Corrosion resistance mechanism of postmortem corundum-mullite refractories used in hot stoves

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ABSTRACT
Alkali attack of aluminosilicate refractories has been a long-term problem in the industry. In this paper, XRD, SEM, and CT scanning methods were used to analyze the phase and structure characteristics of postmortem corundum-mullite refractory used in hot stoves for more than 10 years, and the anti-corrosion mechanism of the refractory was explored. Results show that the corundum-mullite refractory after long-term corrosion by hot stove gas maintains excellent physical properties, and its cold compressive strength can still reach 92.7 MPa. The mullite network formed by the interpenetration of short columnar mullite endows the corundum-mullite refractory with excellent resistance to gas corrosion: Under the working conditions of the hot stoves, mullite network plays a role in dispersing impurities in refractory, so that the CaO entrained in hot stove gas can be transformed into high melting point CAS$_2$ instead of low melting point phase with high Ca content in the working layer of refractory; CAS$_2$ has good resistance to alkaline gases such as K$_2$O(g) and Na$_2$O(g), and the blocking of pores in the working layer of refractory by CAS$_2$ finally makes the refractory free from the corrosion of hot stove gas.

1. Introduction

It is significant for realizing the long service of the entire ironmaking system to extend the service life of hot stove. According to the expected generation of hot stoves to match two generations of blast furnaces, the service life of hotstoves needs to reach more than 30–40 years, while the average service life of current hot stoves is only more than 10 years, which is far from expected.

At present, only silica bricks and aluminum-silicon-based low-swell bricks can keep long service life under the cruel working conditions of hot stoves. For aluminum-silicon refractories, corundum-mullite refractories with mullite as the main crystal phase exhibit excellent performance due to the bridging and pinning effects of short columnar mullite [1–4]. The mullite phase in corundum-mullite refractories is generally introduced in two ways: pre-synthesized and in-situ reaction of aluminosilica minerals, such as andalusite, kyanite, and mullite [5–9]. Studies of the mullitization of aluminosilica minerals show that trace impurities in minerals can reduce the formation temperature of mullite by forming a liquid phase at high temperatures, and the mullitization temperatures of andalusite, kyanite, and sillimanite are 1200–1450°C [10], 1100°C [11,12] and 1550–1600°C [13], respectively. At the same time, the impurities introduced by alumina-silicon minerals have a series of impact on the performance of the refractory, especially corrosion resistance.

When the corundum-mullite refractory is used as the working lining of the hot stove, it only comes into contact with gas, not with molten metal or slag. To date, the effects of H$_2$, steam, and CO vapor on the microstructure, crystal compositions, and physical properties of mullite-based refractories have been investigated [14–19]: The silica in mullite is preferentially corroded by H$_2$, resulting in a porous alumina-rich surface; In high-temperature steam, the water vapor corrosion of silica component in mullite can be accelerated by a small amount of sodium, which leads to its decomposition into alumina phase; With respect to the CO(g) atmosphere, the primary cause of material damage at high temperature arises from the catalytic decomposition of mullite by CO(g), and the impurities accelerating generation of the liquid phase in Al$_2$O$_3$-SiO$_2$ system significantly affect the stability of mullite in a CO(g) atmosphere. The reported reaction between mullite and CO(g) is given by Eq. 1 [20,21].

\[
3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2(s) + 2\text{CO}(g) \rightarrow 3\text{Al}_2\text{O}_3(s) + 2\text{SiO}(g) + 2\text{CO}_2(g)
\]  

(1)

The main factor affecting the service life of the corundum-mullite refractory for hot stove is the alkali attack of aluminosilicate refractory [22,23]. It is worth mentioning that although studies have shown that mullite will decompose into low melting point silicate phase under the action of alkali gas [24–27], corundum-mullite
refractories can still be used in high-temperature furnaces for more than 10 years. Therefore, it is necessary to investigate the corrosion resistance of corundum-mullite refractories for hot stove. This paper explores the phase and structure characteristics of the postmortem corundum-mullite refractory used in hot stoves for more than 10 years, and the anti-corrosion mechanism is also analyzed.

