Influence of Sucrose Binder on the Oxidation Resistance of MgO-C Refractory

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Abstract: In this study, novel MgO-C refractories using environmentally friendly sucrose as binder were prepared. To solve the harmful effects of formaldehyde and phenolic compounds that cause serious harm to the environment and human health released during the development, production and use of phenolic resin binders for MgO-C refractories, MgO-C refractories using environmentally friendly sucrose instead of phenolic resins as binders were prepared. The phase, microstructure, oxidation resistance and the antioxidant mechanism of MgO-C refractories prepared by adding sucrose as binder at different temperatures were analyzed. The formula between the weight loss of the material and the temperature is $y=1.6225x+0.215$ ($600^\circ C$ $\sim$ $1200^\circ C$). The addition of aluminium resulted in the formation of Al\textsubscript{2}O\textsubscript{3} inside the refractories. Meanwhile, MgAl\textsubscript{2}O\textsubscript{4} crystals were synthesized by Al\textsubscript{2}O\textsubscript{3} and MgO at high temperature. The formation of Al\textsubscript{2}O\textsubscript{3} and MgAl\textsubscript{2}O\textsubscript{4} played an important role in improving the oxidation resistance property of MgO-C refractories using sucrose as binder.

1. Introduction

With the rapid development of iron and steel metallurgical industry, the requirements of refractory quality for relevant enterprises are increasingly stringent.\textsuperscript{[1-2]} Refractories are the necessary basic materials for the development of high-temperature industries such as iron and steel, non-ferrous materials, building materials, electric power, chemical industry, machinery, et al. They have made great contributions to the safe and reliable production of the national high-temperature industry and the sustainable development of the national economy.\textsuperscript{[3-4]}

Relevant research shows that although the total output of refractories in China is in the forefront of the world, the proportion of advanced refractories with high performance characteristics such as energy saving, long life and environment friendly is still at a low level. At present, the total demand for refractories may not increase substantially, but the total demand for high-performance advanced refractories will have an urgent demand to a certain extent, especially for functional, energy-saving and environment-friendly refractories. Among them, the carbon-containing refractory is an important part of the refractory system. It has excellent properties such as high thermal conductivity, low thermal...
expansion, good thermal shock resistance and slag erosion resistance.[5-7] Carbon-containing refractories can be divided into Al₂O₃-C, MgO-C and MgO-CaO-C according to their materials.

MgO-C refractory is a kind of carbon-containing refractory which combines high melting point magnesia and carbon raw materials.[8] Among them, magnesia has high melting point, high temperature performance and good chemical stability, but magnesia is easy to be eroded and peeled by slag, and its thermal expansion coefficient is higher, so the slag corrosion resistance and thermal shock resistance are not good enough.[9] Graphite has high heat conductivity and is difficult to be wetted by slag. Therefore, magnesia combined with graphite can make up for the shortcomings of high thermal expansion coefficient and slag corrosion of magnesia. However, due to the easy oxidation of carbon raw materials and the great difference of thermal expansion coefficient between magnesia and carbon raw materials at high temperature, the MgO-C refractories have the shortcomings of easy loosening, easy oxidation, poor erosion resistance and low high temperature strength.[10-11]

Because the reaction between carbon materials and magnesia is very difficult and the bonding is very poor, it is necessary to use binders to combine the two materials.[12] The common organic binders of MgO-C refractories are phenolic resin and coal tar pitch. However, when used as a binder of carbon-containing refractories, a certain amount of harmful gases (e.g. ethylene, phenol, cresol and xylol) will be emitted in the process of development, production and use, which will cause air pollution and odor. Therefore, the development of high performance, low cost and low pollution binders has become the focus of the research field of carbon-containing refractories.[13] In this study, sucrose were used to prepare carbohydrate binder, and then carbohydrate was combined with MgO-C refractories to prepare environmentally friendly and high performance MgO-C refractories. Sucrose is widely available, environmentally friendly, and relatively inexpensive compared with phenolic resins. It is suitable for large-scale application as binders for carbon-containing refractories.

