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Corrosion Study of MgO-C Bricks in Contact with a Steelmaking Slag

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Abstract

The MgO-C bricks are extensively used as lining work on different steel containers. Due to the high temperatures of the process, these refractories are subjected to severe wear and corrosion processes, principally in the area of contact with the slag. These slags have variable contents of CaO, SiO₂, Al₂O₃, MgO and FeO, varying in composition according to the process stage. In this paper, cup tests were performed at 1650 °C during 2 hours in air, using three kinds of commercial MgO-C bricks. They were put in contact with a high basicity slag. The corrosion degree and decarburization level suffered by the refractories were analyzed and compared. Microstructural observations were performed in order to postulate the probable corrosion mechanisms acting on each material.

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1. Introduction

The MgO-C (magnesia-carbon) bricks are widely used in the steel industry. The success of the use of basic magnesia-carbon refractory in different steel containers is based on its good properties of resistance to erosion, corrosion and thermal shock. Degradation of these materials results from the interactions among these chemical, thermal and mechanical phenomena. These linings suffer corrosion and wear processes that take place mainly in the...
area of contact with the slag. Steelmaking slags are complex mixtures of various oxides including: CaO, SiO₂, Al₂O₃, MgO, and FeO. Furthermore, the compositions of the slag can vary according to the stage of the process considered.

These refractories have resulted in better performance in the steel manufacturing process, Pena et al. (2010). Basically consist of grains (or aggregates) of MgO (1-7 mm in size) representing about 70 wt% of the refractory and the matrix (or filler) composed of graphite and finer magnesia (50-500 μm). Refractory brick is complemented by bond (or cement), which is used to form a strong connection between the matrix and aggregates, and the addition of antioxidants such as: Al, Si, Mg, B₄C, SiC, CaB₆ and ZrB₂, Zhang et al. (2001). The compositions usually contain 80-93 wt% MgO, between 7-20 wt% graphite and the additions of antioxidants are between 2-3 wt%, Baudin et al. (1999).

The degree of corrosion resistance of these materials is linked to percentage, size and quality of the MgO grains among other variables. These MgO grains should have a low level of impurities (SiO₂, Fe₂O₃ and B₂O₃) and the porosity of grains should be low, Lasquibar and Ribera (1989). The bond and graphite containing these materials are other important factor to determine their corrosion resistance. While carbon gives higher thermal conductivity, the main drawback is that the carbon is oxidized in air atmosphere (at process temperature), generating pores in the structure of the refractory. The presence of these pores promotes the penetration of the slag and consequently decreases the protective quality of the lining. Carbon is incorporated by natural graphites and it should be noted its impurities, since they influence its oxidation. To minimize oxidation, antioxidants are added (non-oxide powders) which react with oxygen to form gases that move in opposite direction to the entry of O₂, retarding the diffusion of oxygen into the refractory. Moreover, bond material must moisturize ceramic grains and graphite to press them properly. For this reason, resins and/or derivatives of the pitch are used. Although the bond contributes with carbon, which protects the refractory before the attack of the iron oxide and calcium oxide, they burn easily and the protection appears to be transient, Lasquibar and Ribera (1989).

In the present work different grades of magnesia-carbon bricks were characterized. The resistance to the attack by a slag with a high ratio CaO/SiO₂ was analyzed through a static corrosion test at 1650 °C. The microstructures observed after test, were associated to the degree of corrosion and decarburization suffered by the samples.

2. Experimental

Three MgO-C bricks of different qualities -designated as A, B and C- were analyzed. Samples of the original bricks were obtained to determine porosity and bulk density, which were determined by the Archimedes method using kerosene as the immersion liquid.

In the static corrosion test (cup test) was used a high basicity slag whose chemical composition, determined by X-ray fluorescence, is listed in Table 1. According to these values, the binary basicity index of slag CaO/SiO₂ = 6.7. For the cup test were prepared crucibles with the following dimensions: base = 5 cm x 5 cm and height = 7 cm. A hole ~ 20 mm in diameter and ~ 30 mm in depth was made on each crucible.

<table>
<thead>
<tr>
<th>Mn</th>
<th>MgO</th>
<th>CaO</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>FeO</th>
<th>Cr₂O₃</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15</td>
<td>7.04</td>
<td>57.4</td>
<td>25.3</td>
<td>8.55</td>
<td>0.53</td>
<td>0.02</td>
<td>0.54</td>
</tr>
</tbody>
</table>

Table 1. Chemical composition of the slag.