2. Materials and methods

The postmortem corundum-mullite refractories were taken from the regenerator cone of the hot stove which had been working for more than 10 years. The raw material composition of corundum-mullite refractories shows in Table 1. The main composition and content of hot stove dust shows in Table 2.

The phase composition of the samples were identified by X-ray diffraction (XRD, PANalytical X’Pert Powder diffractometer, Holland) using Cu Kα radiation (λ = 1.5406 Å). The microstructure was observed using a scanning electron microscope (SEM) (Quanta FEG450, FEI) equipped with an energy-dispersive spectroscope (EDS) to analyze the elemental composition in specific areas. The pore distribution was measured according to YB/T 118–2020. Industrial CT (FF35 X-CT, YXLON) was used to perform X-ray tomography on the used corundum-mullite refractory to construct a three-dimensional model of the sample.

3. Results and discussion

3.1. Physical properties of postmortem corundum-mullite refractory

In the hot stove with a total height of 52 m, the position of low creep high alumina brick is about 25–30 m. Refractories built above low creep high alumina bricks include silica wall bricks, silica lattice bricks and silica vault bricks (Figure 1). The masonry height of H22 low creep high alumina brick in the hot stove is about 28 m. After calculation, the load it can bear in the stove can reach 0.39 MPa.

Despite the extremely cruel working conditions, the postmortem corundum-mullite refractories not only maintain low impurity content and high strength retention rate, but also have better high-temperature volume stability than the original. It is mainly reflected in the smaller permanent change in dimension on heating and creep rate of postmortem bricks than the original bricks. The chemical composition, physical properties and creep rate performance (0.2 MPa) of corundum-mullite refractories before and after used are shown in Table 3, Table 4 and Figure 2.

3.2. Phase composition of postmortem corundum-mullite refractory

Figure 3 shows the XRD pattern of working layer and interior of the postmortem corundum-mullite refractory (10 cm from the working layer). It can be seen that the interior of the brick includes corundum (Al2O3), Reference pattern: 01–088-0826, mullite (Al4.68Si1.32 O9.66, Reference pattern: 96–900-5503) and trace sillimanite (Al2SiO5, Reference pattern: 01–083-1562); In addition, calcium aluminosilicate (CAS) (NaAlO2CaO55 Al1.35Si2.45O16, Reference pattern: 01–078-0433) due to the corrosion of high-temperature flue gases in hot stove is also detected in the working layer.

Figure 4 shows the SEM views of the unused corundum-mullite refractory. Figure 5 and Figure 6 show the SEM views of working layer and interior of the postmortem corundum-mullite refractory. EDS results of the selected area in the figures are shown in Table 5. Combining the SEM with EDS results, it can be seen that compared with the original brick, the postmortem brick shows a better sintering degree, which is considered to be the result of ion diffusion during long-term use, because Fe, Ca, Mg elements are not detected in the mullite crystals in the both interior or working layer of the postmortem brick; The impurities in the hot

Table 1. Raw material composition of corundum-mullite refractories (wt %).

| Raw materials | Sintered corundum | Sillima-nite | Sintered mullite |
|---------------|------------------|-------------|-----------------|
| Content       | 33               | 10          | 26              |

Table 2. Main composition and content of hot stove dust (wt %).

| Composition | S | Zn | SiO2 | Al2O3 | TFe | CaO | MgO | Na2O | K2O |
|-------------|---|----|------|-------|-----|-----|-----|------|-----|
| Content     | 2.88 | 5.11 | 14.65 | 4.79 | 46.71 | 9.75 | 1.43 | 1.89 | 12.79 |

Table 3. Chemical composition of original brick and postmortem brick (wt %).

| Samples                  | SiO2 | Al2O3 | Fe2O3 | CaO | MgO | TiO2 | K2O | Na2O | C   |
|--------------------------|------|-------|-------|-----|-----|------|-----|------|-----|
| Unused brick             | 16.04 | 82.90 | 0.26  | 0.01 | 0.06 | 0.24 | 0.22 | 0.27 |     |
| Interior of postmortem   | 15.71 | 82.99 | 0.40  | 0.13 | 0.03 | 0.26 | 0.15 | 0.17 | 0.16 |
| Working layer of postmortem brick | 16.19 | 82.07 | 0.70  | 0.22 | 0.05 | 0.13 | 0.26 | 0.19 | 0.19 |
3.3. Corrosion resistance mechanism of corundum-mullite refractory for hot stove

