Anti-oxidant Additions to Refractories: Roles and Effects*

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Introduction

Although it may not be explicitly stated, almost all carbon containing refractories have some type of antioxidant added. This material is usually thought of as a "metal addition" although it may not consist of one. Among the most common additions used for this purpose are Al or Si metal, but Mg and different alloys can also be found as are carbides, borides and nitrides (SiC, CaC, AlC, B4C, ZrB2, Si3N4, etc.) singly or in combination with metals. Criteria for selecting what to add is a function of the main refractory constituents and expected field requirements. These additions work not only as antioxidants ensuring carbon retention, but can play a role in the ease of drying of a castable, improve the refractory's hot strength, decrease its porosity, improve its corrosion resistance or, affect several of these properties at the same time.

The additions can be found in blast furnace tap hole clays, iron trough refractories, alumina-carbon, magnesia-carbon, alumina-magnesia-carbon, etc. refractories. This presentation will review the role of the major metal/boride/carbide species added to the different refractories, their expected effect on properties and how they manifest themselves.

Background

The refractory wear improvement as a result of having carbon present was explained by Herron et.al. [1], who showed how the carbon in pitch impregnated burned magnesia brick prevented slag from penetrating its pores. Subsequent studies showed that a dense zone formation protected this carbon from oxidation. This led to the development of techniques to encourage an efficient process for its formation which was accomplished by adding metals to the refractory. Although this technology was not implemented until the 1980s the idea was not new. The first mention can be found in a 1935 patent [2] that starts out by saying

"The present invention is related to the last type (coke residue bond), and has for its object the provision of a lasting protection against oxidation of such a bond, when exposed to oxygen and oxidizing conditions at the various temperatures..."

and goes on to state

"This protection is accomplished, in the course of manufacture, by uniformly incorporating in the mixture one or more inclusions of oxidizable metal, metals, alloys, metalloids or carbides of same. These metallic inclusions, if properly selected, are capable of having their oxides form a molten and viscous glass."

In 1983 a patent [3] was issued for the addition of metallic Mg to a chemically, pitch, bonded brick. The idea was to increase the amount of Mg gas generated which would lead to a thick dense zone. The refractory could be made out of magnesia, dolomite or alumina. This concept was applied in the laboratory development of brick formulations which showed promise. Then, a commercial product was successfully manufactured: a pitch bonded magnesia brick containing Mg metal.

Other refractory types containing carbon were subsequently developed and the advantage of an addition to protect their carbon from oxidation was equally applicable. Through these studies the role of metals was expanded and the use of other additions explored.

Initial work was carried out on tar/pitch bonded magnesia refractories which were mainly used in BOFs. This steelmaking process was started in the late 1950s, but advancement in refractory performance was needed for it to succeed. High strength burned MgO brick were introduced in the late 1960s and by the 1970s BOFs were being lined with pitch bonded magnesia brick, and pitch impregnated burned MgO brick. Subsequently the amount of carbon, in the form of graphite contained in the brick, was greatly increased and had to be protected from oxidation. This gave rise to the current technology of magnesia carbon refractories. Much work has been carried out studying the reactions that take place in magnesia –carbon (MgO-C) brick, the effect of the different additions and, how they

	Atmosphere	Al	Mg	Si
Zone I	CO2, CO, N2	MgO + MA MA = MgO Al2O3 Spinel	MgO	MgO + M2S M2S = 2MgO SiO2 forsterite
Zone II	CO, N2	> 1807°C MgO + AlN + C < 1,807°C MgO + MA + C	MgO + C	> 1527°C MgO +M2S + C < 1527°C MgO + SiC + C
Zone III	N2	MgO + AlN + C	> 1327°C M gO + Mg + C < 1327°C MgO + Mg3N2 + C	> 1427°C MgO + SiC + C < 1427°C MgO + Si3N4 + C
Zone IV	Neutral Atmosphere	> 1107°C MgO + Mg + C < 1107°C MgO + Al4C3 + C	MgO + Mg + C	> 1537°C MgO + M2S +Mg + C < 1537°C MgO + SiC + C
Zone V	Unchanged Material	MgO + Al + C	MgO + Mg + C	MgO + Si + C

Table 1: Reactions of Al, Mg, or Si additions to MgO brick with some carbon as a function of temperature and atmosphere [5]

behave in contact with slags and different atmospheres.

