Research on Corrosion Resistance of Al₂O₃-MgAl₂O₄ Refractories and SiC-MgAl₂O₄ Refractories to Gasifier Slag

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Abstract. Spinel-containing refractory is a kind of potential chromium-free refractory for coal gasification because MgAl₂O₄ spinel has good slag resistance. Corundum-spinel refractories with w(Al₂O₃)=94%, w(MgO)=5% and SiC-spinel refractories with w(SiC)=64%, w(Al₂O₃)=5% were prepared. The crucible specimens were tested for slag corrosion with commercial gasifier slag at 1500°C for 1 h in reducing atmosphere. XRD analysis were researched on the sidewall of the crucible after slag test. Microstructure and chemical composition of samples in slag corrosion zone were analyzed by SEM and EDS. The results show that the slag resistance of SiC-MgAl₂O₄ refractory was significantly better than Al₂O₃-MgAl₂O₄ refractory. The corundum particles were decomposed into fine particles by the slag, and the microstructure was destroyed. The oxidation of the surface of the silicon carbide particles formed a high-viscosity glass phase with the infiltrated slag, which was benefit to prevent the slag penetration into the interior. And a solid solution of (Mg, Fe)O·Al₂O₃ composite spinel was formed in matrix of the sample after slag penetration because MgAl₂O₄ absorbed FeO in the slag. It is speculated that the spinel solid solution repairs and strengthens the structure of the matrix, which improves the slag resistance.

1. Introduction
Coal gasification is an ideal way of clean and efficient utilization for coal resource. Fluidized bed with high temperature, high pressure and liquid slag discharge is the mainstream of coal gasification because of its high efficiency and large capacity [1]. Coal-water slurry gasifier is one of the typical representatives. Its operating temperature is about 1500°C, and pressure is 2.0-8.7 MPa in a reducing atmosphere [2]. The slag after gasification corroded the lining seriously. In practice, high chromium refractory has to be used as lining because chromium oxide has excellent corrosion resistance to slag [3,4]. However, high chromium refractories are expensive. Particularly, they have potential hazards of hexavalent chromium in production, use and after use. It is great significance to develop chromium-free refractories for coal gasification [5]. A large number of research results have show that erosion, penetration, spalling and wear are the main forms of damage to high chromium refractories used in gasifiers [6,7]. The comprehensive improvement of multiple properties may be a way out of the predicament of using only chromium refractories in coal gasification environment.
Magnesia-alumina spinel has high refractoriness, good chemical stability and slag resistance. Spinel-containing refractories have been applied in many fields. Magnesite-spinel bricks used in cement rotary kiln have replaced magnesia-chrome bricks [8]. Magnesite-spinel-ZrO2 bricks have been used in steelmaking furnace with RH vacuum degassing [9]. Corundum-spinel castable used in ladle has shown good slag resistance and prolonged service life [10]. Spinel-based refractories for improved performance in coal gasification environments have been researched [11]. And they are considered as potential new refractory materials for application in coal gasification environments with the laboratory testing and evaluation [12].

Oxide-nonoxide composite refractories are not wetted with slag and show good slag resistance [13]. Silicon carbide as a synthetic non-oxide material is widely used in refractories. SiC-spinel refractory with SiC particles as aggregate and MgAl2O4 spinel powder as matrix may combine the advantages of SiC and spinel and will have good properties. However, few studies have been reported in this field. In this study, SiC-spinel refractory and corundum-spinel refractory were prepared and their chemical and physical properties were tested. In order to preliminarily explore whether these materials can be applied in coal gasification environments, slag resistance test to industrial gasifier slag was evaluated and discussed by static crucible method.

2. Experimental procedure

1. Preparation and properties of specimens

SiC-spinel mixture was prepared by mixing fused silicon carbide particles (≤3mm, 65mass%), sintered magnesia-alumina spinel(≤45μm, 25mass%), alumina powder (≤45μm, 10mass%) and water-soluble resin binder. While, Al2O3-spinel mixture consisted of fused white corundum and tabular alumina particles(≤3mm, 65mass%), sintered magnesia-alumina spinel (≤45μm, 25mass%), alumina powder (≤45μm, 10mass%) and water-soluble resin binder. The two mixtures were pressed into the crucible specimens respectively, which were the cylinder with φ70mm, h 70mm, and the hole with φ35mm, h 40mm. And the green bodies of SiC-spinel were fired at 1600°C in carbon bed, marked as S#. Al2O3-spinel green bodies were fired at 1650°C in air, marked as A#. The chemical and physical properties of the specimens are shown in Table 1.

| Specimens | SiC mass% | Al2O3 mass% | MgO mass% | Porosity | Bulk density g·cm⁻¹ | CCS MPa | CMOR MPa |
|-----------|-----------|-------------|-----------|-----------|---------------------|---------|---------|
| S#        | 64        | 30          | 5.5       | 18.3      | 2.72                | 63.2    | 5.7     |
| A#        | --        | 94          | 5         | 21.0      | 2.95                | 77.9    | 9.7     |

