Development of a new process for the inhibition of oxidization in MgO-C refractory

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Graphite, used as a carbon source in a conventional magnesia-carbon (MgO-C) refractory, was coated with an inorganic precursor to prevent the contact between graphite and oxygen. The coating layer thus generated could effectively protect graphite from oxygen, compared to common antioxidants. The coating reagent was composed of silicate and metal alkoxide, generally called the inorganic precursor, which modified the graphite surface. The modified graphite showed excellent stability at 1000 \(^\circ\)C in an ambient atmosphere, whereas the graphite in a conventional MgO-C refractory reacted with oxygen and showed a significant weight loss. The coating reagent was coated uniformly on the graphite surface and it was very efficient in preventing the oxidation of graphite. Furthermore, the shape of prepared refractory samples remained fixed, even when the content of phenol resin was low. Consequently, ecofriendly MgO-C refractories with high oxidation resistance were successfully prepared by the coating of an inorganic precursor onto graphite.

Key words: Inorganic precursor, Sol-gel reaction, Refractory, Graphite, Coating, Oxidation resistance.

Introduction

Recently, the magnesia-carbon (MgO-C) refractory has been used in basic furnaces, electric arc furnaces, and steel ladles because of its high refractoriness, excellent thermal shock, and corrosion resistance [1, 2]. The presence of graphite, used as a carbon source in the MgO-C refractory, offers many desirable properties, such as corrosion resistance, due to its low wettability with a molten metal, and excellent thermal shock resistance, due to low thermal expansion, high thermal conductivity, and low elasticity. However, graphite in the MgO-C refractory is highly vulnerable to oxidation, causing deterioration in the mechanical properties of refractory owing to spalling phenomena and pore generation. Therefore, so-called antioxidants that have notable reactivity with oxygen are usually added into refractory batches during brick fabrication to impede the oxidation of graphite. These include metals/ alloys such as Al, Al/Mg, carbides such as B\(_2\)C and SiC, and borides such as CaB\(_6\) and ZrB\(_2\) [3]. An antioxidant used in the MgO-C refractory has stronger oxidation properties than graphite. Theoretically, it means that graphite does not react with oxygen until the oxidation of the antioxidant has progressed considerably. However, the antioxidant cannot totally prevent the oxidation of graphite. The antioxidant has further disadvantages, such as volume expansion, low purity, limited content, and high cost, and so on.

In this study, graphite was coated with a coating reagent, generally an inorganic precursor composed of a silicate and metal alkoxide. The generated coating layer will restrict the access of oxygen to graphite, and hence adequately control the oxidation of graphite. Therefore, the coating reagent should be homogeneously coated onto the surface of graphite to achieve sufficient coating efficiency of the inorganic precursor. Two key points regarding the coating reagent were considered: (1) a liquid phase coating reagent would be used to improve the coating efficiency and dispersibility of inorganic precursor on the surface of graphite, and (2) the coating reagent would be converted into solid phase by a sol-gel reaction to restrict totally the contact between oxygen and graphite [4, 5]. The antioxidant content was controlled to investigate the oxidation resistance of coated graphite in the MgO-C refractory. The content of phenolic resin used as an organic binder was also controlled to study the production of an ecofriendly MgO-C refractory. The oxidation behavior of the MgO-C refractory is discussed based on its observed microstructure and the measured fracture strength during the development of the new process.

Experimental Procedures

The commercial fused magnesia (MgO, particle...
Table 1. Formulations used to prepare MgO-C refractory and oxidation test conditions.