The amount of slag used in each crucible was 4 g, covering up to approximately half depth of the hole. All crucibles (brick + slag) were heat treated at 1650 °C (2 hours in air), with heating rate of 5 °C/min. In this case, the oxidizing atmosphere was used to evaluate the oxidation degree of bricks measuring the thickness of decarburization layer on the outer wall of the crucible.

After the corrosion test, the three crucibles were embedded in resin, to prevent degradation to the environment and cut in half to observe the structures developed in reacted areas. After cutting, the exposed surfaces were polished with SiC papers and diamond paste.
The observations of the structure were performed by light microscopy (Olympus SZ61 and Olympus GX51) with image analyzer system (Leco IA 32) and scanning electron microscopy (SEM) in a Philips XL30 CP microscope, the latter with energy dispersive analysis (EDS).

3. Results

3.1. Physical properties and microstructure of the bricks

The values of porosity and bulk density of the bricks are listed in Table 2. On order to determine these values five specimens of each brick were used.

Table 2. Bulk density and open porosity of the MgO-C bricks.

<table>
<thead>
<tr>
<th>Brick</th>
<th>Density (g/cm³)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2.94</td>
<td>2.2</td>
</tr>
<tr>
<td>B</td>
<td>3.00</td>
<td>1.9</td>
</tr>
<tr>
<td>C</td>
<td>2.97</td>
<td>2.7</td>
</tr>
</tbody>
</table>

Previous to the corrosion test, the microstructure of the bricks was observed by light microscopy. Figure 1a shows an image (x100) of as received brick A. It is observed a grain of electrofused-MgO (ME) with sub-grains inside and the matrix containing finer MgO grains (size < 500 μm), graphite and antioxidants.

Fig. 1. Microstructure of brick A (virgin): (a) fused MgO grain, and (b) detail of the matrix.

Figure 1b (x200) shows, in greater detail, the matrix of brick A. This highlights the presence of antioxidants (A) and graphite (G) surrounding small grains (≥ 100 μm) of fused magnesia (ME). The antioxidant material is identified by its brightness (size < 50 μm), while graphite is presented as "flakes", Lee et al. (2004).

In the brick B (Figure 2a), electrofused (ME) and sintered (MS) MgO grains of different sizes were observed. Fused-MgO grains are dense while the sintered-MgO grains have a porous microstructure. In general, the ME grains are greater than the MS ones. The matrix shows the presence of antioxidants (bright spots) and "flakes" of graphite.

Finally, the brick C (Fig. 2b) shows large amount of sintered periclase grains and a higher area occupied by fine particles (<300 μm). In this area both type of magnesia grains, fused and sintered, are present. Visually, in brick C there is a higher percentage of sintered-MgO than in brick B.
In summary, according to optical microscopy analysis, a greater volume occupied by the fine fraction (matrix) is observed in the brick C. In turn, this brick has the highest amount of sintered periclase grains. Moreover, in the brick A the presence of sintered MgO grains is not observed.

3.2. Microstructure of bricks after corrosion test

After to the corrosion test, the cross section of the crucibles clearly shows the decarburized area (oxidation of graphite) in the immediate region to the outer wall. It is clear that this zone has not been in contact with the slag. Figure 3 shows the decarburized layer of brick A, exposed through an optical microscope image (x 0.67).

Thickness of decarburized layer ($L_D$) was measured in the three crucibles, taking the average of 50 measurements along the entire wall. Values (average) of $L_D$ obtained for each sample were: $L_D$ (A) = 2.6 mm, $L_D$ (B) = 3.2 mm and $L_D$ (C) = 3.7 mm
Regarding the degree of corrosion suffered by the refractory, it was not possible to determine a thickness of penetration of the slag on brick A, since there are only few areas where the slag has reacted with magnesia grains as presented in Figure 4a.

![Image 1](image1)

![Image 2](image2)

Fig. 4. (a) Reacted MgO grain in brick A, and (b) SEM image of a magnesia grain.

Oxide content of the phase called "slag" and identified as S_A in Figure 4a, is presented in Table 3. It corresponds to an approximate composition of the original slag (Table 1) somewhat richer in Mg and Fe oxides.