2. Experiment

2.1. Experimental raw materials
Cylindrical MgO-C refractories were prepared with fused magnesia (≥ 97wt.% Beijing Lier High Temperature Materials Co., Ltd.) and flake graphite (≥ 97wt.% Zhengzhou Jinchuan Metallurgical Materials Co., Ltd.) as main raw materials, 4% sucrose (ARXilong Chemical Co., Ltd.) binder and aluminum powder (≥ 99.5wt.% Tianjin Guangfu Fine Chemical Research Institute) as antioxidant. The strength of MgO-C refractories bonded by sucrose binder at low temperatures is improved by curing sucrose binder.

2.2. Design of experimental formula
In this experiment, MgO-C refractories were prepared with fused magnesia, flake graphite and metal aluminum powder as main raw materials and added sucrose binder. The specific quality of the raw materials used in the experiment was shown in table 1.

| Raw materials Mass fraction/wt.% |
|-------------------------------|
| Fused magnesia 0-0.074 mm 23 |
| Fused magnesia 0-1 mm 35 |
| Fused magnesia 1-3 mm 30 |
| Flake graphite 9 |
| Aluminum powder 3 |
| Sucrose Binder (Added) 4 |

2.3. Experimental preparation
Firstly, sucrose binder was prepared. Sucrose is dissolved in water (the mass ratio of sucrose binder to water is 1:1), heated in a resistance furnace and stirred continuously with glass rod until the sucrose binder is completely dissolved, sealed with a fresh-keeping film after cooling.
According to table 1, fused magnesia (0-0.074 mm) and metal aluminum powder are weighed and milled in planetary ball mill for 2 hours (agate ball is the medium of ball milling, and the mass ratio of ball to material is 1:1), so that fine powder is mixed evenly and the mixture is taken out for use. Coarse and medium particles of fused magnesia with particle sizes of 1-3 mm and 0-1 mm, respectively, were added in the order of coarse and medium particles, binder, fine powder mixture and flake graphite, then fully mixed and trapped in the sample bag for 24 hours. Cylindrical specimens with diameter of 25 mm (ratio of height to diameter of 1:1) were pressed by powder press moulding (forming pressure is 20 MPa, holding pressure is 1 minute). The pressed sample was placed in the oven and cured at 180 °C for 24 hours. The samples were placed in muffle furnace and oxidized in air. Five groups of oxidation temperatures were designed, which were 600 °C, 800 °C, 1000 °C, 1200 °C and 1400 °C, respectively. The oxidation time was 2 hours.

3. Results and discussion

The appearance and cross section of the oxidized samples at different temperatures are obtained as shown in Figure 1. It can be seen from the figure that after oxidation for 2 hours at 600 °C, the sample is still grey-black, and the oxide layer cannot be seen clearly. With the increase of oxidation temperature, it can be clearly seen that the sample gradually oxidized, the oxidation area gradually increased, and the color changed from gray-white to yellow-brown. It can be seen more intuitively from the section diagram that the sample has been oxidized seriously at 1000 °C. When the temperature rises to 1200 °C, the gray-black original sample layer cannot be seen in the sample, and it is completely oxidized to gray-white. The graphite in the sample was completely burnt at 1400 °C, and large brown MgO particles were exposed.

![Image of oxidized samples at different temperatures](image.png)

**Figure 1.** Digital photos of samples added with 4% sucrose oxidized for 2 h at different temperatures.

The mass loss rate after oxidation at different temperatures was tested, as shown in Figure 2. As shown in the figure, the mass loss rate of samples basically increases with the increase of oxidation temperature before 1200°C, and the mass loss rate reaches the maximum value at 1200°C, which is 6.69%. It can be seen that the mass loss rate of samples basically increases linearly when the oxidation temperature does not exceed 1200°C. The linear formula that the mass loss rate changes with temperature is obtained through linear fitting, which is shown in the figure. According to the analysis figure, when the oxidation temperature does not exceed 1200°C, the samples maintain a basically stable oxidation rate, and the oxidation is basically complete at 1200°C. When the temperature
continues to rise to 1400°C, the mass loss rate decreases somewhat. It is speculated that some gases are fixed by the chemical composition of the sample, leading to the increase in mass.