The alumina systems did not undergo this type of development until the need for improved slide gate refractories became of importance, alumina-magnesia-carbon brick technology was developed, alumina-silicon carbide-carbon refractories were installed in blast furnace runners and torpedo cars, etc. The development of their addition technologies was based on the knowledge acquired previously.

Refractories: The Reactions

Yamaguchi [4] and Rymon-Lipinski's [5], work provided the early theoretical basis for determining which phases were expected to be formed as a result of the addition of Al, Mg or Si metals to a MgO-C brick as a function of atmospheres and temperatures. Table 1 shows the expected reactions with Zones I through V representing the transition from the refractory's hot face to its unaltered cold face.

Microscopy work, carried out on BOF brick samples, recovered after tear outs, showed the presence of many of the predicted phases (Figure 1) confirming the theoretical work [6].

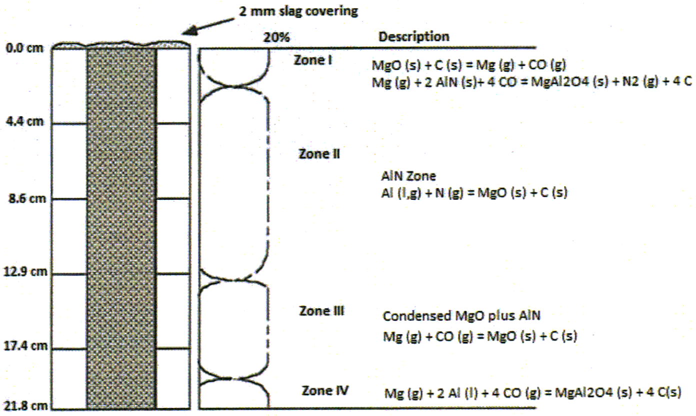


Figure 1: Typical mineralogical zones in used BOF brick [6]

Calculations of the standard free energy of reaction for Si and SiC in MgO-C brick have been carried out and are shown below [7].They confirm that these phases can be formed in the temperature ranges of interest.

$Si(s) + C(s) \longrightarrow SiC(s)$

$\Delta G = -53943 + 7.29T$ 298K (25C)<T<1686K (1413C) (1)

$Si(s) + O2\ (g) \longrightarrow SiO2(s)$

$\Delta G = -902070 + 173.64T$ 700K (427C)<T<1700K (1427C) (2)

$3Si(s) + 2N2\ (g) \longrightarrow Si3N4(s)$

$\Delta G = -731118 + 320.31T$ 298K (25C)<T<1686K (1413C) (3)

$3SiC(s) + 2N2\ (g) \longrightarrow Si3N4(s) + 3C(s)$

$\Delta G = -569289.00+298.44T$ 298K (25C)<T<1686K (1413C) (4)

$SiC(s) + 2CO\ (g) \longrightarrow SiO2(s) + 3C(s)$

$\Delta G = -732587+356.23T$ 700K (427C)<T<1700K (1427C) (5)

$SiO2(s) + 2MgO(s) \longrightarrow Mg2SiO4(s)$

$\Delta G = -67200+4.31T$ 298K (25C)<T<1700K (1427C) (6)

Additional reactions have been noted. In particular around 1200°C Si can react with CO to form SiC and, SiC can also react with CO to form SiO and then SiO2 adding to the steps shown in equations 1 and 5. This SiO2 can subsequently react to become forsterite in the presence of MgO (eq. 6). Other reactions leading to forsterite are also possible.

