Effects of alkalis and zinc on the damage of the tuyere composite brick of a blast furnace

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Abstract. The distribution of foreign elements and its true mineral forms in the tuyere composite brick extracted from a 2800 m³ industrial blast furnace were examined to gain a better understanding of the damage mechanism of the brick. The X-ray diffraction (XRD) and the scanning electron microscopy-energy dispersive spectroscopy (SEM-EDS) were applied to characterize the brick. The results show that the potassium is easier to permeate into the brick than zinc. The potassium is prone to react with Al-Si compounds in the brick to form kalsilite or leucite while the zinc is apt to react with the corundum in the brick to produce zinc-aluminum spinel. In addition, the zinc can interact with the blast furnace gas to form zinc oxide and zinc sulfide filled in the cracks of the brick. The mineral phases of the residual brick change from the original corundum and mullite to corundum, gahnite, zincite, sphalerite, kalsilite and leucite. The main cause of the damage of the brick is found to be potassium and zinc attack. In the case of degradation of the raw materials, it can choose the micro corundum brick instead of the corundum-mullite or mullite brick to prolong the life of the tuyere composite brick.

1. Introduction
Silicon-aluminum composite refractory is one of the refractories used in blast furnace. The composite brick arranged around the tuyere is in such harsh environment (high temperature, multiphase coexistence and so on) that its damage is inevitable in a working blast furnace [1-4]. With the deterioration of the raw materials as well as the application of the high blast temperature and pulverized coal injection technology [5,6], the significant damage of the tuyere composite brick is found [4]. Therefore, it is necessary to figure out the damage mechanism to develop and choose proper tuyere composite brick. Previous researches [1-2,7] on tuyere composite brick mostly focused on composition analysis of the residual bricks. However, limited studies have considered inorganic elements in their true mineral forms rather than in oxides or element forms. Besides, previous studies [1,4,7] usually focused on the properties of the tuyere composite brick affected by potassium and zinc separately, while potassium and zinc simultaneously influence the performance of tuyere composite brick in the actual production of the blast furnace. Although researchers have studied the effect of potassium on Al-Si bricks, the studied environment is different from the environment of blast furnace near the tuyere zone [8-12]. Accordingly, in order to prolong the life of the tuyere composite brick, it is necessary to identify its real phases of the residual brick and make clear the actual behavior simultaneously degraded by potassium and zinc vapors.
In this paper, the microstructure of tuyere composite brick and its composition as well as mineral phases were investigated in detail with samples obtained from a 2800 m³ blast furnace during its overhaul. In addition, the formation process of the foreign phases in the tuyere composite brick was investigated thermodynamically. Finally, the damage mechanism of the tuyere composite brick was analyzed.

2. Samples and methods

2.1. Introduction of blast furnace and the sampling position

In the present study, the samples were obtained from an industrial blast furnace with an inner volume of 2800 m³, 30 tuyeres and 3 tap holes. The relevant parameters are listed in the previous paper [13]. After the blow-out and cool-down of the furnace, some tuyere composite brick samples collected manually. The tuyere composite brick installed around the tuyeres was the corundum-mullite brick. It was comprised of Al₂O₃ (87.72%), SiO₂ (11.03%) and Fe₂O₃ (0.35%). In this paper, the neighboring part of hot surface, the vicinity part of macroscopic crack and the inside part of tuyere composite brick around No. 6 tuyere at layer 2 were studied, and the sampling positions were shown in the figure 1.

![Figure 1](image1.png)

**Figure 1.** The schematic diagram of the sampling positions. (a) Sampling position in the blast furnace; (b) Sampling position in the residual brick.

2.2. Analysis methods and sample preparation

The samples were prepared, ground and polished similar to the previous study [13]. Then the samples were examined with a Zeiss Evo18 Special Edition SEM-EDS. In order to identify the mineral phases of the residual brick, the samples obtained from different positions were crushed to passing less than 74um and then examined using a Rigaku diffractometer (DMAX-RB 12 kW; Rigaku Corporation, Tokyo, Japan) using Cu Ka as radiation. During this analysis, samples were scanned with 20 in the range of 10 to 90 deg at a scan rate of 5 deg/minute.

