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DIFFERENT TYPES OF *IN SITU* REFRACTORIES

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ABSTRACT

The use of refractories formed i*n situ* to resist corrosion is widespread throughout the materials processing industries. This paper aims to define exactly what is meant by the term "*in situ* refractories" and to describe the various types arising in practice.

INTRODUCTION

Refractories invariably undergo some changes in use due to the high service temperatures pushing them towards equilibrium. This is particularly true when refractories are in contact with liquids and vapors as occurs in most materials processing, such as iron and steel making and glass production, and in waste incineration. A surprisingly large proportion of refractories also contain liquid and vapor phases formed under service conditions. Consequently, what is used to line a furnace is not what is present during use. These changes, which occur once the refractory is installed, lead to production of what have come to be termed *in situ* refractories. Since refractories are designed to give the longest campaign possible it is important that the in service changes are understood and controlled. A recent review[1] described the evolution of *in situ* refractories in the twentieth century and suggested that several types of *in situ* refractories can form. The purpose of this paper is to give a clear definition of what is meant by the term *in situ* refractories and to specify possible different types of *in situ* refractories.

DEFINITION

In situ refractories may be defined as the in use product(s) of reaction within a refractory system or between the refractory and furnace contents leading to improved refractory behavior.

DIFFERENT TYPES OF *IN SITU* REFRACTORIES

For simplicity 4 types of *in situ* refractories will be described but, as shall become apparent, there is the possibility of extensive overlap between these groups. Also, there may be additional types of which the authors are unaware.

Type I

Type I *in situ* refractories are those arising due to reactions solely within the components of the brick or monolith without any external contribution (Figure 1).

These arise from reactions between refractories components due to the high temperature and so may occur e.g. during heat up of a refractory system. Included in Type I are those *in situ* refractories in which useful phases are generated throughout the matrix often during production/installation. Fine powders are often used in the batch which (due to their high surface area) react to form desired phases. The most common bond phases formed in Type I *in situ* refractories are spinels (of various compositions), forsterite and mullite[2]. Often their formation leads to a direct bond between the individual grains of the refractory aggregate system such as in $MgCr_2O_4$ spinel bonded mag-chrome bricks[3]. Critical features of the reactions leading to Type I *in situ* refractories are the volume changes associated with the reactions[2] and the competition between this volume change and other temperature-induced microstructural changes such as thermal expansions of other phases present and shrinkage contraction arising from liquid phase or solid state sintering. Beneficial behavior may result if these lead to a tightening of the texture so improving resistance to liquid penetration and strength. The morphology of the product is also important, e.g. formation of acicular or tabular mullite or calcium hexaluminate (CA6) may open up a microstructure and have an adverse affect on thermo-mechanical properties.

A good example of a Type I refractory is self-formed spinel in castables arising from reaction of fine, matrix additions of alumina and magnesia on firing often in the presence of silica and calcium aluminate cement[4]. The volume increase associated with the spinel formation may tighten the refractories texture helping to resist liquid penetration. Calcium aluminates such as CA6 also form in the matrix of such systems from reaction of the cement and alumina components. The tabular CA6 crystals formed are believed to link other phases (such as tabular grain and spinel), interlocking the microstructure and improving strength[5,6].

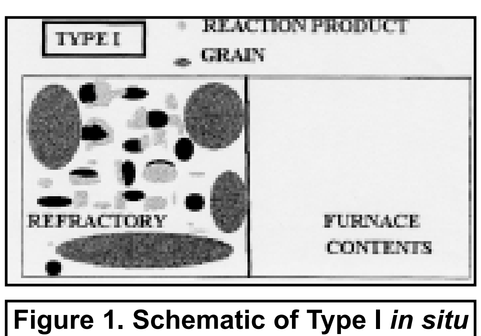

Figure 1. Schematic of Type I *in situ* refractories.

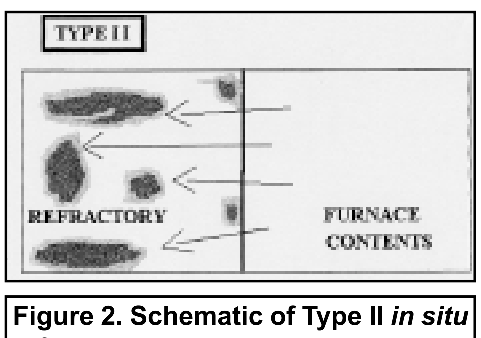

Figure 2. Schematic of Type II *in situ* refractories.