![Graph showing mass loss rate vs. temperature](image)

**Figure 2.** Mass loss rate of samples with 4% sucrose added after oxidation at different temperatures.

![X-ray diffraction patterns](image)

**Figure 3.** X-ray diffraction pattern of oxidized samples with 4% sucrose at different temperatures.

Phase transformation of sucrose-bound MgO-C refractories at different oxidation temperatures is shown in Figure 3. It can be seen from the figure that after oxidation at 600°C, in addition to the original three phases of periclase, graphite and Al, there are also very weak α-Al2O3 diffraction peaks, indicating that part of the Al powder in the sample is oxidized at this temperature. After oxidation at 800°C, the content of graphite in the sample decreases, and a small amount of MgAl2O4 spinel is found. At this temperature, oxygen in the air reacts with graphite as the sample pore penetrates into the
sample. Owing to less oxygen and limited pore space in the sample, an anaerobic environment is formed, and graphite is excessive. At this time, graphite reacts with oxygen to form CO, which forms a decarbonization layer and makes the surface of the sample powdered. When the oxidation temperature rises to 1000°C, the diffraction peak of graphite can hardly be observed. By 1200°C, the samples have been completely oxidized, and the amount of spinel MgAl₂O₄ increases. The diffraction peaks of MgAl₂O₄ decrease after oxidation at 1400°C, while the diffraction peaks of periclase become stronger, indicating that some MgAl₂O₄ decomposes at this temperature.

Figure 4. Field emission scanning electron microscopy images and Energy dispersive spectroscopy pattern results of 4% sucrose-added samples oxidized at different temperatures (a-600°C; b-800°C; c-1000°C; d-1200°C; e-1400°C; f- Linear scanning results of right marker line in c).

The cylindrical samples oxidized at different temperatures were cut along the middle line perpendicular to the high to obtain the cross section. The SEM images and EDS results were obtained as shown in Figure 4. It can be seen from the figure that after oxidation at 600°C, there is no obvious boundary between the original sample layer and the oxide layer, and the internal structure of the sample is relatively loose. When the samples were oxidized at 800°C and 1000°C, the loose original sample layer, denser oxide layer and denser intermediate transition layer could be seen clearly. Figure 4-f is the results of linear scanning elemental distribution of the oxidized samples at 1000°C. The graphs show that the distribution of Mg and O elements in the oxide layer is almost the same as that in
the original sample layer, while the presence of C element is almost invisible in the oxide layer, and the content of C in the transition layer is very small. Figure 4-d and e is the micro-morphology of the sample after oxidation at 1200°C and 1400°C, respectively. It can be seen that there is almost no loose original sample layer inside the sample, indicating that the sample has been basically oxidized at 1200°C. As can be seen in Figure 4-e, the particles in the sample are closely stacked in layers, which is caused by internal sintering of the sample at this temperature. The results of micro-morphology are consistent with those of digital photographs.

4. Oxidation resistance mechanism of sucrose-bound MgO-C refractories

The oxidation of MgO-C refractories is mainly due to the oxidation of graphite. There are two forms of graphite oxidation: one is gas phase oxidation, that is, reaction with oxidized gases such as oxygen and carbon dioxide in the air into CO; the other is solid phase oxidation, under high temperature, MgO and graphite are oxidized and reduced to replace Mg vapor. Combining the XRD spectra of MgO-C refractories prepared by adding sucrose binder at different temperatures, we can know the main reactions in the oxidation process and their thermodynamic formulas as follows:

\[
C (s) + \frac{1}{2}O_2(g) \rightarrow CO(g) \quad \Delta G^0 = -114400 - 85.77T \text{ (J/mol)} (1)
\]

\[
C (s) + CO_2(g) \rightarrow 2CO(g) \quad \Delta G^0 = 166550 - 171T \text{ (J/mol)} (2)
\]

\[
MgO(s) + C(s) \rightarrow Mg(g) + CO(g) \quad \Delta G^0 = 600020 - 279.49T \text{ (J/mol)} (3)
\]