<table>
<thead>
<tr>
<th>zone</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>CaO</th>
<th>Fe₂O₃</th>
<th>SO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>S_A (slag)</td>
<td>13.89</td>
<td>27.71</td>
<td>9.25</td>
<td>47.82</td>
<td>1.33</td>
<td>-</td>
</tr>
<tr>
<td>T_A (triple point)</td>
<td>34.04</td>
<td>14.09</td>
<td>23.06</td>
<td>25.52</td>
<td>0.54</td>
<td>2.75</td>
</tr>
</tbody>
</table>

The same table shows the EDS analysis of the area marked as "triple point" (T_A in fig.4a), in which the relationship CaO/SiO₂ ~ 1.1. At this point the MgO content is increased by the proximity of magnesia grain.

A electrofused periclase grain (unreacted) of brick A is shown in Fig. 4b. This image shows cubic fracture in the grain and a liquid/white area (L) with a ratio CaO/SiO₂ ~ 2.4. EDS analysis of both phases (grain and L phase) are listed in table 4.

<table>
<thead>
<tr>
<th>zone</th>
<th>MgO</th>
<th>Al₂O₃</th>
<th>SiO₂</th>
<th>CaO</th>
<th>Fe₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO grain</td>
<td>94.21</td>
<td>0.93</td>
<td>1.57</td>
<td>2.04</td>
<td>1.25</td>
</tr>
<tr>
<td>L (white phase)</td>
<td>19.86</td>
<td>0.87</td>
<td>23.12</td>
<td>55.64</td>
<td>0.50</td>
</tr>
</tbody>
</table>

The brick B, as well as brick A, has no continuous reaction zone, but rather isolated regions where penetration by the slag may be detected. Figure 5 shows a reaction zone: slag-refractory B, where magnesia grains dissolved in the slag (area S_B) are observed. Here, a part of the brick has been detached from the mass of the refractory as a product of reaction with the slag.
In the same figure, there are various triple points within the MgO grain (point $T_B$). The EDS analysis of the triple point $T_B$ is presented in Table 5. It is noted that the CaO/SiO$_2$ ratio in the triple point is $\sim 1.1$ (similar to the triple point $T_A$).

<table>
<thead>
<tr>
<th>Zone</th>
<th>MgO</th>
<th>Al$_2$O$_3$</th>
<th>SiO$_2$</th>
<th>CaO</th>
<th>Fe$_2$O$_3$</th>
<th>P$_2$O$_5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S_B$ (slag)</td>
<td>20.50</td>
<td>27.22</td>
<td>6.04</td>
<td>43.81</td>
<td>1.71</td>
<td>0.72</td>
</tr>
<tr>
<td>$T_B$ (triple point)</td>
<td>38.02</td>
<td>1.10</td>
<td>28.92</td>
<td>30.70</td>
<td>0.45</td>
<td>0.82</td>
</tr>
</tbody>
</table>

The brick C has the highest degree of degradation by the slag attack showing significant detachment of the refractory material. Figure 6a presents an attacked area with the presence of MgO grains disaggregated ($\leq 500$ μm) immersed in a liquid phase ($S_C$). In this picture is observed a large sintered MgO grain ($\sim 3$ mm).

Table 6 shows the EDS analysis of the phase called "slag" ($S_C$) and the area of a "triple point" ($T_C$) located in the center of the sintered-MgO aggregate.
Table 6. EDS composition of phases analyzed in Figure 6.

<table>
<thead>
<tr>
<th>zone</th>
<th>MgO</th>
<th>Al2O3</th>
<th>SiO2</th>
<th>CaO</th>
<th>Fe2O3</th>
</tr>
</thead>
<tbody>
<tr>
<td>S_c (slag)</td>
<td>14.14</td>
<td>29.04</td>
<td>6.02</td>
<td>49.37</td>
<td>1.44</td>
</tr>
<tr>
<td>T_c (triple point)</td>
<td>27.86</td>
<td>8.01</td>
<td>21.16</td>
<td>42.29</td>
<td>0.69</td>
</tr>
<tr>
<td>MgO-without attack</td>
<td>91.96</td>
<td>2.17</td>
<td>2.24</td>
<td>2.81</td>
<td>0.83</td>
</tr>
</tbody>
</table>

The basicity at the triple point is CaO/SiO2 ~ 2.0. The same table lists an analysis (EDS) of a sintered-MgO grain no corroded, whose image is presented in Figure 6b. In this case the purity of magnesia grain is approximately 92 wt% and the ratio Ca/SiO2 ~ 1.2.