Type II

Type II includes those *in situ* refractories in which reactions occur within the refractory but which may be assisted by reaction with the (liquid or vapor) furnace contents (Figure 2).

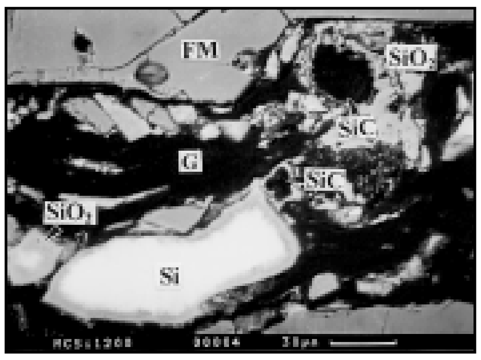

Figure 3. Direct and indirect silica formed in MgO-C brick with added Si at 1200°C.

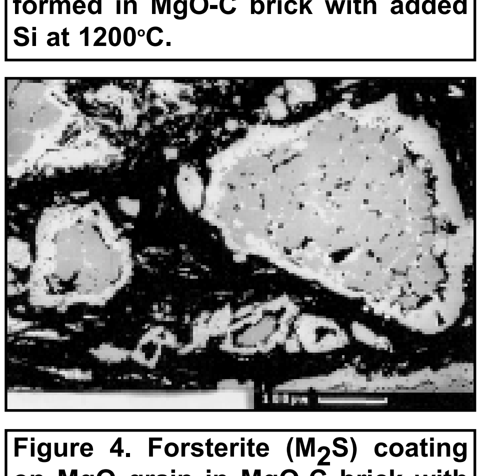

Figure 4. Forsterite (M_2S) coating on MgO grain in MgO-C brick with added Si at 1600°C (courtesy R. Artir, University of Sakarya, Turkey)

These include formation of dense layers within the refractory adjacent the contents (such as fine MgO in BOF vessels via the MgO-C reaction aided by availability of oxygen from the slag or atmosphere first seen in 1967[7]). Also, included in this category are the MgO-C bricks containing ceramic additives such as B_4C which react to form ceramic/glass phases at high temperature improving oxidation resistance[8]. Similarly, MgO-C bricks with metal additives such as Al, Si, Mg and alloys[e.g.9,10] can be included here since they may react with gases from the atmosphere to form ceramic phases which beneficially getter oxygen and interlink other phases so improving hot strength. The ceramic phases which form are a strong function of the local conditions at the metal location in the brick. The morphologies of the phases formed often indicate their formation mechanism. In Figure 3 two forms of SiO_2 occur. Silica from direct oxidation of silicon metal is present as a shell on the original metal particle. Silica formed indirectly via SiO vapor e.g.

$$Si_s + C_s \longrightarrow SiC_s\,(+CO_g) \longrightarrow SiO_g + CO_g \longrightarrow SiO_{2s} + C_s$$
$$Si_s + CO_g \longrightarrow SiC_s\,(+CO_g) \longrightarrow SiO_g + CO_g \longrightarrow SiO_{2s} + C_s$$

occurs as a rim around the original location of the Si particle.

As with Type I the critical features of Type II *in situ* refractories include the properties of the phases formed. Consequently, while oxidation of additive B_4C to give B_2O_3 rich glass improves oxidation resistance it leads to poorer high-temperature strength since the glass becomes fluid. Often the phase formed covers the grain phase leading to protective coatings which may e.g. be spinel or forsterite (Figure 4).

Type III

Type III includes those refractories which react with the furnace contents generating a protective interlayer between the refractory and furnace contents (Figure 4).

Often the interlayer forms as a result of indirect corrosion of the refractory solid by penetrating liquid[11]. If the interlayer passivates further attack it is a Type II *in situ* refractory. Commercial examples of such Type II interlayer formation include clinker coatings in the burning zones of cement kilns and viscous glass layers adjacent Al_2O_3-ZrO_2-SiO_2 blocks in glass tanks.