Experimental evidence for equation 1 was provided by Chan et al. [8] who found that the Si addition had mostly become SiC after exposure to ~1500°C

Similarly, the reactions of Al, Si, SiC and Si3N4 additions to an Al2O3-SiO2-SiC-C brick or castable were studied [8, 9, 10, 11]. The following reactions were observed after exposure to 1200°C

$4Al\ (s,l) + 3C\ (s) \longrightarrow Al4C3\ (s)$ (7)

The carbide can then react with either N or CO:

$Al4C3\ (s) + 2N2\ (g) \longrightarrow 4AlN\ (s) + 3C\ (s)$ (8)

$Al4C3\ (s) + 6CO\ (g) \longrightarrow 2Al2O3\ (s) + 9C\ (s)$ (9)

Lower temperatures of formation have also been reported to lead to the formation on these phases [12]. In addition, at 1500°C, almost all the Al2O3 generated had reacted to become a spinel (MgO Al2O3).

Microscopy work carried out on laboratory mixed, pressed and fired MgO-C brick samples showed the sequence of reactions 7 and 9 to occur (Figure 2). The core or pore was assumed to initially have been filled with Al.

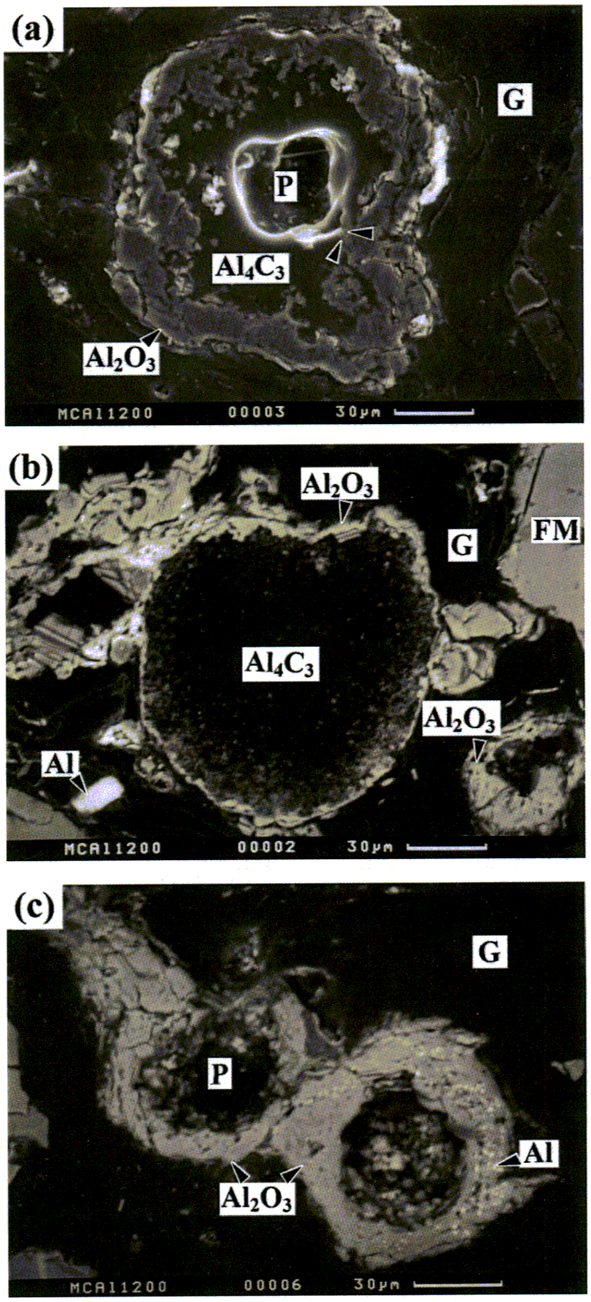
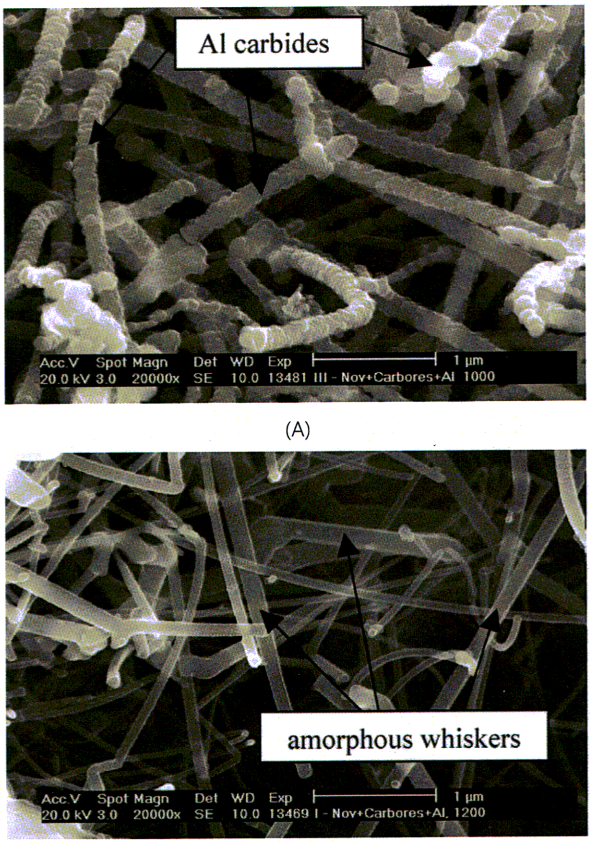


