The Behavior of Slag Resistance of MgO-C Refractory Prepared by Sucrose as Binder

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Abstract: The harmful components such as formaldehyde and phenolic compounds released during the development, production and use of MgO-C refractories prepared by using phenolic resin as a binder can cause serious harm to the environment and human health. In this paper, MgO-C refractory material with sucrose as binder and metal aluminium powder as antioxidant is prepared. Different slag temperature and time factors have a largely influence on the slag corrosion resistance of as-prepared samples. By analyzing the microstructure and composition of the samples, it is found that under the condition of constant time, the higher the temperature, the more obvious the slag corrosion phenomenon; under isothermal conditions, the longer the time, the more obvious the slag corrosion phenomenon. At the same time, it is revealed that the main corrosion process of MgO-C refractories prepared by adding sucrose as a binder is carbon oxidation and slag corrosion, which provides a theoretical basis for optimizing the slag resistance of MgO-C refractories.

1. Introduction

MgO-C refractory material, as one of the three major categories of carbon-containing refractories, is a sintering-free refractory sintered by fused magnesia or sintered magnesia as magnesia raw material, graphite or carbon black as carbon raw material, auxiliary with various antioxidants and carbonaceous binders. MgO has a high melting point and is resistant to alkali slag erosion. However, due to its large coefficient of thermal expansion, the thermal shock stability of MgO refractory products is poor and easy to peel off. Graphite has a high melting point, high thermal conductivity, and excellent properties that are difficult to be wetted by slag. MgO-C refractory material overcomes the fatal shortcoming of magnesia sand which is easy to crack due to thermal shock and is easily peeled off and damaged by steel slag, thus exerting good erosion resistance, thermal shock resistance and thermal conductivity, and low linear expansion coefficient. And excellent properties such as resistance to metal melt and high temperature slag. Due to the presence of carbon in the MgO-C refractory, its anti-erosion performance is significantly stronger than oxide refractories such as dolomite brick, magnesium dolomite and magnesia chrome brick. It is mainly used in clean steel smelting ladle, hot metal storage
tanks, continuous casting, iron making blast furnace body and other parts. It plays a vital role in the technological advancement and safe production of the iron and steel metallurgical industry.

Binder is the core of strength acquisition of MgO-C refractories. The commonly used binder is phenolic resin. Because it is a synthetic resin formed by condensation of phenol and formaldehyde, formaldehyde and phenols will be released when heated, accompanied by odor, which will have adverse effects on the environment and human health. Therefore, it is urgent to develop a new type of binder with good wettability, high residual carbon rate, good bonding strength, environmental protection, pollution-free and relatively strong oxidation resistance. As environmentally friendly sugars, sucrose is a new type of binder widely studied by scientists in recent years. Sucrose has a certain viscosity and is more environmentally friendly than phenolic resin, so it has the potential to replace phenolic resin as a binder. Due to the difference of carbonization process between carbohydrate and phenolic resin at elevated temperature, the ultimate porosity and microstructure of refractories are different, resulting in different slag corrosion resistance of refractories. Up to now, there are few studies on the application of saccharides as binders in refractories.

In this paper, MgO-C refractories were prepared with fused magnesia and flake graphite as main raw materials, aluminum powder as antioxidant and sucrose as additives. The corrosion resistance of MgO-C refractories with sucrose as binder under different temperature and time conditions was studied. The slag corrosion resistance of MgO-C refractories with sucrose as binder was compared with that of phenolic resin as binder, and the slag corrosion resistance mechanism of MgO-C refractories with sucrose as binder was explored.

2. Experiment

The experimental steps are divided into three parts: firstly, the sucrose binder is prepared; secondly, the MgO-C refractory is prepared; finally, the slag erosion resistance experiments at different temperatures and at different times are carried out.

Preparation of sucrose binder: Sucrose is dissolved in water (the mass ratio of sucrose to water is 1:1), heated in resistance furnace and stirred continuously with glass rod until sucrose is completely dissolved, sealed with fresh-keeping film after cooling.

MgO-C refractory material preparation: According to the proportion of 23% and 3%, fused magnesia (0-0.074 mm) and metal aluminum powder are weighed respectively, and ball milled in planetary ball mill for 2 hours (agate ball, mass ratio of ball to material is 1:1), so that fine powder can be mixed evenly. The flake graphite and crude, medium of fused magnesia with particle size of 1-3 mm and 0-1 mm were weighed according to the proportion of 9%, 30% and 35%, respectively. And then the trapped material was fully mixed in the sample bag for 24 hours. The crucible samples of 50 mm (outer diameter) * 25 mm (inner diameter) were pressed by powder press moulding (forming pressure 20 MPa, holding pressure 1 min). The pressed sample was placed in the oven and cured at 180°C for 24 hours.

Resistance to slag erosion: After solidifying at 180°C for 24 hours, the sample is filled with converter slag of about 2/3 volume in the crucible. The sample is placed in a corundum crucible with carbon buried at the bottom. The slag erosion resistance experiments are carried out in muffle furnace at 1400°C and 1500°C temperatures, respectively. Five groups of slag etching time were designed for sucrose samples, which were 15 min, 30 min, 45 min, 1 h and 2 h, respectively.