Significant properties of liquid interlayers formed in Type III *in situ* refractories include their viscosity and the solubility of adjacent solid phases in them. In AZS refractories the liquid formed is rich in Al_2O_3 which makes it viscous and so it acts as a barrier between the refractory and the fluid soda-lime-silica glass in the tank. The solid ZrO_2 in adjacent refractory is also slow to dissolve in the alumina-rich glass interlayer.

Solid *in situ* refractory interlayers are observed to form in many refractory-slag interactions[11] and are often multiphase. Slag attack of MgO often leads to formation of a magnesiowustite boundary layer in Fe-rich slags[12] and a spinel layer in alumina or chromia rich slags. Complex spinel and calcium aluminate phases (CA2, CA6 and gehlenite, C2AS) often form between alumina and slag[13]. Critical features of such interlayers include whether they are complete and fully cover the (often) aggregate or grain phases being attacked. Incomplete coverage leaves gaps through which aggressive liquid can penetrate. The morphology of the phases in the interlayer is also important. Acicular or tabular phases such as CA6 or mullite may grow into and penetrate the grain phase, opening up the interface to further attack. Thermal expansion mismatch between the interlayer and other solid phases present may lead to stress and crack formation although the presence of liquid may often alleviate this problem.

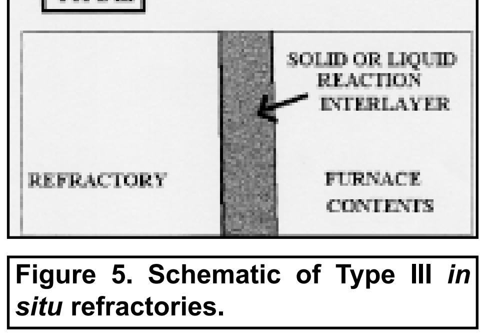

Figure 5. Schematic of Type III *in situ* refractories.

The mechanisms by which solid Type III interlayers may passivate further attack vary. Open crystal structures, such as spinel or rock salt (MgO), can accommodate cations such as Fe, Mn, Mg and Cr so removing these cations from the adjacent local liquid rendering it more viscous and less penetrating. Zhang *et al.*[13] observed a change in composition of spinel from Mg aluminate adjacent alumina being corroded to Mg, Al, Fe, Cr, Mn spinel into the slag. This would suggest that the Mg aluminate spinel acted as a nucleus and as the spinel grew into the slag it incorporated the various cations, rendering the local slag more viscous. Another mechanism is when complete layers of refractory phases (such as CA6) simply act as a prophylactic coating.

A subtle distinction needs to be made here between Type II and Type III *in situ* refractories. As discussed above the formation of an interlayer between slag and solid grain in a crucible-type slag test is Type III. However, if the slag has penetrated the matrix of a refractory brick and then attacks the grain in an identical manner this is Type II, since now reactions occur within the refractory but assisted by reaction with the liquid slag from the furnace contents.

Type IV

Finally, Type IV are those in which the furnace contents are deposited on the refractories to themselves act as the refractory such as slags splashed onto BOF vessel walls.

In BOF vessels the nature of the bond between the slag and refractory is as yet not well defined. If a reaction occurs between the splashed slag and the refractory lining then depending on the nature of the interlayer formed this may introduce some Type II or Type III component. Refractory systems are often designed to freeze liquid either at the refractory surface or at a specific location in the brick at a specified isotherm. Air or water cooling in high thermal conductivity refractories may be used to control the location of the isotherm. In carbon blocks in iron blast furnaces the

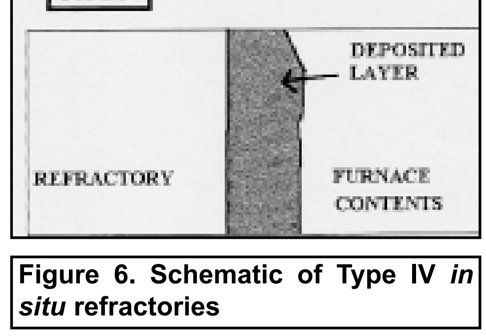

Figure 6. Schematic of Type IV *in situ* refractories

important isotherm is that at 1150°C (the temperature at which iron + 4% C freezes). In Al reduction cells the 800-850°C isotherms (at which the eutectic bath components freeze) are important. If the slag is frozen at the surface this is a Type IV *in situ* refractory whereas if it is internal to the brick it is Type II.

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