Figure 2: Microstructures of MgO-C brick with Al as antioxidant, fired for 3hrs at 1200°C. (a) a pore surrounded by an Al4C3 core then covered by an Al2O3 shell, (b) a solid Al4C3 grain covered by an Al2O3 shell, (c) an Al2O3 shell containing Al particles, enclosing a pore [13]

Much higher magnification shows the Al addition in a MgO-C brick coked in air to 1000°C to form Al4C3 whiskers [14], which remained present even after the temperature was increased to 1200°C. In the process they become smooth and amorphous (Figure 3: A & B)



(A)

(B)

Figure 3: MgO-C brick with Al addition coked in air: (A) after 1000°C Al carbide whiskers, (B) after 1200°C mostly amorphous whiskers [14]

Under oxidizing conditions SiC can react to form SiO2 (eq. 5) which can be observed as a SiO2 rim surrounding SiC grains protecting them from further oxidation. Similarly Si can oxidize to SiO2 and surround its source metal (Figure 4).

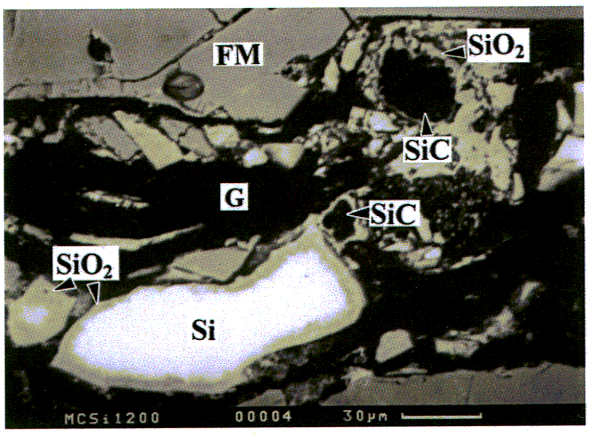


Figure 4: Micrograph of MgO-C brick with Si showing formation of an SiO2 rim covering SiC or unreacted Si [13]

The presence of SiO2 and Al2O3 can lead to the formation of mullite at ~1500°C, but it is not a stable phase as, with increasing temperature, it will dissociate back to Al2O3 and SiO2 and the latter can further react to form SiC [8].

B4C, a common carbide additive, does not behave like traditional antioxidants as it becomes a liquid which fills pores. At ~1000°C B4C will react with CO or N according to

$$\mathrm{B4C\ (s) + 6CO \longrightarrow 2B2O3\ (l) + 7C\ (s)} \tag{10}$$

or

$$\mathrm{B4C\ (s) + 2N\ (g) \longrightarrow 4BN\ (s) + C\ (s)} \tag{11}$$

When B4C is added to an MgO-C refractory it reacts with CO to form B2O3 which, in the presence of MgO, forms the low melting point 3MgO B2O3 phase.

The high temperature effect of Si as an antioxidant can be enhanced with the addition of a small amount of B4C. This is shown in Figure 5 for an Al2O3-SiO2-SiC-C castable containing 10% carbon [15].