2. Slag test

The crucible sample was filled with an industrial gasifier slag. The weight of slag added to each crucible was a certain 45 gram. The composition of slag is shown in Table 2. The slag test was carried out at 1500 °C for 1 hour in reductive atmosphere, which was a relatively closed space consisting of carbon blocks and the illustration is shown in Figure 1.

| Compositions | SiO2 | Al2O3 | Fe2O3 | CaO | MgO | Na2O | K2O | TiO2 |
|--------------|------|-------|-------|-----|-----|------|-----|------|
| Mass%        | 38.2 | 20.9  | 11.5  | 18.7| 3.6 | 3.8  | 1.1 | 1.0  |
3. Analytical apparatus and method
After cooling, the specimens were cut along the axis. The photograph of section after slag test is shown in Figure 2. The macrostructure and microstructure of the two slag eroded specimens were compared and analyzed. The microstructure and element distribution of the specimens were analyzed by scanning electron microscope (SEM, EVO-18, Zeiss company) and energy-dispersive X-ray spectroscopy (EDS, X-Max50, Oxford company). The phase composition of the specimens after slag test was analyzed by X-ray diffractometer (XRD, Empyrean, PANalytical company). The sampling locations of SEM and XRD are shown in Figure 2.

4. Results and discussion
5. Comparison of the slag test results
The profile of crucibles after slag test is shown in Figure 2. We can see from it that the original contour of the side wall and bottom of the two crucibles was obvious. This indicates that the corrosion of the two kinds of refractories by the slag is slight. And there was almost no residual slag in both crucibles after slag test. The slag may evaporate or penetrate the refractories during the slag test.

Crucible sidewalls were sampled for XRD analysis, and the results are shown in Figure 3. For sample S#, in addition to the original SiC and spinel in the bricks, an anorthite phase as new product were formed because of the reaction between slag and refractory. While for sample A#, the new phase was nepheline.
Figure 3. XRD patterns of the specimens after slag test.

The microstructure at the reaction interface of crucible after slag test was observed by SEM in Figure 4. We can see that the slag reacted with the refractory at the interface, and some of the slag penetrated the refractory in Figure 4. For sample S#, as shown in Figure 4(a), there were slag layer, penetration layer and unreactive layer, and their demarcation lines were obvious. But for sample A#, as shown in Figure 4(b), there was just penetration zone in the field of vision, neither slag zone nor unreactive zone. Through further analysis, we observed unreactive zone and found that the penetration of slag was deeper for sample A#.

Figure 4. SEM photograph of crucible after slag test at the reaction interface.
Calcium oxide is one of the main substances in the slag. And there was no calcium oxide in the two original refractory specimens. It was found by SEM and EDS that the distribution of calcium oxide in refractories coincided with that of slag in refractories after slag test. So, in this study the distribution of CaO by EDS analysis was used to judge the penetration depth of molten slag. The concentration distribution of CaO in slag penetration zone is shown in Figure 5. The concentration of CaO decreases with the distance from the reaction surface for the two specimens. And that in sample S# is lower than sample A#. When the concentration of calcium oxide decreases to about 1 mass% by EDS analysis, it can be considered that there is no slag in the sample. It can be judged from Figure 5 that the slag penetration depth of sample A# is 10 mm and that of sample S# is 2 mm.

To sum up, both refractories were eroded and penetrated by molten slag during slag test. Erosion was slight and slag permeation was huge in both Al$_2$O$_3$-MgAl$_2$O$_4$ refractories and SiC-MgAl$_2$O$_4$ refractories to gasifier slag. SiC-MgAl$_2$O$_4$ refractories had better slag penetration resistance than Al$_2$O$_3$-MgAl$_2$O$_4$ refractories.

Figure 5. The concentration distribution of CaO in slag penetration zone and permeation depth of slag.

![Figure 5](image_url)

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Figure 6. SEM and EDS analysis of specimen S# in slag corrosion zone.

(a) **SEM photograph**  
(b) **Element distribution by EDS**

Figure 6. SEM and EDS analysis of specimen S# in slag corrosion zone.
6. Slag resistance mechanism of SiC-MgAl₂O₄

The original microstructure of SiC-MgAl₂O₄ refractory was silicon carbide particles dispersed in MgAl₂O₄ spinel matrix. The matrix was not dense, and there were some fine pores in the matrix. During the slag test, the molten slag penetrated into the pores. The graphs of specimen S# by SEM and EDS analysis in slag corrosion zone are shown in Figure 6. We can see from Figure 6(a) there is a clear boundary between slag and refractory. The upper part is slag and the lower part is refractory. And combining with the elemental surface distribution by EDS in Figure 6(b), the main elements in slag are Ca, Si, Al and a small amount of Mg. The matrix is mainly spinel composed of Mg and Al. While Ca and Si are also sporadically distributed in the matrix. This indicates that slag infiltrated between spinel particles, but the reaction between them was not intense.