The working temperature of the corundum-mullite refractory taken from the cone of the regenerator is about 1500°C. Although the temperature does not reach the ideal thermodynamic conditions for the formation of mullite, the extremely long use time provides sufficient kinetic conditions. At this condition, mullite can be formed in the refractory through the following reaction: Mullite formed by diffusion and solid solution between mullite and corundum; Mullite formed by mulliteization of sillimanite (Reaction 2); Mullite formed by the reaction of SiO$_2$ and Al$_2$O$_3$ (Reaction 3); Mullite formed by the reaction of SiO(g) and corundum particles, in which SiO(g) comes from the deoxidation of SiO$_2$ under reducing atmosphere (Reaction 4). The continuous formation of mullite in the refractory enables it to form a continuous and uniform mullite network in the refractory through mutual insertion, which is the main structural feature of the corundum-mullite refractory.

\[
3(\text{Al}_2\text{O}_3 \cdot \text{SiO}_2)(s) = 3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2(s) + \text{SiO}_2(s) \quad (2)
\]

\[
3\text{Al}_2\text{O}_3(s) + 2\text{SiO}_2(s) = 3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2(s) \quad (3)
\]

\[
2\text{SiO(g)} + \text{O}_2(g) + 3\text{Al}_2\text{O}_3(s) = 3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2(s) \quad (4)
\]
The XRD and SEM results show that a large amount of calcium aluminosilicate phase (CAS₂) are enriched in the working layer of the postmortem refractory. CAS₂ has good alkali corrosion resistance, and its filling in the pores of the working layer effectively improves the corrosion resistance of the refractory. Figure 9 shows the CaO-Al₂O₃-SiO₂ ternary-phase diagram. It can be seen that when the corundum-mullite refractory is corroded by the hot stove flue gas, the CaO in the flue gas adheres to the surface of the mullite, causing its micro-domain composition to shift toward the direction of the line connecting A₃S₂ and CaO. When the content of CaO in the micro area is less, the composition is within ΔA₃S₂-CAS₂-A, and the formation temperature of the liquid phase in the area is 1512°C (Reaction 5). If the CaO content increases, the composition of the micro area will leave ΔA₃S₂-CAS₂-A and enter ΔCA₆-CAS₂-A and ΔCA₆-CAS₂-C₃AS in turn, and the formation temperature of the liquid phase will also decrease to 1495°C and 1380°C. The XRD results show that no CA₆ or C₃AS is detected in the working layer of the postmortem corundum-mullite refractory, so it is believed that there is no CaO aggregation in the working layer during long-term use of the refractory.

\[
\text{L(l)} + \text{Al}_2\text{O}_3(s) \rightleftharpoons 3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2(s) + \text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2(s)
\]  

(5)
Figure 4. SEM views of unused corundum-mullite refractory.

Figure 5. SEM views of the interior of postmortem corundum-mullite refractory.

Figure 6. SEM views of the working layer of postmortem corundum-mullite refractory (a, b: Longitudinal section, c, d: Surface).
Mullite will decompose under the action of Na₂O(g) and K₂O(g) in the flue gas of hot stove. Fig. 10 shows the phase diagrams of K₂O-Al₂O₃-SiO₂ and Na₂O-Al₂O₃-SiO₂. It can be seen that pure alumina has good corrosion resistance to Na₂O and K₂O, and it can be transformed into β-alumina (NaAlO₁·7 and KAlO₁·7) instead of liquid phase with the solid solution of Na₂O and K₂O; compared with the pure corundum, the Al₂O₃-SiO₂ system is much more complicated, and the Na₂O-Al₂O₃·SiO₂ and K₂O-Al₂O₃·SiO₂ ternary systems contain various compounds such as Na₂O-Al₂O₃·6SiO₂ (NAS₆) (~1104°C), Na₂O-Al₂O₃·2SiO₂ (NAS₂), K₂O-Al₂O₃·6SiO₂ (KAS₆) (It decomposes into KAS₄ and L at 1140°C), K₂O-Al₂O₃·4SiO₂ (KAS₄) (~1686°C), K₂O-Al₂O₃·2SiO₂ (KAS₂) (~1800°C) and K₂O-Al₂O₃·SiO₂ (KAS).