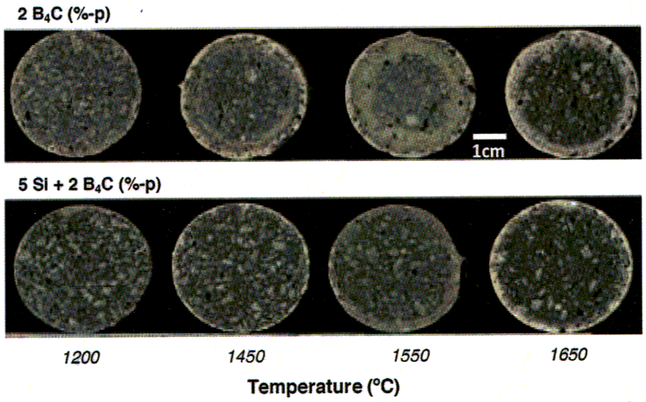


Figure 5: Effect of adding Si to B4C on the rate of oxidation after firing for 3 hours in an oxidizing atmosphere [15]

Several borides have also been used to prevent oxidation. A commonly added one is ZrB2, which can be found in submerged entry nozzle slag line material. At temperatures around 650°C or greater it dissociates according to

$$\mathrm{ZrB2\ (s) + 5\ CO\ (g) \longrightarrow ZrO2\ (s) + B2O3\ (l) + 5\ C\ (s)} \tag{12}$$

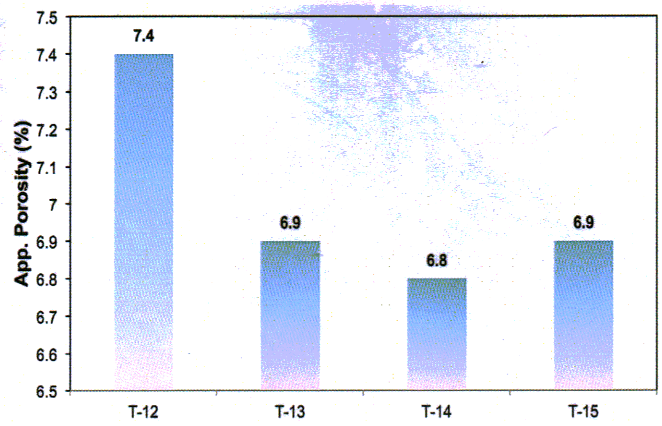
ZrB2 often contains some SiC. The presence of this SiC, or its addition, improves the ZrB2 oxidation resistance at temperatures above ~1100°C

Effect on Properties

Porosity

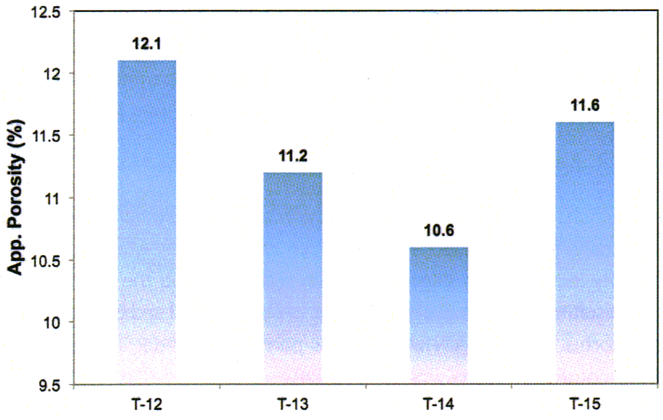
The effect of metallic additions to the refractory's porosity was determined early on. In general, the mechanism is the oxidation of the Al and/or Si which results in the in-situ formation of their carbides (Al4C, SiC). This leads to a finer pore structure thereby decreasing the refractory's permeability. Among the studies, Sadrnezhaad et al.[7] reported experimental results from studying MgO-C refractories. They found that samples without antioxidants or those with only 1% Si or Al, all behaved in a similar manner. On the other hand, if the Si level was increased to 3% to 5%, and the refractory heated to between 1000°C to 1100°C, then the open porosity decreased as a result of the formation of silica containing phases. This led to a lowering of the ability of gas to diffuse through the refractory sample thereby decreasing its oxidation rate. At temperatures > 1500°C, the apparent porosity increased again [8].