3. Results and discussion

Figure 1 shows the appearance of sucrose-bonded MgO-C refractories before and after slag corrosion at 1400°C for different time, the cross section after slag corrosion and the erosion thickness at the bottom of crucible. It can be seen from Figure 1(a) that the outer surface of the sample is oxidized to white after slag corrosion. When the slag corrosion time is low, the converter slag cannot be completely melted and the sample is hardly eroded by slag. When the slag corrosion time is more than 30 minutes, irregular slag corrosion layer can be seen on the sample. When the slag corrosion time is prolonged to 2 h, it can be seen that the converter slag filled in the crucible is completely melted and
the crucible is corroded by the slag. Figure 1(b) shows the erosion thickness at the bottom of the crucible as slag erosion time increases. The analysis in the figure shows that the longer the sample is eroded by converter slag at 1400°C, the greater the erosion thickness at the bottom of the sample. When the corrosion time is less than 30 minutes, the corrosion degree of sample is low because only a few parts of converter slag melt into it. When the erosion time is more than 45 minutes, the melting state of converter slag increases and the erosion thickness at the bottom of the sample increases greatly. When the erosion time is 2 h, the erosion thickness at the bottom of the specimen reaches the maximum value of 2.95 mm.

![Figure 1](image1.png)

**Figure 1.** Sucrose-bonded MgO-C refractories at 1400°C: (a) appearance and cross section of slag-etched specimens before and after slag corrosion at different time; (b) erosion thickness of crucible bottom.

The figure shows that the appearance of sucrose-bonded MgO-C refractories before and after slag corrosion at 1500°C for different time, the cross section after slag corrosion and the erosion thickness at the bottom of crucible. It can be seen from Figure 2 (a) that, compared with the slag etched specimens at 1400°C, the converter slag melts completely at 1500°C regardless of the length of slag.

![Figure 2](image2.png)

**Figure 2.** Sucrose-bonded MgO-C refractories at 1500°C: (a) appearance and cross section of slag-etched specimens before and after slag corrosion at different time; (b) erosion thickness of crucible bottom.
etching time. The slag etching degree of the specimens is more serious, the slag etching area is larger, and the outer layer of the specimens is oxidized to a deeper yellow-brown color. It can be seen from the section diagram after slag corrosion that with the increase of slag corrosion time, the degree of slag corrosion of crucible increases gradually. Figure 2 (b) shows the bottom erosion thickness data of the specimens after slag etching at 1500°C for different time. According to the data in the analysis chart, the erosion thickness at the bottom of the sample increases with the increase of slag corrosion time. It shows that the longer the slag corrosion time is, the more serious the slag corrosion is. When the slag corrosion time is less than 30 minutes, the slag corrosion degree is relatively low, and the slag corrosion thickness at the bottom is not more than 2.00 mm. When the slag corrosion temperature is more than 45 min, the slag corrosion speed is accelerated and the slag corrosion degree at the bottom is aggravated. When the slag corrosion time reaches 2 h, the bottom slag corrosion thickness has a maximum value of 2.98 mm. Compared with the slag-etched specimens at 1400°C for 2 h, the bottom erosion thickness of the slag-etched specimens at 1500°C for 2 h is larger. It shows that the higher the temperature is, the more easily the slag penetrates into the sample structure.

Figure 3 shows the SEM images of sucrose-bonded MgO-C refractories after slag corrosion at 1400°C for different time. It can be seen from the figure that when the slag corrosion time is less than 30 minutes, the boundary between the slag corrosion layer and the original sample layer is not obvious, but it can also be seen that the original sample layer is looser and the slag corrosion layer is more compact. When the slag corrosion time is more than 30 minutes, the obvious boundary between slag layer, slag corrosion layer and original sample layer can be seen. The slag layer is formed by the cooling of converter slag after melting, and a large number of holes with a diameter of 200 microns are distributed on the slag layer. Besides, liquid slag penetrates into the original sample layer filling the pore causes the formation of a denser slag corrosion layer on the surface.

![Figure 3. SEM photographs of sucrose-bonded MgO-C refractories after slag corrosion at 1400°C for different time: (a) 15 min; (b) 30 min; (c) 45 min; (d) 1 h; (e) 2 h.](image)

SEM photographs of sucrose-bound MgO-C refractories after slag etching at 1500°C for different time are shown in Figure 4. It can be clearly seen from the diagram that there are many porous slag layers, denser slag corrosion layers and the boundary between the original sample layers with loose structure. When the slag corrosion temperature is low, the pore size of the slag layer cooled after melting is large, and with the increase of slag corrosion time, the pore size of the slag layer decreases and the pore size decreases. This is because, on the one hand, the slag intrudes into the original sample layer and fills the voids in the sample, which makes the slag corrosion layer dense. On the other hand, the elements in the original sample permeate into the slag and fill the voids in the slag.
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Figure 4. SEM photographs of sucrose-bonded MgO-C refractories after slag corrosion at 1500°C for different time: (a) 15 min; (b) 30 min; (c) 45 min; (d) 1 h; (e) 2 h.

