Magnesia-Carbon Brick: a Retrospective

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Introduction

The steel industry is the biggest consumer of refractories and the main user of magnesia based ones. Consequently, improvements and new developments of magnesia based refractory types reflect the demands of this industry.

The continual need to increase process vessel availability, improve life and decrease refractory lining cost has been the driver of many technological changes. The development of what today is understood as a magnesia-carbon brick, a resin bonded magnesia brick with graphite and often antioxidant additions, resulted from the quest to develop better refractories for the high wear areas of converters. This overview will cover the early days of magnesia-carbon brick and some of the developments that have taken place with this technology.

History

Since, at least, the 1870s, pressed basic raw materials, in particular bonded dolomite, mixed with pitch have been available for lining vessels for use in different processes.

The advent of the BOF in the late 1950s and early 60s was accompanied with developments in tar bonded dolomite, mag-dolomite and magnesia brick [1]. High strength bonded MgO brick was introduced in the late 1960s and by the 1970s BOFs were being lined with pitch bonded brick or forced into the brick's pores as in burned pitch bonded brick. The graphite used in refractories is a naturally occurring flake material which was the beginning of lining developments [2]. Pitch bearing brick required some manufacturing fine tuning in order to facilitate their installation at the user's site as excess pitch covered the brick bonding them together, while in transit to the installation site, made them slippery to handle and modified their dimensions. During this time period the expected converter life was in the 200 to 500 heat range. By the late 1970s the need for better refractories became acute as a result of moving from ingot to continuous casting which increased the maximum temperature of the steel in the converter from the 1500 oC - 20,000 to 35,000 heats while a European one after 2,500 to 3,000 heats [3] and these numbers have almost doubled by today.

Magnesia

Much confusion can arise from the term magnesia refractory. The American Society for Testing and Materials (ASTM) defines it as “a dead-burned refractory material consisting predominantly of crystalline magnesium oxide”, but that is not the terminology found in the literature. The terms magnesite, magnesia and MgO are used interchangeably to signify magnesium oxide. In addition, older publications use the term periclase for MgO, even though this is the name of the naturally occurring mineral of that composition. Over time different raw materials have been the source for the MgO used in refractories. These changes have been driven by technology, economics, availability and the expectation of continuously improving refractory properties. Today, most magnesia refractories contain sintered and/or fused grain, both being a synthetic product. Sintered magnesia, also called dead burned magnesite, is produced by heating, sintering, a Mg bearing mineral or a synthetic compound to drive off volatile gasses. When the resultant product is further beneficiated by melting in an electric arc furnace, it becomes fused magnesia. The amount and chemistry of the impurities present affect the high temperature grain properties. Many papers contain sections discussing the properties of magnesia grain, the changes that have taken place in its production over time and the effect of impurities at high temperature [1,5,6, etc.]. It should be noted that there has been a continuous improvement in magnesia grain quality. This has resulted in the availability of bigger grains with higher density and the continuous lowering of the SiO2 and other impurities which lead to slow melting point phases at high temperature [6]. The decrease in SiO2 can be observed in the changes in lime to silica ratios from 2.6. In the early days, to about 4 with improvements in technology and the current level of 10 or higher. Use of these improved grains has contributed to the production of brick with better physical properties and slag resistance.

Carbon

Carbon is added to refractories because it is not wetted by slags. Traditionally, refractory chemical corrosion resistance was improved by decreasing the size or number of pores, but this could make them more sensitive to thermal shock damage. Consequently, methods were developed to incorporate carbon to fill to the spaces between the magnesia, or other refractory oxide grains. The carbon then forms a film blocking the slag penetration thereby minimizing the damage it causes the brick. The early carbon sources were tars which have been replaced by pitches or resins. The carbon level so achieved can be further increased with the addition of carbon black and graphite.

The concept of adding a metallic component to a refractory was already patented in 1935 [11], a long time before the technology was available to produce magnesia-carbon brick. In 1983 a patent for the addition of metal Mg to a chemically bonded brick was issued. The idea was to increase the amount of Mg2 gas generated which should lead to a thicker dense zone [22]. This concept was reduced to practice, and a commercial product was successfully manufactured. To carry out production several hurdles had to be overcome, not the least of which was to handle metallic Mg, a spontaneously flammable material in the presence of nitrogen, carbon dioxide, oxygen and/or water.

With the increased use of magnesia-carbon refractories came the realization that graphite, in the 10% and higher level, behaved in a completely different manner than the residual carbons from pitch or resins. Figure 4 shows that the higher C levels decreased slag penetration, increased the brick’s thermal conductivity leading to more efficient cooling of the hot face, and reduced its modulus of elasticity (Young’s modulus) with the latter two improving its thermal shock resistance.