Another study showed the effect of varying the levels of antioxidants, Al and B4C, added to a MgO-C refractory. The results are shown in Figure 6 for tempered and coked porosity where T-12 had no antioxidants, while T-13, T-14 and T-15 had ever increasing amounts of Al and decreasing amounts of B4C while keeping the carbon, types and amount, and the MgO levels constant [16].



(A)

Al	0.0	0.5	0.75	1.0
B4C	0.0	0.5	0.25	0.0



(B)

Al	0.0	0.5	0.75	1.0
B4C	0.0	0.5	0.25	0.0

Figure 6: MgO-C brick: effect of amount of antioxidant on apparent porosity: (A) after tempering at 200°C, (B) after coking at 1000°C [16]

Strength

It is often stated that antioxidant additions improve hot strength. The explanation is that they form bridges between the different refractory components. Figure 7 shows the effect of Si or Al on the fired strength of the refractory. The changes are the result of the formation of additional phases when the Al or Si reacted with the prevailing atmosphere and the other constituents in the refractory.

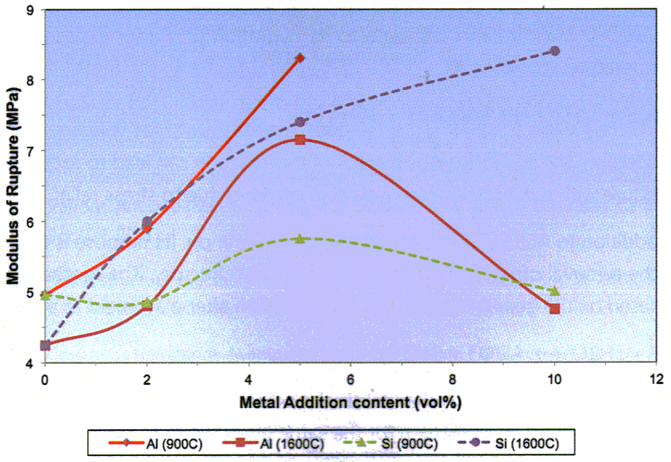


Figure 7: Modulus of rupture of 80:20 alumina-graphite composites as a function of additive content, fired to 900°C and 1600°C [17]

Addition of B4C to slide gate plate refractory material showed an increase in hot strength as a function of the amount added (Figure 8) [18].

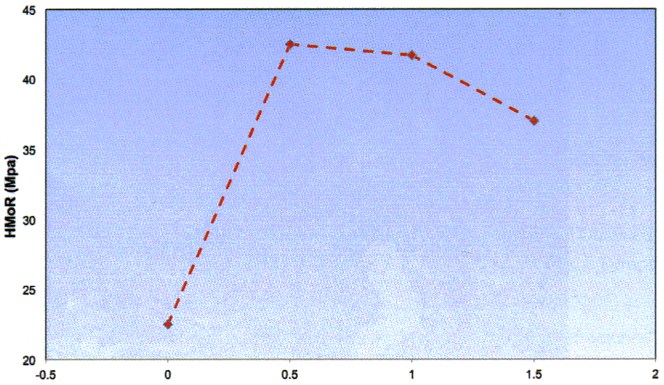
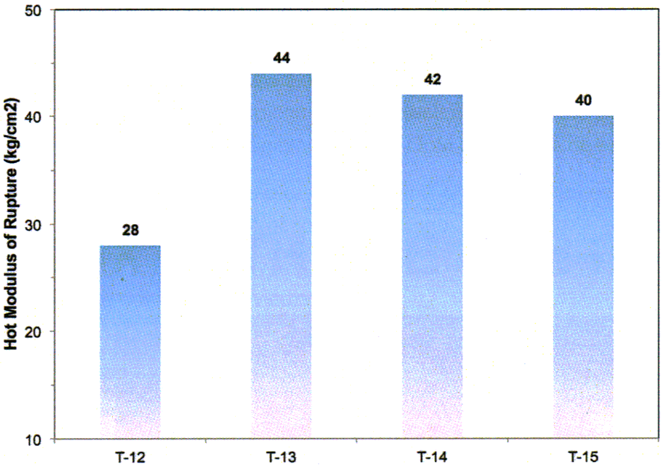


Figure 8: Hot modulus of rupture with various amount of B4C addition; test temperature 1400°C [18].