The equilibrium-phase regions of Na₂O-Al₂O₃·SiO₂ and K₂O-Al₂O₃·SiO₂ ternary systems at 1500°C are plotted in Fig. 10, and the equilibrium phases are shown in Table 6. It can be seen that KAS₆ and NAS₆ will be formed first when Na₂O and K₂O are introduced into the Al₂O₃·SiO₂ system, and the formation temperature of the liquid phase in the system will be lowered to...
and 1104°C, respectively. If the content of Na₂O and K₂O in the system is further increased, the mullite phase will disappear, which is inconsistent with the actual results. Therefore, KAS₆ and NAS₆ are considered to be the reaction products of Na₂O(g) and K₂O(g) with corundum-mullite refractories under the working conditions of hot stove (Reactions 6 and 7), and the equilibrium phases after corrosion are A₃S₂, α-Al₂O₃ and a liquid phase composed of Na₂O-K₂O-Al₂O₃-SiO₂.

\[
\text{Na}_2\text{O(g)} + 3(3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2)(s) = \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2(l) + 8\text{Al}_2\text{O}_3(s) \tag{6}
\]

\[
\text{K}_2\text{O(g)} + 3(3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2)(s) = \text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2(l) + 8\text{Al}_2\text{O}_3(s) \tag{7}
\]

At the same time, Na₂O(g) and K₂O(g) can also directly enter the liquid phase formed by impurities in the refractory at high temperature, thereby causing damage to the refractory by reducing the viscosity of the liquid phase and expanding the amount of the liquid phase. However, the analysis results of the
postmortem corundum-mullite refractory show that Na$_2$O(g) and K$_2$O(g) do not corrode the refractory deeply despite the existence of various corrosion pathways, such as decomposing mullite and increasing the amount of liquid phase.

Fig. 11 shows a schematic diagram of the corrosion resistance mechanism of corundum-mullite refractories for hot stoves. Corundum-mullite refractories show excellent corrosion resistance under the working conditions of hot stoves, and the reason is inseparable from the formation of mullite network in refractories: In conventional refractories, granular minerals accumulate in the refractory to form channels for gas intrusion (Fig. 11 A and D), and CaO accumulates in the refractory until a low melting point phase with high Ca content is formed (Fig. 11B), which leads to the damage of the refractory; The mullite network in the corundum-mullite refractory effectively divides the CaO intruded into the refractory by reducing the gas diffusion channels in the refractory, which in turn leads to the CaO transformation into CAS$_2$ with low calcium content and high melting point instead of low melting phase (Fig. 11 C and E). Finally, the corrosion resistance of corundum-mullite refractory is improved because the pores in the working layer of the refractory are blocked by the generated CAS$_2$ (Fig. 11F).

4. Conclusions

XRD, SEM, and CT scanning methods were used to investigate the phase and structure characteristics of postmortem corundum-mullite refractories used in hot stoves for more than 10 years, and the anti-corrosion mechanism of the refractories was also analyzed. Results show that:

(a) After being used for more than 10 years, the performance of postmortem corundum-mullite refractory remains good, and the corrosion trace of hot stove gas is only detected in the working layer of the refractory.
(b) The postmortem corundum-mullite refractories are mainly composed of corundum and mullite, and have the structural characteristics of short columnar mullite distribution in a network.
(c) The separation of impurities in the corundum-mullite refractory by mullite network makes the CaO in the hot stove gas change into high melting point CAS$_2$ in the working layer of the refractory. And the refractories are endowed with excellent resistance to hot stove gas corrosion because that CAS$_2$ blocks the pores of the working layer of the refractory.

Figure 11. Schematic diagram of corrosion resistance mechanism of corundum-mullite refractories for hot stoves.
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