EFFECTS OF ALUMINUM, SILICON AND FERRO-SILICON ANTI-OXIDANTS IN MgO-C REFRACTORIES

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Abstract...Three different materials (aluminum, ferro-silicon and silicon) were used as anti-oxidants in order to prevent the decarburization process and to keep and/or increase the final properties in MgO-C refractories. Their effects were compared by measuring the physical and mechanical properties as well as oxidation and the resultant phases and microstructures, in the temperature range of 200-1600 °C. High temperature oxidation was measured up to 1000 °C. The impurities of the aluminum and silicon powders were less than 1%. The ferro-silicon contains 2-5% Al, and 10-20% Fe. Results indicate that the oxidation of the samples were much better in the ferro-silicon than aluminum and silicon cases. The CCS measurements indicate more improvements due to the effects of ferro-silicon than silicon case. Results indicate that aluminum is more effective at low temperature. However, at higher temperatures, the other two anti-oxidants are more effective. The phase analysis indicates that the reaction of M2S phase with other phases might cause some reduction of high temperature behaviors. Also, Phase analysis indicates the formation of MgO-FeO/Fe2O3 phase, aluminum and silicon carbides as well as Spinel phase in the samples.

Key Words MgO-C Refractory, Anti-Oxidants, Aluminum-Silicon, Ferro-Silicon

1. INTRODUCTION

MgO-C refractories have been used in various applications with different performance, depending on where they are located in the service. It has been reported that MgO-C and MgO containing bricks with graphite can serve under more sever conditions. This is due to the special properties of these refractories, such as relatively low thermal expansion coefficient, high thermal conductivity, good...
thermal shock resistance and low contact angle with molten materials. The oxidation of the carbon in this kind of refractories is one of the main problems of the refractories. It has been shown that this behavior causes the reduction of the strength and reduces the lifetime of the products.

It is reported (1-7) that one can reduce the oxidation by using different anti-oxidants and via a complex reaction between these additives and refractory component. Although there is not a unique way to explain the behavior of different additives, but previous research results indicate the formation of gaseous compound and molten and glassy phases at porosity which can prevent the diffusion of oxygen into the brick and reduce carbon oxidation. During the reaction, carbides, nitrides and oxide phases form which are very important and play an important rule in final behavior of the refractories.

The phase transformations and thermo-chemical reaction are very complicated, but there are useful information in the articles. The interpretation of

<table>
<thead>
<tr>
<th>Sintered magnesia</th>
<th>Chemical composition</th>
<th>Bulk density g / cc</th>
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<td></td>
<td>MgO</td>
<td>CaO</td>
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<tr>
<td>W%</td>
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<th>Ash of the graphite</th>
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<td>CaO</td>
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<tr>
<td>W%</td>
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<table>
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<tr>
<th>Metallic silicon</th>
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<tr>
<td>W%</td>
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Figure 1. SEM picture of the flaky graphite.
the results depends on the kind of raw materials and additives (3-10).

Different types of additives have been tested such as aluminum, silicon, magnesium alloys and carbides. It was observed (5-15) that with these types of additives, MgO-C brick improves and or maintains most of its properties. It should be mentioned that one must pay attention to negative aspects of additives, especially for high temperature properties.

In this paper, the effects of three anti-oxidants were

**Figure 2.** Strength vs. temperature of the sample with aluminum.

**Figure 3-A.** The formation of spinel phase in the system.

**Figure 3-B.** The formation of aluminum carbide within the system.
compared; aluminum, ferro-silicon and silicon, and the formation of the different phases and properties were evaluated.

2. EXPERIMENTAL PROCEDURE

The raw materials used in manufacturing of MgO-C refractories were Chinese sintered magnesia, Canadian graphite, Novaluk resin (Sepahan Chemistry Co., Isfahan, Iran), silicon, and aluminum and ferro-silicon powders as additives. The amount of antioxidant additives was 0-5%. The magnesia contained 97% pure MgO with CaO / SiO₂ ratio of 2.16 (Table 1 shows the chemical analysis of the magnesia). The average of bulk density measured by user was approximately 3.3 g/cm³. The graphite was flaky one (Figure 1 shows the SEM picture of the
flake) with 1.41% ash (Table 2 shows the chemical analysis of the ash). Ferro-silicon contained 78% silicon and SiO₂, 2% Al, and about 20% Fe. The industrial grades of silicon with impurities of less than 1% (Table 3 shows the analysis of the silicon) and aluminum powders with impurities of less than 0.1% were used.

The mixed raw materials were formed into a cylindrical shape with dimension of 30 mm (Diameter), 46 mm (Height) with 250-350 MPa pressure. The samples were tempered at 200 °C for 24 hrs. Then they were located within graphite powder bed and heated at 670 °C, 1070 °C and 1570 °C for 3 hrs and after that the furnace was cooled-down, normally.