3. Results and discussion

3.1. The composition and microstructure analysis of the hot surface of the tuyere composite brick

The composition and microstructure of the hot surface of the brick is presented in figure 2. The residual brick is composed of corundum particles (black phases in figure 2(a)), potassium aluminosilicates (grey phases in figure 2(a)), oxide and sulfide of zinc (white phases in figure 2(a)). In the neighboring part of the hot surface of residual brick, various foreign elements (K, Zn and S) penetrated into the brick as shown in figure 2(b). A great deal of zinc was primarily observed in the hot surface and the internal cracks, while the potassium is mainly distributed with Al and Si inside the brick. It is indicated that the permeation ability of potassium into the brick is stronger than that of zinc, which is in agreement with previous studies [7]. A layer of oxide and sulfide of zinc with a thickness
of about 2 mm (figure 2(a)) is observed in the hot surface. Thus, the liquid slag and hot metal are prevented from penetrating into the tuyere composite brick. From this perspective, the layer of foreign elements is contribution to the protection of the brick to some extent.

![Image](image1.png)

**Figure 2.** Composition and microstructure of the hot surface of the tuyere composite brick. (a) SEM micrograph; (b) EDS maps showing the distribution of Si, Al, K, S, Zn and O in residual brick.

The micro and macro cracks in the vicinity part of hot surface of brick were presented in figure 3. The residual brick was cut along the vertical direction of the hot surface and its profile is shown in figure 3(b). The residual brick cracked with numerous laminations in parallel with the hot surface of the brick. Part of the cracks pass through the brick, as shown in figures 3(a) and 3(b). The micro and macro cracks decrease the strength of the brick and are very detrimental to the life of the brick. The maximum crack width of the residual brick is about 3 mm. Some cracks are completely filled with foreign matters while the others are only partially filled, indicating that the foreign matters in the cracks is gradually accumulated. The cracks provide a special channel for the harmful elements into the brick. The thermal conductivity of the corundum-mullite brick (3.2 W/(m•K) [3]) is about 128 times that of gas (0.025 W/(m•K)). That is to say, the thermal resistance of air gap with a 3 mm thickness is equivalent to that of a brick with a thickness of 384 mm. Therefore, the cracks filled with gas are bad to the heat transfer of the brick. Besides, non-uniform distribution of the cracks cause uneven thermal stress distribution of the bricks. It may leads to the emergence of the new cracks and damage to the brick.

![Image](image2.png)

**Figure 3.** The micro cracks and macro cracks in hot surfaces of tuyere composite brick. (a) SEM micrograph; (b) Macro picture.

The XRD spectra of the brick at different positions is shown in figure 4. The original brick is composed of corundum and mullite, which is in accordance with the previous studies [14-16]. The absence of mullite peak in the diffraction pattern of the tuyere composite brick was confirmed, while
the mineralogical phases in the neighboring part of hot surface of the brick were determined to be zincite (ZnO), sphalerite (ZnS), gahnite (ZnAl₂O₄), kalsilite (KAlSiO₄) and corundum (Al₂O₃), as shown in figure 4. Thus, foreign elements in the brick were proved to be mainly alkalis and zinc. With the exception of the corundum, the other phases are absent from original brick, indicating that mullite in the original brick is easy to interact with potassium to form kalsilite and the corundum can react with zinc to form zinc-aluminum spinel. Also, the blast furnace gas permeating the composite brick can interact with zinc to form ZnO and ZnS concentrated on the brick cracks or pores. Previous studies have shown that the transformation from zinc to zinc oxide, from zinc to zinc sulfide, from zinc to gahnite and from potassium to kalsilite is accompanied by a volume expansion of about 54% [7], 83% [7], 15% [17] and 36% [18], respectively, which may lead to the generation of new cracks and deteriorate the brick.