Al2O3-SiC-C monolith and MgO-C studies have shown that a combination of additives, in particular a metal together with B4C, are more effective in improving hot strength than a single additive (Figure 9) [16].



Al	0.0	0.5	0.75	1.0
B4C	0.0	0.5	0.25	0.0

Figure 9: MgO-C brick: effect of the amount and type(s) of antioxidant on hot modulus of rupture at 1400°C [16]

Effect on Slag Resistance

According to some studies, steelmaking slags rich in iron oxides will result in the oxidation of the carbon and graphite fraction of the refractory. This leads to increased porosity which allows for the penetration of the slag into to refractory. If the slag is alumina and/or silica rich then it will react with the magnesia and or dolomite in the refractory resulting in low temperature melting phases [19].

It has also been shown that iron oxide in a ladle slag can lead to the formation of magnesia-wustite in the MgO-C slag line brick leading to a decrease in its refractoriness. This reaction takes place anytime iron oxide comes in contact with MgO [20].

Decreasing the porosity lowers the ability of the slag to penetrate/react with the refractory constituents while in service thereby improving its overall slag resistance.

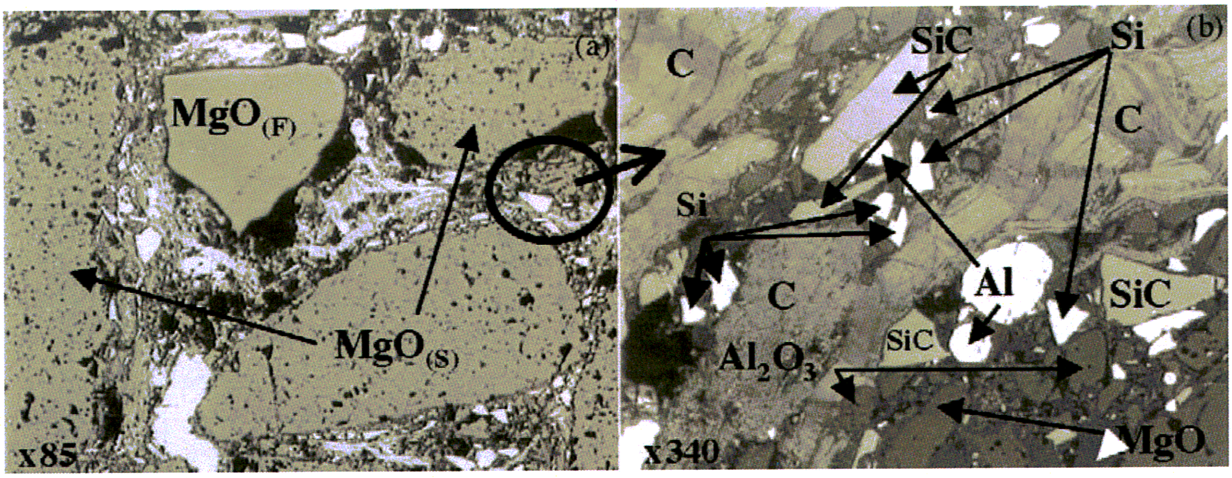


Figure 10: Reflected light micrographs of a MgO-C refractory: (a) low magnification image and (b) higher magnification image of the area in the circle. MgO(F): fused magnesia, MgO(S): sintered magnesia, C: graphite, Al2O3: corundum, SiC: silicon carbide, Si: silicon and Al: aluminum. [21]

Refractories

MgO-C Brick

MgO-C brick have been the most studied of all of the carbon bearing refractories. Innumerable articles discuss the different additives and the resulting reactions. The type and amount of the additives selected for use for a particular application will depend on the environment's severity, the prevailing failure mode and required vessel life. The most common additions are Al and Si, followed by B4C and other borides and, SiC. Figure 10 shows an as received MgO-C brick containing Al, Si and SiC [21].

Dense zone formation is one of the results of the use of metals as an additive. A spinel dense zone, the result of an Al addition to a MgO-C brick, is shown in Figure 11.