The physical properties such as density and apparent porosity were measured (apparent porosity was measured by using kerosene liquid). Cold crushing strength (CCS) was measured with loading rate of 0.2 KN/S. The oxidation of the sintered specimen was conducted in air up to 1000 °C. The heating rate was 60 °C/h. After holding 4 hrs at maximum temperature, it was cooled down to room temperature and the depth of oxidation layer was measured. The microstructure and phase analysis were conducted by using SEM and XRD.

For determination of low content phases, such spinel and aluminum carbide, after grinding the samples, and separating the MgO grains and lowering its amounts, the reminder was analyzed. In this way, the XRD showed existence of other phases. These results were combined with point EDAX evaluation to confirm the formation of those phases.

3. RESULTS AND DISCUSSION
The effect of temperature on CCS of different specimen with and without anti-oxidant has been shown in Figures 2-6.

The CCS of samples without anti-oxidant at 200 °C was higher than at room temperature, due to the effects of polymerization of the adhesive. At higher temperature, the CCS of the specimen was lowered which is due to the pyrolysis of the resin and the destruction of the polymeric structure. Some preliminary data also, indicates the partial oxidation of carbon up to this temperature (13-14).

In the specimen with anti-oxidant and at low temperature, a similar behavior was observed which is due to polymerization process. However, at higher temperature different behaviors were observed.

The sample with aluminum additive, behaves as previous case up to 670 °C. After this temperature,
by forming aluminum containing ceramic bonding, the strength increases and continues to rise at higher temperature, too, (Figure 2 shows the Strength vs. Temperature of the sample with aluminum.). This behavior was observed in the samples with aluminum contain up to 3%. At higher amount of Al,
the strength starts to decrease. The formation of spinel and aluminum carbide phases (Figure 3-A) and destruction of some ceramic bonds might be the main reason for this behavior. This was confirmed by the XRD analyses that showed higher amounts of spinel and carbides phases. Higher amount of
Figure 9-A. Hydration vs. Temperature of the samples with Al.

Figure 9-B. Hydration vs. Temperature of the samples with Si.
aluminum and lower surface energy of anti-oxidant result higher amounts of these phases. This was completed by SEM studies (Figure 3-B). The results indicate the formation of different forms of aluminum, aluminum hydroxide and calcium hydroxide in the system. Formation of hydroxide was (probability) due to the hydration of the calcium oxide (comes from MgO raw material) and aluminum carbide phase. According to the previous results (13-15), hydration of aluminum carbide causes volume expansion, which can cause internal stress and/or create a path for air diffusion into the system (a path for air to reach inside the sample). This in turn can cause the destruction of the internal structure.

\[
\text{Al}_4\text{C}_3 + 12\text{H}_2\text{O} \rightarrow 3\text{CH}_4 + 4\text{Al(OH)}_3
\]

Figure 9-C. Hydration vs. Temperature of the samples with ferro-Silicon.

In the samples containing silicon (as an anti-oxidant), up to 1070 °C, did not show any special phenomenon, except the same behavior as in original case of the sample without any anti-oxidant. The only phenomenon that one might expect is the surface oxidation of silicon particles. So the strength decreases as in the samples without anti-oxidant. At higher temperature (T>1070 °C), the strength starts to increase, (Figure 4), which might be due to the formation of ceramic phase such as M$_2$S (forsterite), SiC, glassy SiO$_2$ and also low temperature ceramic phases such as mervinite (C$_3$M$_2$S$_3$) or montisilite (CMS). The XRD studies reveal the existence of forsterite and SiC phases in the system (Figure 5).

These phases can cause the graphite particles to bond together as well as to other ceramic phases.

Figure 6 shows the effect of temperature on CCS of the samples containing ferro-silicon. The general behavior of this anti-oxidant is similar to silicon. As a result, there was a reduction of the strength up
to 1070 °C. After that, it starts to rise, but there are a few differences, especially at higher temperature and lower amounts of Si. Also, it seems that the existence of Fe in ferro-silicon might be one of the main reasons for the observed differences. According to Figure 6, the final strength of the samples is lower than the silicon case.

Beside the silicate phases, it is possible to have phase and/or phases in the system, which can reduce the mechanical properties at high temperature. Phase analysis by XRD indicates the formation of similar phases (as in the silicon case), as well as Fe₂O₃ and iron spinel in the system, which has been shown in Figure 7.

Figures (8 A-B-C) show the effect of temperature on the apparent porosity.

In the sample without anti-oxidant, the porosity increases with temperature. The effect of temperature on binder materials and carbonization of resin and graphite can understand this. It can also be partially due to the volume expansion of the phases. Samples with anti-oxidants show some differences in this case.

