flows then to the brittle layer of the carbon bricks and finally, solidifies in the brittle layer (Fig. 8(h)). The carbon bricks can easily break along the brittle layer.

4. Reducing the Harm of Zinc in the BF Hearth

4.1. Calculation of the Zinc Balance

The zinc load of a commercial BF was calculated in **Table 2** according to the mass and the zinc content of various raw materials. The calculated values of the zinc discharge are listed in **Table 3**, according to the mass and the zinc content of various products. The zinc balance in a commercial BF is presented in **Fig. 9**. The highest amount of zinc is introduced in the system via the sinter and it accounts for the 69.4% of the total zinc load, followed by the pellet, which accounts for the 23.86%. Most zinc (71.41% of the

total zinc discharge) is carried out by the bag dust, followed by the gravity dust, which accounts for the 17.47%.

4.2. Countermeasures

4.2.1. Optimization of the Sintering Process

It is essential to control the zinc effect inside the root of the BF, since the sintering process is the main source of zinc and the use of materials with an elevated zinc content, such as bag dust, lead to a high zinc level in the sinter. The zinc content of the raw materials should be strictly controlled when choosing them to avoid zinc levels higher than 0.02% in the sinter.

4.2.2. Zinc Discharge

The zinc present in the slag can be discharged by improving its discharge capacity in the tap cinder. Moreover, the temperature and the basicity of the slag must be controlled in a reasonable range.

4.2.3. Optimization for the BF Operation

A reasonable distribution of the BF gas must be ensured by adjusting its upper and lower levels to stabilize the furnace conditions. While the zinc vapor can be eliminated by properly raising the temperature of the furnace, the accretion can be removed by washing the furnace. Moreover, the continuous activity of the hearth must be ensured to guarantee the heat reserve in the hearth.

4.2.4. Zinc Balance Monitoring

The zinc balance after a fixed period of time and a set of targeted measurements, which monitor the zinc content index of the bosh gas of the BF, should be obtained to con-

Table 2. The zinc load of the commercial BF.

Raw materials	Mass, kg/tHM	$\omega(\text{Zn})$, %	Zinc, kg/tHM
Sinter	1 248.1	0.0371	0.4630
Pellet	269.8	0.0590	0.1592
Lump	127.8	0.0090	0.0115
Coke	357.2	0.0047	0.0168
Coal	140.6	0.0118	0.0166
Total	2 143.5	–	0.6671

Table 3. The zinc discharge of the commercial BF.

Products	Mass, kg/tHM	$\omega(\text{Zn})$, %	Zinc, kg/tHM
Fly dust	1.710	0.5622	0.010
Bag dust	3.745	12.3414	0.462
Gravity dust	8.695	1.2993	0.113
Slag	313.350	0.0134	0.042
Molten iron	1 000	0.002	0.020
Total	1 327.5	–	0.647

Fig. 9. Zinc balance of the commercial BF. (Online version in color.)

trol the zinc accumulation.

4.2.5. Comprehensive Utilization

The dust and mud produced during the iron-making and steel-making production processes contain a large amount of zinc.^{30,31)} When these two components are mixed together in the sintering process an increase in the zinc load of the BF has to be expected. Therefore, techniques which make use of dust and mud containing iron, such as rotary kiln, rotary hearth furnace, shaft furnace, gravity separation, magnetic separation, and flotation, improve the utilization rate of these compounds and reduce the zinc load of the BF.

5. Conclusions

In order to clarify the erosion mechanism of carbon bricks due to the zinc action in the hearth of a BF, a dissection investigation of a commercial BF was carried out. The distribution of zinc along the height of the BF was obtained, the carbon bricks present in regions subject to high erosion were sampled, and their hot face and interior were observed via SEM and EDS. The results of these observations are:

(1) The zinc content in the tuyere coke (0.59%) is the highest measured along the height of the entire BF; the zinc load of the BF dissection is 0.67 kg/t and the zinc content in the dissection bosh gas is 4.59 kg/t due to the cyclic accumulation of zinc, which is high enough to destroy the carbon bricks.

(2) Zinc was detected between the molten iron and the carbon bricks: the high blast pressure and the high zinc content in the bosh gas of the BF caused the zinc vapor to dissolve into the molten iron surface. The zinc vapor and the molten iron mixed together and zinc vapor migrated into the carbon bricks.

(3) The erosion process of the carbon bricks due to the zinc action was explained: the calculated volume expansion rate measures 56.94% when Zn oxidizes into ZnO. This oxidation process may constitute the main cause at the basis of the erosion of the carbon bricks. Countermeasures to reduce the damages induced by zinc were suggested based on the zinc balance calculations.

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