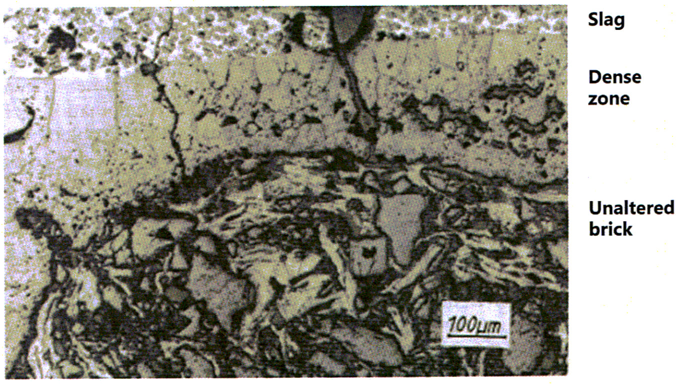


Figure 11: Microstructure of a dense zone. [22]

Al2O3-C Refractories

Alumina graphite refractories generally have additions of Si, SiC and/or B4C, although others have also been reported. These additions improve the oxidation resistance of the refractory body following the same mechanisms as described in MgO-C refractories: Si reacts with CO, a gas, forming SiO which leads to the deposition of C. The SiO can further react with CO forming SiO2. These reactions are accompanied by a volume expansion sealing pores.

Slide gate plates, made out Al2O3-C, and, submerged entry nozzles often contain B4C in addition to Si. This enhances their strength at temperature (Fig. 7) and also positively affects their oxidation resistance. Slide gate plates also benefit from the addition of Si and Al in the presence of microsilica. This combination has been shown to reduce the apparent porosity by decreasing the pore size and distribution [23].

Al2O3-MgO-C (AMC) Brick

The reactions that pertain to this discussion are the recrystallization of the MgO grains from reduction with C which can coat any grain within the refractory increasing its slag and erosion resistance and the formation of spinel resulting from the use of additives, in particular, Al and Si. In addition, the Al forms Al4C3 or AlN which act as part of the binder increasing the strength of the refractory when in use [24].

Al2O3-SiC-C (ASC) Refractories

These can be brick or castable. The SiC in these refractories acts mainly as a structural element although it will also behave like an antioxidant. For use as an antioxidant, Si can also be added. Al can be present in brick formulations, but can be a drawback if added to a castable as will be discussed in the next section. The primary application of these castables is in blast furnace troughs were they are exposed to thermal cycling and iron/slag attack. The SiC is highly abrasion resistant, has high thermal conductivity which minimizes the thermal cycling stresses and, in its antioxidant role, it closes off the pores to slag attack.

Disadvantages of Additions

So far, the discussion has centered on the benefits accrued as a result of metal additions, but Al additions can also be detrimental. If Al is added to MgO-C brick it can contribute to its hydration [25] after exposure to temperature according to

$$\mathrm{Al4C3 + 12H2O \longrightarrow 4Al(OH)3 + 3CH4\ (g)} \qquad (13)$$

In addition, the gas formed as a result of this reaction can lead to excessive pressure within the brick which results in cracking due to stress relief.

Al addition to Al2O3-SiC-C monoliths is very common. Its purpose is to aid in the removal of water during the firing of the refractory. The mechanism is based on the generation of hydrogen gas soon after placement as shown

$$\mathrm{2Al + 3H2O \longrightarrow Al2O3 + 3H2\ (g)} \qquad (14)$$

For the gas to exit it forms channels in the setting refractory which, later on, are reused by the water/steam for the same purpose.

This reaction can also compromise the monolith's integrity as excessive amounts of gas can lead to crack formation or may even be explosive. In order to avoid this problem, coated Al powders have been used but their effectiveness should be determined in each case [26]. Lastly, this reaction can be a safety issue if it takes place in an enclosed area displacing air or leading to an explosion.

Conclusions

In conclusion, the addition of metals, carbides and/or borides singly or in combination to carbon containing refractories is ubiquitous. The possible reactions that take place within the refractory are many and complex. The understanding of the effect of these additions should be integrated into the selection of the appropriate refractory to ensure the most compatible physical properties for maximum unit availability.

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