Figure 4. XRD spectra of the different positions of the tuyere composite brick. T-Inner: the sample in the internal brick; T-Crack: the sample near the crack; T-Hot: the sample of hot surface of residual brick.

Figure 5. The composition and microstructure of hot surface of the tuyere composite brick. (a) SEM micrograph; (b) EDS maps showing the distribution of Si, Al, K, S, Zn and O.

Figure 5 shows the composition and microstructure of the internal cracks in the tuyere composite
bricks near the hot surface. The tuyere composite brick can be divided into four different layers along the arrow direction: kalsilite layer (Layer 1 in the figure 5), ZnO-ZnS layer (Layer 2 in the figure 5), gahnite layer (Layer 3 in the figure 5) and corundum layer (Layer 4 in the figure 5). The potassium is not found in corundum layer while the potassium content is high in the place where Al and Si coexist in the original brick. It can be seen that potassium is apt to react with the Al-Si compounds of the original composite brick to form kalsilite or leucite with about 15-36% [18] volume expansion. Volume expansion or uneven thermal stress leads to the new cracks. Subsequently, zinc permeates into the brick along the cracks and reacts with the corundum particles at the edge of the crack to form the zinc-aluminum spinel, which is accompanied by a volume expansion of about 15% [17]. When the Zn-Al spinel accumulates to a certain extent, zinc can not contact with corundum particles, begin to react with the permeated blast furnace gas to form ZnO-ZnS and accumulates in the crack until the entire crack is filled.

3.2. The composition and microstructure analysis of the tuyere composite brick near the macro crack

The composition and microstructure of the residual brick near macro crack presents in figures 6 and 7. Figure 7 is the magnification photo of a partial region of figure 6. The ZnO-ZnS layer with a thickness of about 40 microns was observed at the crack edge. Therefore, zinc permeates the composite brick along the pores and micro cracks, and accumulates continuously in the form of oxides and sulfides. When a certain thickness is reached, the micro cracks are expanded into the macro cracks which is visible to the naked eye. The mineral phases near the macro cracks of the brick were confirmed to be zincite (ZnO), sphalerite (ZnS), gahnite (ZnAl2O4), kalsilite (KAlSiO4) and corundum (Al2O3), as shown in figure 4. From the figure 7, we can see that the brick can be divided into five different layers: kalsilite layers, ZnO layers, ZnS layers, gahnite layers and corundum layers. It is similar to the results of the brick near the hot surface (figure 5).

Figure 6. The composition and microstructure of the tuyere composite brick near macro crack. (a) Macro picture; (b) SEM micrograph; (c) EDS maps showing the distribution of Si, Al, K, S, Zn and O in residual brick.
3.3. The damage mechanism of the tuyere composite brick

As can be seen from figure 4, the minerals inside the brick were confirmed to be zincite (ZnO), sphalerite (ZnS), gahnite (ZnAl₂O₄), kalsilite (KAISiO₄), leucite (KAISi₂O₆) and corundum (Al₂O₃). The main reactions between zinc or potassium and the composite brick components are as follows:

\[
2K + CO + 2\left[3Al₂O₃ \cdot 2SiO₂\right] = K₂O \cdot Al₂O₃ \cdot 4SiO₂ + 5Al₂O₃ + C
\]  
(1)

\[
2K + CO + 3Al₂O₃ \cdot 2SiO₂ = K₂O \cdot Al₂O₃ \cdot 2SiO₂ + 2Al₂O₃ + C
\]  
(2)

\[
2K + CO + Al₂O₃ = K₂O \cdot Al₂O₃ + C
\]  
(3)

\[
Zn + CO + 1/3\left[3Al₂O₃ \cdot 2SiO₂\right] = ZnO \cdot Al₂O₃ + 2/3SiO₂ + C
\]  
(4)

\[
Zn + CO + Al₂O₃ = ZnO \cdot Al₂O₃ + C
\]  
(5)

\[
Zn + CO = ZnO + C
\]  
(6)

Figure 7. The composition and microstructure of tuyere composite brick near macro crack. (a) SEM micrograph; (b) EDS maps showing the distribution of Si, Al, K, S, Zn and O.