At lower amounts of aluminum and at lower temperature, the anti-oxidant prevents the carbon oxidation and results in lower porosity in the system (Figure 8-A). The data indicates a small increase of porosity at higher amount of aluminum. This effect might be due to the nature of formed phases, specially, porous spinel and flaky-shape Al₄C₃ particles. According to our observation these phases initially prevent the oxidation process, but by increasing their amounts and opening the structure (increasing the porosity), oxygen can diffuse into the system. The XRD result and SEM pictures show the formation of these phases in the system containing Al additive (Figures 3 A and B).

In the case of silicon additive, the amount of porosity is lower than the samples without anti-oxidant (Figure 8-B). The filling pores with Si additive can explain this observation. With increasing of temperature up to 1070 °C, the porosity continues to increase. At T> 1070 °C, porosity starts to decrease which can be understood from the formation of forsterite and silicon carbide in the system (Figure 5). The decrease of the porosity was more significant at lower amounts of Si anti-oxidant. This phenomenon has significant effect on the hydration of the samples.

The effect of temperature on the porosity of the samples containing ferro-silicon anti-oxidant has been shown in Figure 8C. According to this, the behavior of the system with and without anti-oxidant does not change significantly after annealing at 200 °C. At 670 °C, the overall the behavior is similar to silicon anti-oxidant. But due to the existence of Al and Fe in the system, some differences have been observed. As the temperature increases up to 1070 °C, the overall porosity is lower than in the Si case. This might be due to the effect of other impurities (such as Al and Fe in the ferro-silicon).

At temperatures above 1070 °C, the system acts like silicon, although the overall porosity is somehow lower. By increasing the amount of ferro-silicon, the porosity has been lowered significantly. This can be understood by the formation of MF, M₂S, SiC and some other phases (Figure 7). It is believed that according to MgO –FeO / Fe₂O₃ phase diagram, after the oxidation of Fe and formation of FeO and /or Fe₂O₃, this oxide can dissolve in MgO and form solid solution.

These phases form at the porosity and lower the amount of the porosity and also, lower the hydration of the samples.

The hydration of the samples was measured by the depth of carbon removed layer from the surface. Figures (9-A, B and C) show the effect of temperature on hydration process in the samples with different additives.

Data of the samples without anti-oxidant indicates an increasing hydration with temperature. It has been mentioned in the literature that this process begins from active surface defects such as point and line defects and pores. One should, therefore, expect to have more hydration by increasing the porosity in the system.

By adding aluminum anti-oxidant, the hydration process was lowered up to T=670 °C. It is believed that this is due to oxidation of aluminum and formation of other ceramic phases. The data show that at higher temperature (T > 670 °C), although there is some hydration in the samples, but the overall depth of carbon removed layer is lower than the samples without aluminum. The amount of open porosity and higher speed of carbon and oxygen reaction at high temperature are important factors for this process. According to the graph (Figure 9-A), the higher the amount of aluminum, the lower the depth of carbon removed layer.

Figure 9-B shows the effect of temperature on
hydration process in the samples with silicon additives. In the sample treated at low temperature (T<1070 °C), the effect of Si on hydration is minimal. It is believed that the small differences in samples with different amount of Si at lower temperature (T<1070 °C) is due to absorption of oxygen on the surface of Si. The Si additive causes some reduction of hydration process in the sample treated at higher temperature (T>1070 °C). The higher the amount of silicon, the lower the depth of carbon-removed layer would then be. When temperature exceeds 1070 °C, Si atoms start to react with other materials and oxygen in the system and form some phases, which are resistive to oxidation or act as a barrier for further more oxygen diffusion. This phenomenon is more significant at higher temperature (T>1500 °C). This was studied with SEM; specially the boundary between removed and remained carbon layers. It was observed that the formation of ceramic phases between particles act as a barrier, and increase the oxidation resistance of the samples.

In the case of ferro-silicon, the thickness of the carbon removed layer decreases with adding more anti-oxidant (Figure 9-C). A comparison between three anti-oxidants shows that ferro-silicon is more effective than silicon at lower temperature, (T<1070 °C). The existence of Fe and Al metals and other impurities in ferro-silicon can explain this observation. Formation of low temperature phases and filling the open porosity are the main reasons for lowering the oxygen diffusion into system. At higher temperature (when T>1070 °C), ferro-silicon acts like silicon.

4. CONCLUSIONS

The effects of three anti-oxidants (aluminum, ferro-silicon and silicon) were compared in MgO-C refractories. The CCS of the samples with anti-oxidants was higher than the samples without anti-oxidants. Samples with anti-oxidants show lower apparent porosity. Hydration of the samples is lowered significantly by using anti-oxidants.

The results indicate that the formation of ceramic phases reduces the porosity and increases the CCS and improve the oxidation resistance and hydration of the refractory.

The overall results show that aluminum is more effective anti-oxidant than silicon at low temperatures, but decomposition of aluminum contains ceramic phases at higher temperature reduces its effect. As a result, ferro-silicon and silicon are more effective anti-oxidants than aluminum at higher temperatures.

The results indicate that ferro-silicon is more effective than silicon, at moderate temperatures.

5. REFERENCES