Figure 5 (a). The distribution sketch of each element was scanned by profiles after slag erosion for 15 min at 1500°C.

In the process of mutual penetration, the slag erosion layer acts as an intermediate bridge. In this area, the atomic migration rate increases, and the flow of liquid Al also exists, which makes the distribution of particles in the slag erosion layer tend to be uniform and stable, and the particles gradually become compact accumulation, and the porosity decreases. Therefore, it can be seen that the slag corrosion degree deepens and the density of slag corrosion layer increases with the slag corrosion time. It was also found that the edges of the specimens contacted with the slag were white and bright under scanning electron microscopy, which indicated that these parts were replaced by high-altitude atomic substances in the slag.

Figure 5 shows the linear scanning results of the specimens after slag etching at 1500°C for different time. The main original compounds in the original sample layer are MgO, C and Al. The
original elements in the slag are mainly 30.13% CaO, 39.13% Fe₂O₃, 18.26% SiO₂, and a small amount of MgO and Al₂O₃. After slag corrosion, graphite in the original sample layer is oxidized to form decarbonized layer, and the gas phase product formed by oxidation escapes, increasing the porosity of the sample. From the SEM photos, it can be seen that there are pores on the decarbonized layer. From the line scan results, it can be seen that there is almost no C in the decarbonized layer, and the Fe element in the decarbonized layer is less than that of Ca and Si, which indicates that the iron oxides in the slag are prior to that in the decarbonized layer. The slag penetrates into the sample along the channel formed by gas escaping and the crack formed by thermal stress, forming slag corrosion layer. The surface of slag corrosion layer is smooth and compact from SEM. From the results of line scanning, it can be seen that there are more Mg, Ca, Si, Al and O elements in slag corrosion layer. It shows that CaO, Fe₂O₃, SiO₂ and Al₂O₃ in slag and MgO in magnesia sand form low melting point. The solid solution of C, Fe, Si, Ca and other elements can also be seen in the original sample layer, which indicates that the slag penetrates into the sample structure through the slag corrosion layer, resulting in the damage of the internal structure of the structure.

The erosion process of converter slag on MgO-C refractories can be summarized into two parts: one is the penetration of slag into the sample, the other is the melting of the sample into the slag. In the process of slag corrosion, Al in the sample is oxidized to form Al₂O₃, and with volume expansion, the internal structure becomes dense, which hinders the penetration of slag to a certain extent. The high melting point spinel phase MgAl₂O₄ was synthesized from Al₂O₃ and MgO in the sample, which prevented the formation of low melt and improved the slag corrosion resistance of the material. In addition, the Mg vapor produced by MgO reduction at high temperature is oxidized to form a continuous MgO protective layer when it diffuses to the surface of the sample. The MgO in this layer continues to react with SiO₂ in the slag to form a high melting point solid solution 2MgO·SiO₂ (melting point is 1890°C), which further prevents the penetration of the slag. However, the 2MgO·SiO₂ continuous phase is less and the structure is looser. When molten slag penetrates through the protective layer, it will enter the decarbonized layer with more pores, and continue to dissolve magnesia in the sample, resulting in material damage.

![Figure 5 (b). The distribution sketch of each element was scanned by profiles after slag erosion for 30 min at 1500°C.](image-url)
Figure 5 (c). The distribution sketch of each element was scanned by profiles after slag erosion for 45 min at 1500°C.

Figure 5 (d). The distribution sketch of each element was scanned by profiles after slag erosion for 60 min at 1500°C.
Figure 5 (c). The distribution sketch of each element was scanned by profiles after slag erosion for 120 min at 1500°C.

4. Conclusion

MgO-C refractories were prepared by adding sucrose as binder and using aluminum powder as antioxidant. The slag corrosion resistance of MgO-C refractories was analyzed and compared at 1400°C and 1500°C at different time, respectively. The positive correlation between temperature, time and slag corrosion degree was explored by means of morphology analysis, microstructure analysis and component analysis. Under the condition of equal time, the higher the temperature, the more obvious the slag corrosion phenomenon; under the condition of equal temperature, the longer the time, the more obvious the slag corrosion phenomenon. At the same time, it is revealed that the main erosion processes of MgO-C refractories prepared by adding sucrose as binder are carbon oxidation and slag erosion. The high melting point spinel phase MgAl$_2$O$_4$ is synthesized from Al$_2$O$_3$ formed by oxidation of Al powder and MgO in the sample, which prevents the formation of low melt and improves the slag corrosion resistance of the refractories.

Acknowledgement

This work was supported by the National Key Research and Development Program "Solid Waste Resource" Key Project "Key Technologies for Large-scale Production of High Value Mineral Materials from Low-order Solid Waste" Project 3 "Research and Demonstration of High Temperature Resistant Materials Prepared by Shielding Control of Ceramic Solid Waste Microstructure" (Grant No.2018YFC1901503), the National Natural Science Foundations of China "Basic Research on Environmental Protection Carbon Bonded Carbon-containing Carbon Oxide-Non-oxide Composite Refractories"(Grant No. 51472222)and the Fundamental Research Funds for the Central Universities(Grant No. 2652018320,2652018321).

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