Figure 8. The relationship between Gibbs free energy and temperature in the standard state.
The Gibbs free energy of each reaction is calculated using FactSage 7.1 thermodynamic software [19], as shown in figure 8. The Gibbs free energy of the reactions (1) - (3) is always negative at temperatures below 1600°C, and the Gibbs free energy of the generation of kalsilite and leucite is smaller than that of the other reactions at the same temperature. Therefore, potassium is easier to react with mullite in the brick to produce kalsilite or leucite. This is consistent with the previous SEM-EDS analysis. When the temperature is below 1050°C, the free Gibbs energy of reaction (4) and (5) is always negative while the Gibbs free energy of reaction (6) is always negative when the temperature is lower than 950°C. The Gibbs free energy of reaction (5) is less than that of reaction (4) at the temperature range from 900 to 1050°C. As potassium more easily penetrates into the tuyere composite brick than zinc and is apt to react with mullite, the infiltrated zinc primarily reacts with corundum in the brick to generate zinc-aluminum spinel. The Gibbs free energy of the reactions (4) and (5) is always smaller than that of the reaction (6) at the same temperature, indicating that zinc prefers to react with corundum in the tuyere composite brick. When the reaction product (zinc-aluminum spinel) accumulates to a certain extent, zinc begins to react with the permeated blast furnace gas to generate ZnO and ZnS filled in the cracks and the open pores in brick.

Potassium, zinc and blast furnace gas penetrate into the brick as the gaseous phase through the pore and crack, and they react with the brick or each other. Based upon the results of the SEM-EDS and thermodynamics analysis, potassium is apt to react with Al-Si compounds in the composite brick to form kalsilite or leucite while zinc prefers to react with corundum to form zinc alumina spinel. The formation of the new phases results in volume expansion and new cracks. When the thickness of the new phases reaches a certain extent, the contact reaction between the alkali metal, zinc and the self-components of the tuyere composite brick will be hindered. Then, the CO and S in the gas react with zinc vapor to form high melting point ZnO and ZnS, and accumulate in the pores or cracks eventually filling the pores or cracks. At last, there will be some distinct layers in the brick, namely, kalsilite layer, ZnO layer, ZnS layer, gahnite layer and corundum layer. The expansion coefficient of different layers is different. When the furnace condition fluctuates (such as the edge gas flow becomes stronger), the non-uniform volume expansion between the foreign matters filled in the cracks or pores and the brick can lead to the generation of new cracks, which in turn loops over the above destruction process. The long-term accumulation eventually causes macro cracks. The fluctuations of the gas and liquid slag and iron will make the brick peel off along the macro cracks layer by layer.

4. Conclusions

- The main cause of the damage of the tuyere composite brick is found to be alkalis and zinc attack due to penetration of alkalis and zinc vapor through the pore or crack.
- Potassium is easier to permeate into the composite brick than zinc. Potassium is easy to react with Al-Si to form kalsilite or leucite while zinc is apt to react with the corundum in the composite brick to produce zinc-aluminum spinel. In addition, zinc can react with the blast furnace gas and the products are filled in the cracks of the composite brick.
- After more than nine years’ use of the tuyere composite brick, the mineral phase of the residual tuyere composite brick changed from the original corundum, mullite and glass phase to zincite (ZnO), sphalerite (ZnS), gahnite (ZnAl2O4), kalsilite (KAlSiO4), leucite (KAlSi2O6) and corundum (Al2O3).
- In the case of degradation of the raw materials, it can choose the micro corundum brick instead of the corundum-mullite or mullite brick to prolong the life of the tuyere composite brick.

Acknowledgment
This project was supported by the National Key R & D Program of China (2017YFB0304300 & 2017YFB0304302).
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