![Fe-Si alloy in slag](image.png)

![Partial oxidation of SiC](image.png)

**Figure 7.** SEM and EDS analysis of specimen S#.

SEM photographs of the local details with specimen S# are shown in Figure 7. SEM photographs of residual slag adhered to the surface of the specimen is Figure 7(a). As can be seen from Figure 7(a), there are some bright white spherical aggregates in the slag layer, which are inferred to be Fe-Si alloy by EDS. This may be due to the reduction of iron oxides in slag by silicon carbide at high temperature and in reducing atmosphere. The reaction equation is as follows:

\[
SiC(s) + FeO(s) \rightarrow Si(l) + Fe(l) + CO(g)
\]  \hspace{1cm} (1)

As can be seen from Figure 7(b), the morphology and structure of SiC particles are not smooth and compact. This indicates that SiC particles may be partially oxidized. The reaction equations are as follows [14]:

\[
C(s) + 1/2O_2(g) \rightarrow CO(g)
\]  \hspace{1cm} (2)

\[
SiC(s) + CO(g) \rightarrow SiO(g) + 2C(s)
\]  \hspace{1cm} (3)

\[
SiO(g) + CO(g) \rightarrow SiO_2(s) + C(s)
\]  \hspace{1cm} (4)

In the slag test, the carbon block was surplus, so it can be considered that CO atmosphere was in the sagger as in equation (2). Silicon carbide particles at the reaction interface were preferentially oxidized by CO gas, such as equation (3). This oxidation reaction was slow. And the smaller SiC particles were, the easier they were to be oxidized. Generally, the edges of particles were first oxidized. According to equation (4), silicon dioxide film was generated and coated on the surface of silicon carbide, which could hinder and delay the oxidation of internal silicon carbide. At the surface, the slag infiltrated into the matrix along the micropore. CaO in slag, corundum in matrix and SiO₂ formed by
oxidation of SiC react to anorthite (CaAl$_2$Si$_2$O$_8$), as in Figure 3. The oxidation of the silicon carbide particles on the surface formed glass phase with the infiltrated slag, which had a high viscosity because of high silica content. This is benefit to prevent the slag penetration into the interior.

7. Slag resistance mechanism of Al$_2$O$_3$-MgAl$_2$O$_4$

The experimental results showed that the penetration of molten slag into the Al$_2$O$_3$-MgAl$_2$O$_4$ specimen was deeper. The main infiltrated elements in slag were Ca, Fe, Si, etc. The SEM of specimen A# in slag corrosion zone, corresponding element surface distribution by EDS, are shown in Figure 8. Corundum particles are encapsulated by spinel matrix and have compact microstructure. The distribution regions of Mg, Al and Fe elements are overlapping except corundum particles. While which of Ca and Si elements are similar. Mg, Al and Fe elements exist in spinel, and Ca and Si elements with others in slag form to glass phase, which has low melting point and is easy to penetrate.

![Figure 8. SEM and EDS analysis of specimen A# in slag corrosion zone.](image)

![Figure 9. SEM and EDS analysis of specimen A#.](image)

Unlike SiC-MgAl$_2$O$_4$ specimen, the Fe element in the slag were not reduced to metal due to the absence of SiC in the Al$_2$O$_3$-MgAl$_2$O$_4$ specimen. So, corrosion and penetration of Fe element in the slag to refractories cannot be neglected. Previous studies have found that magnesia-alumina spinel can capture and absorb Fe element in slag [15]. In this study, further analysis showed that iron in slag was
dissolved into magnesia-alumina spinel, and the concentration of FeO decreased with the increase of penetration depth. And we can see from Figure 9(a), the spinel in the penetrated area was composed of Mg, Al, Fe and O elements by EDS analysis. So we can infer that the spinel detected by XRD is (Mg,Fe)O·Al2O3 solid solution in Figure 3(b).

The glass phase consisting of Ca, Si and Na elements in the slag slowly dissolved spinel and corundum particles, and which make its composition more complex. The glass phase promoted ion diffusion and made the microstructure of matrix in penetration layer more compact. Nepheline precipitated from the glass phase during cooling at the slag test. As can see from Figure 3(b), nepheline was detected by XRD. The glass phase also infiltrated into the corundum particles along the pores and cracks. And large corundum particles were dismembered into small pieces in Figure 9(b), which lead to collapse of refractory skeleton structure.

8. Conclusions

It is shown that both materials have good corrosion resistance to gasifier slag by slag test of static crucible in reducing atmosphere. Silicon carbide, corundum and spinel were still the main components in the slag-eroded samples. SiC-MgAl2O4 specimens have better slag permeability resistance. This is due to a viscous glass phase formed from infiltrated slag and composition in bricks, which prevents the further infiltration of slag into the material. SiC particles were locally oxidized in the reaction zone, and iron in slag was reduced to Fe-Si alloy for SiC-MgAl2O4 specimens after slag test. But for Al2O3-MgAl2O4 specimens after slag test, iron in slag was absorbed by magnesia-alumina spinel to form spinel solid solution with iron. Corundum particles were dismembered because of the infiltration of molten slag. In conclusion, it is considered that SiC-MgAl2O4 material is a potential refractory for coal gasification.

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