4. Discussion

Although the three materials have low open porosity (<3%), due to the higher percentage of MgO grains sized <100 μm displayed in the matrix, and the large proportion of sintered MgO grains (with internal pores), make the brick C is more prone to slag attack, Zhang et al. (2000). This is reflected in the highest degree of degradation observed in this material.

According to the dissolution mechanism of the refractory into the slag, it may be direct (congruent) or indirect (incongruent), Lee and Zhang (1999). In the case of direct mechanism, the attack is controlled by the reaction rate in the slag-refractory interface or diffusive transport through the slag. The indirect process is controlled by diffusive transport through the slag or a new solid phase formed in the slag-refractory interface. Previous work, Zhang and Lee (2000), with this type of refractories emphasizes the formation of a spinel layer (MgO-Al2O3) surrounding MgO grains, thus promoting an incongruent mechanism of corrosion. Although the original slag composition has a content of Al2O3 (~25%) which could justify spinel formation, analyzing the equilibrium diagram CaO-MgO-SiO2-(25%) Al2O3, spinel formation is not expected on MgO-slag interface due to the high ratio CaO/SiO2 (~ 7) of the slag. In the present study the presence of MgO-Al2O3 was not detected in any of the analyzed reaction zones.

According to the wear mechanisms of magnesia bricks, slag rich in lime (CaO), alumina (Al2O3) and silica (SiO2) penetrates between the grains of MgO by capillarity and chemical reaction. The formation of liquid silicates among MgO grains, leads to decohesion thereof, causing its detachment from the mass of the refractory. Carbon presence prevents penetration in the area of the matrix because the carbon does not melt and is not wetted by slag. However, both Fe oxide and silica oxidize carbon.

In the brick C, which has a large amount of aggregates of sintered magnesia, the amount of impurities plays an important role, since these impurities may maintain separate MgO crystals within the aggregate and not allow direct joining during MgO-MgO sintering production, Landy (2004). In this case, the ratio CaO/SiO2 plays a fundamental role. Then, during the high temperature metallurgical applications, the softening of grain boundaries leads to loss of the aggregate stability generating critical paths for entry of slag. Considering that in the triple points and grain boundary of sintered MgO aggregates of brick C, the relationship CaO/SiO2 is ~ 1.2 (see Fig. 6b and Table 6). Then, using the phase equilibrium diagram MgO-CaO-SiO2, one can expect the presence (among aggregates of MgO) of a combination of phases merwinite (3CaO·MgO·2SiO2) whose melting temperature T_M ~ 1575 °C and monticelite (CaO·MgO·SiO2) with T_M ~ 1490 °C.

For the brick B, it is considered that the zone of greater reaction with the slag is conducted through sintered grains or smaller electrofused MgO, since they can be more easily disaggregated or dissolved by the slag rich in CaO. According to the composition of the triple point, it is again possible to expect the formation of both phases monticelite and merwinite that at the test temperature (1650 °C) promote the formation of liquid.

For brick A, the greater resistance to the slag attack may be associated with better quality of MgO grains (electrofused). In this case, in triple points the ratio CaO/SiO2 is approximately 1. However, in this case significant content of alumina (~ 25%) is observed. Thus, considering the equilibrium diagram MgO-CaO-SiO2-(25%) Al2O3, it can be expected the presence of both merwinite and dicalcium silicate (2CaO·SiO2), the latter with liquid formation temperature at ~ 2130 °C.
It is noteworthy that, due to the presence of impurities such as iron oxide can be expected that the liquid formation might be present at lower temperatures.

In all cases, it is observed that the slag attack (rich in CaO) proceeds through the grain boundaries in MgO aggregates and through the fine grains zone (matrix). This differs from attack by a slag rich in FeO, where penetration takes place by grain boundaries and through MgO grains (inter and intra-granular attack) as reported by Galbiatti et al. (2003).

5. Conclusions

The bricks A and B presented higher number and size of electrofused-MgO grains, while brick C had a higher proportion of fines and sintered MgO grains. The quality of the periclase raw material of bricks A and B appears to play a major role in the minor extent of corrosion suffered by both materials.

The analysis of microstructure of the corroded zone allowed to observe that the penetration of slag, with high basicity (CaO/SiO₂ ~ 7), is carried by the grain boundaries of MgO, primarily moving through the fine grain region (matrix), and disaggregating sintered MgO grains.

Acknowledgements

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References