At low, medium and high temperatures, Al in the sample can react with oxygen in the air to form Al₂O₃, forming a dense oxide layer on the surface of the sample, and the unreacted elemental Al can continue to be oxidized by CO gas to form Al₂O₃. The formation of Al₂O₃ crystals is accompanied by volume expansion, which fills the internal pore of the structure, makes the sample compact and prevents the air from penetrating into the sample. Enter the sample. At high temperature, MgO in the sample is reduced to Mg vapor by graphite. During the process of Mg vapor escaping from the sample, the generated oxygen gas is fixed to regenerate the continuous MgO layer, which prevents the further invasion of oxygen. At the same time, spinel MgAl₂O₄ was synthesized by MgO and Al₂O₃ at high temperature. The increase of high temperature phase not only improved the oxidation resistance of the sample, but also enhanced the high temperature strength of the sample. The possible chemical reactions are speculated as follows:

\[
2Al(s) + 3/2O_2(g) \rightarrow Al_2O_3(s) \quad \Delta G^0 = -1675100 + 313.2T \text{ (J/mol)} (4)
\]

\[
3CO(g) + 2Al(s) \rightarrow Al_2O_3(s) + 3C(s) \quad \Delta G^0 = -1331900 + 570.51T \text{ (J/mol)} (5)
\]

\[
1/2O_2(g) + Mg(g) \rightarrow MgO(s) \quad \Delta G^0 = -732700 + 205.99T \text{ (J/mol)} (6)
\]

\[
Al_2O_3(s) + MgO(s) \rightarrow MgAl_2O_4(s) \quad \Delta G^0 = -32220 - 3.79T \text{ (J/mol)} (7)
\]

The standard Gibbs free energy of formulas 4-4 to 4-7 in the temperature ranging from 600°C to 1400°C is calculated. It shows that these chemical reactions can be carried out spontaneously in this temperature range. In the standard state, MgO and C can react at higher than 1800°C, but in the closed muffle furnace, the gas released from the binder and carbon oxidation in the sample, together with the high temperature environment, leads to the increase of pressure in the furnace, and the partial pressure of Mg vapor and CO gas in the sample increases, which greatly reduces the reaction temperature of MgO and C, and can occur at higher than 1400°C.

5. Conclusion

MgO-C refractories are widely used in modern steelmaking industry because of their excellent thermal shock resistance and slag erosion resistance. The excellent performance of MgO-C refractories depends mainly on the use of phenolic resin binders. However, phenolic resin, as a commonly used binder for MgO-C refractories, releases a certain amount of harmful components such as...
formaldehyde and phenolic compounds in the process of development, production and use. The prominent problems that cause serious harm to the environment and human health have not yet been clearly solved. In this paper, MgO-C refractories were prepared by using sucrose as binder, fused magnesia and flake graphite as main raw materials and aluminum powder as antioxidants. The effects of sucrose binder on high temperature oxidation resistance were studied. The conclusions are as follows:

Sucrose-bound MgO-C refractories begin to oxidize at 800°C with relatively small oxidation area, and almost completely oxidize at 1200°C, and the change rate of oxidation mass varies with temperature by linear fitting. The relationship of transformation is $y=1.6225x+0.215$ (600°C -1200°C).

The oxidation of MgO-C refractories is mainly due to the oxidation of graphite. Adding metal aluminum powder as antioxidant to sucrose-bound MgO-C refractories and producing $\text{Al}_2\text{O}_3$ and MgAl$_2$O$_4$ at high temperature are beneficial to the strength acquisition and structure compactness of the materials, and to the oxidation resistance and slag resistance of MgO-C refractories.

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