Figure 2: Annual production of MgO-C refractories [3]

Figure 3: Laboratory fired pitch containing 10% MgO brick, showing “bridging” of MgO grains (×120) [10]

Figure 4: Magnesia carbon brick micrograph showing the graphite flake alignment: A) perpendicular and B) parallel to brick’s long dimension [7]
To ensure the brick’s carbon would be available for a long time its rate of oxidation had to be reduced. The formation of the dense zone to protect it was already known and ways to increase its speed of formation and/or its stability were being investigated. To this end Al and/or Si metals were added to commercial magnesia-carbon brick, but a major problem remained, the laboratory determined dense zone could not be detected in post mortem brick [14]. It was speculated that the technique used for brick removal from actual field installations somehow destroyed it or that slag penetration during cooling was to blame. By 1997, this problem was no longer an issue and dense zones from used brick were being analyzed [15].

Rymon-Lipinsksi [16] with his seminal work, provided the theoretical basis for the effect of Al addition. Al, and Si metals react to provide the carbon protection in a magnesia-carbon brick. Table 1 shows the expected reactions as a function of temperature and position within the BOF lining.

<table>
<thead>
<tr>
<th>Zone I (CO2, CO, N2)</th>
<th>MgO = MA</th>
<th>MgO = MA, Al2O3</th>
<th>MgO = C</th>
</tr>
</thead>
<tbody>
<tr>
<td>0,20 K</td>
<td>MgO + Al + C</td>
<td>MgO + SiC + C</td>
<td>MgO + MA + C</td>
</tr>
<tr>
<td>0,20 K</td>
<td>MgO + Al + C</td>
<td>MgO + SiC + C</td>
<td>MgO + MA + C</td>
</tr>
<tr>
<td>Zone II (C, N2)</td>
<td>MgO = MA</td>
<td>MgO = MA, Al2O3</td>
<td>MgO = C</td>
</tr>
<tr>
<td>&gt; 2,00 K</td>
<td>MgO + AlN + C</td>
<td>MgO + SiC + C</td>
<td>MgO + MA + C</td>
</tr>
<tr>
<td>&gt; 2,80 K</td>
<td>MgO + AlN + C</td>
<td>MgO + SiC + C</td>
<td>MgO + MA + C</td>
</tr>
</tbody>
</table>

Table 1: Reactivity products for Al, Mg and Si with the refractory at different temperatures in a BOF lining with Zone 1 representing the hot face and Zone II the received brick (18).

Figure 5 shows the expected dense zone morphology of a metal containing magnesia-carbon brick. Compare this to the one shown in Figure 3 which is more of a bridging between grains. In the latter case the amount of contained carbon is considerably lower than that found in a modern magnesia-carbon brick which makes the MgO grains being very close to each thereby providing a scaffold for the newly precipitated material.

If the metal added to the brick was Al then the dense zone will consists of an MgAl spinel not pure MgO. Figure 6 shows the reaction products from the hot face to the cold face of a used magnesia-carbon brick with Al addition. Note, that in addition to the MgAl spinel, nitride and carbide phases also formed while the brick was in service.

At the same time that the early research on antioxidants was being carried out, magnesia and carbon as raw materials and in contact with each other were studied to establish the important parameters for achieving good refractory properties which would lead to increased life in actual applications [25].

Dolomite
Baker, et. al. [10] showed evidence of a dense zone formation in pitch bonded dolomite, similar to that observed in magnesia brick. Following up on this work, studies with antioxidant additions showed that boron containing compounds were more effective than metals in forming a dense zone, but their presence had a detrimental effect on slag corrosion [26] so it was not pursued.

Summary
Although magnesia-carbon refractories showed low wear in actual applications the move from the laboratory to the steel plant was slow until the rate of carbon oxidation could be controlled. Much research was carried out to determine its role and how to reduce its oxidation. This work traced the development of the early magnesia-carbon brick and the role of antioxidants in the dense zone formation. Their role can be summarized as follows:

- At low temperatures, less than around 1200°C, there is a decrease in the brick’s porosity.
- Above about 1400°C graphite will oxidize in the presence of MgO and both Mg and C will be lost from the refractory.
- If the refractory is above about 1500°C for long periods of time and in the presence of carbon, an Mg vapor forms which reacts to form the MgO or an MgAl -spinel dense zone at the brick’s hot face. This prevents the ingress of air or slag into the brick thereby “resisting” oxidation.
- The commonly added antioxidants of Al and Si are used because they are less lost and afford effective protection.

It is interesting to note that brick based on this technology are used with great success, not only in the BOFs, but also in most EAFs and ladles and the metal addition concepts were expanded to encompass Al2O3-SiC-C (ASC) brick, SENs, slide gate plates, etc.

Post script: the biggest challenge to writing this overview was acquiring copies of the cited papers and many others that I used for background. I would like to thank all the libraries which have kept journals and conferences proceedings from years gone by.

References
I would like to thank N. Sullivan for his critical reading of this manuscript.
[7] W S Lee @ http://cmm.mater.info.ac.uk

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