<table>
<thead>
<tr>
<th>Run Number</th>
<th>MgO (g)</th>
<th>Graphite (g)</th>
<th>Antioxidant (g)</th>
<th>Phenolic resin (g)</th>
<th>Heat treatment (hr)</th>
<th>Fracture strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run-1-1</td>
<td>0</td>
<td>2.97 ± 1.19</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Run-1-2</td>
<td>1</td>
<td>3.89 ± 0.70</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Run-1-3</td>
<td>11</td>
<td>1.18 ± 0.56</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run-1-4</td>
<td>22</td>
<td>1.07 ± 0.10</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run-2-1</td>
<td>0</td>
<td>1.88 ± 0.68</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run-2-2</td>
<td>1</td>
<td>3.34 ± 1.13</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run-2-3</td>
<td>11</td>
<td>6.35 ± 0.16</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run-2-4</td>
<td>22</td>
<td>1.67 ± 0.52</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>Run-3-1</td>
<td>0</td>
<td>1.83 ± 0.15</td>
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<td></td>
<td></td>
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<tr>
<td>Run-3-2</td>
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<td>3.13 ± 1.09</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run-3-3</td>
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<td>5.66 ± 1.34</td>
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<td></td>
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<td></td>
</tr>
<tr>
<td>Run-3-4</td>
<td>22</td>
<td>1.69 ± 0.09</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run-4-1</td>
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<td>2.57 ± 1.37</td>
<td></td>
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<tr>
<td>Run-4-2</td>
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<td>3.75 ± 0.15</td>
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<tr>
<td>Run-4-3</td>
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<td>2.98 ± 1.43</td>
<td></td>
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<td>Run-4-4</td>
<td>22</td>
<td>0.63 ± 0.04</td>
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</tbody>
</table>

Fig. 1. Schematic diagram showing preparation of the MgO-C refractory sample with high oxidation resistance.

Results and Discussions

The reactions involved in the preparation of the inorganic precursors, TEOS and NaOMe, used as coating reagent in this study are as follows.

Sol-gel reaction:

\[
\text{Si(OEt)}_4 + 4\text{H}_2\text{O} \rightarrow \text{Si(OH)}_4 + 4\text{EtOH} \quad (1)
\]

\[
\text{Si(OH)}_4 \rightarrow \text{SiO}_2 + 2\text{H}_2\text{O} \quad (2)
\]

\[
\text{NaOMe} + \text{H}_2\text{O} \rightarrow \text{NaOH} + \text{MeOH} \quad (3)
\]

where \(\text{Si(OEt)}_4, \text{Si(OH)}_4, \text{EtOH}, \text{SiO}_2, \text{NaOH}, \text{and MeOH}\) denote TEOS, silanol, ethyl alcohol, silica, sodium hydroxide, and methyl alcohol, respectively. TEOS is degraded to silanol and ethyl alcohol via a hydrolysis reaction (eq. 1), and silica is consecutively formed by a condensation reaction between silanol molecules (eq. 2). The series of reactions is generally referred to as a sol-gel reaction [6, 7]. NaOMe is hydrolyzed to form sodium hydroxide (eq. 3). The inorganic precursors of liquid phase coated on the surface of graphite are converted into solid phase via the above reactions. Therefore, the oxidation reaction of graphite can be controlled by the solid phase, affording a continuous coating layer. Furthermore, the synthesized SiO\(_2\) and NaOH are glassified to sodium silicate during heat treatment (eq. 4). We expected that this would lead to an increase in the mechanical properties of refractory.

Heat treatment:

\[
\text{SiO}_2 + 2\text{NaOH} \rightarrow \text{SiO}_2 \cdot \text{Na}_2\text{O} + \text{H}_2\text{O} \quad (4)
\]

Element analysis results for the graphite particles modified by coating reagent are shown in Fig. 2. To
impede the access of oxygen to graphite effectively, the coating reagent should be homogeneously coated on the surface of graphite and the coating efficiency of the inorganic precursor should be adequate. Si and Na atoms, which are the fundamental elements in the coating reagent, were evenly detected on the graphite surface, meaning that the inorganic precursors are uniformly coated on the graphite surface. Therefore, it can be inferred that the oxidation of graphite will be decreased by the oxygen-barrier effect of the coating layer.

Photographs before and after the combustion test carried out on the graphite particles, with and without modification, are shown in Fig. 3. When the graphite was modified with the inorganic precursors, the color of the graphite did not change after heat treatment at 1000 °C, as shown in Fig. 3 (b-2). This indicates that the coating layer is continuously and homogeneously formed on the graphite. However, in the unmodified graphite, the graphite was oxidized after heat treatment (Fig. 3 (a-2)), showing a brown color.

SEM images and element analysis results of the graphite particles, for different conditions, such as with and without coating reagent, and before and after the combustion test, are shown in Fig. 4. The unmodified graphite decomposed during the combustion test and the platy shape changed to an open structure. In addition, the element C was not perfectly detected, and only impurities appeared after the combustion test. However, in the case of graphite with a coating layer, all elements constituting the inorganic precursor and graphite, Si, Na, and C were detected, and the original graphite shape was fully retained. This indicates that the layer of solid phase formed from the inorganic precursors is desirably well coated on the surface of the graphite particles. Furthermore, it is expected that the inorganic materials generated by the sol-gel reactions (SiO₂ and Na₂O) are not degraded or evaporated during the combustion test, but are converted into sodium silicate in the glass phase.

This expectation is in agreement with the fracture strength values measured after heat treatment at 1000 °C for various time periods. The fracture strength values of the prepared MgO-C refractory samples are shown in Table 1. The fracture strength was measured to investigate the oxidation resistance of the refractory. Generally, the degradation of graphite by oxygen causes the creation of pores in the MgO-C refractory, leading to a decrease in fracture strength. However, in the refractory samples modified with the coating reagent, the fracture strengths of samples were significantly increased (runs 2 and 3), compared to those samples prepared without the coating reagent. This is because the oxidation of graphite is disturbed, or retarded, by the coating layer. The SiO₂ and Na₂O, formed by the
sol-gel reactions of the coating reagent, composed of TEOS and NaOMe, mixed with 40 and 60 wt%, is transformed into SiO$_2$ - Na$_2$O under heat treatment at 1000 °C. Furthermore, MgAl$_2$O$_4$ in the spinel phase is formed by MgO and Al$_2$O$_3$ under heat treatment at 1000 °C. The SiO$_2$ - Na$_2$O and MgAl$_2$O$_4$ contribute to the improvement in the mechanical properties of the refractory. Namely, the mechanical properties of MgO-C refractories are significantly increased before the oxidation of graphite commences. Therefore, the increased strengths of refractory samples after heat treatment for specific periods of time (hr) arose from the spinel phase (MgAl$_2$O$_4$) generated between MgO and Al$_2$O$_3$ (except in run 4) and the glass phase (SiO$_2$ - Na$_2$O) synthesized from SiO$_2$ + Na$_2$O (except in run 1). However, in the unmodified refractory (run 1), the strength values decreased significantly after heat treatment for 11 hr, whereas the strength values of the samples prepared with the modified graphite sharply increased after heat treatment for 11 hr, even at 50% content of antioxidant and phenolic resin (run 3). In the sample without antioxidant and with 50% content of phenolic resin (run 4), the fracture strengths of samples were similar to those of samples prepared without the coating reagent (run 1). Consequently, it is evident that graphite coated with inorganic precursors is desirable to prepare MgO-C refractories with high oxidation resistance. Furthermore, the fracture strength is unaffected by the content of phenolic resin.

**Conclusions**

Graphite was coated with an inorganic precursor to prepare a magnesia-carbon (MgO-C) refractory with high oxidation resistance. The liquid phase coating reagent was converted into the solid phase by a sol-gel reaction, which improved the oxygen barrier effect in graphite. The shape of the unmodified graphite was completely deformed and the color changed, whereas no changes were observed in the graphite coated with the inorganic precursors of TEOS and NaOMe. The strengths of the refractory samples gradually increased due to the spinel structure of MgAl$_2$O$_4$ and the glass phase of SiO$_2$ - Na$_2$O, up to specific heat treatment conditions of 11 hrs at 1000 °C, except in the samples with the unmodified graphite. In the samples prepared with the modified graphite, the fracture strengths were significantly improved with up to 50% antioxidant. Even though antioxidant was not added in the samples with the modified graphite, their strengths were similar to the samples with the unmodified graphite. Thus implies that the coating layer is highly efficient for the preserving graphite in oxygen. Furthermore, it is possible to reduce the content of phenolic resin by the solid phase generated from the coating reagent. Consequently, an ecofriendly MgO-C refractory with high oxidation resistance was successfully prepared using modified graphite.

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**References**