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Direct and indirect slag corrosion of oxide and oxide-c refractories

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Penetration and dissolution mechanisms are reviewed for predominantly single-phase oxide, two phase oxide and oxide-carbon composite refractories by liquid silicate slags. Theoretical models of these processes, as well as static (sessile drop, dipping and crucible) and dynamic (rotating finger and rotary slag) experimental tests, along with their practical limitations are considered. Direct (congruent or homogeneous) attack is controlled by the reaction rate at the slag-refractory interface or the rate of diffusive transport of species to it through the slag leading to active corrosion. Indirect (incongruent or heterogeneous) attack is controlled by diffusive transport through the slag or through a new solid phase, which forms at the original slag-refractory interface. This may lead to passive corrosion. Examples of direct and indirect attack in a range of refractory/slag systems are described highlighting the critical influence of the composition and hence viscosity of the local liquid slag adjacent the solid refractory. Penetration and corrosion can be controlled either through the local slag composition via the refractory or the bulk slag or by microstructural control of the refractory by e.g. internal generation of dense layers or external deposition/generation of passive coatings, so-called *in situ* refractories.

Theory of penetration by slags and dissolution of refractories

Attack of refractories in a commercial furnace is a complex phenomenon involving not only chemical wear (corrosion) but also physical/mechanical wear (such as erosion/abrasion) processes that may act synergistically. Lee and Zhang[1] recently reviewed theoretical aspects of chemical attack of solid refractories by liquid slags emphasising both penetration (simple permeation of liquid slag via open porosity) and reaction of the slag with the refractory phases often by dissolution. The rate of slag penetration can be quantified by Poiseulle's Law which, although ignoring much of the influence of the refractories microstructure, does include the effect of slag viscosity which indirectly includes temperature. Lee and Zhang[1] also highlight the importance of surface and interfacial energies on wetting leading to

$$1^2 = (r\cos\theta/2)(\gamma/\eta)t \qquad [1]$$

where r is open pore radius, l slag penetration depth, η slag viscosity, t time, γ is the slag surface tension and θ the wetting or contact angle. Equation [1] assumes straight open pores and a tortuosity factor can be included to account for the more complex form of the pore path in commercial refractories. Equation [1] does, however, indicate that slag penetration can be suppressed by increasing slag viscosity or contact angle or by decreasing its surface tension. This is why a temperature gradient from a cool outside surface to the hot (contact) face can limit penetration (such as the 1150°C isotherm freeze line in iron blast furnaces which is the temperature at which the hot metal freezes). It is also why many isothermal slag tests may be of limited practical applicability.

Viscosity is also an important measure of the rate of diffusive mass transport within the slag after penetration into the refractory. In the Stokes-Einstein relation

$$D = kT/6\pi\eta r \qquad [2]$$

where r is radius of the diffusing species, the ionic diffusivity (D) in the slag is inversely proportional to viscosity so that changes in composition (due e.g. to dissolution of the solid) which reduce viscosity also enhance transport in the slag so accelerating degradation processes dependent on diffusive mass transport.[5] Consequently, during penetration, especially at high temperatures, the liquid and solid react. This then makes some of the variables such as θ and γ in Equation [1] vary with time. The reaction products can be solid, liquid, gas (or a combination) and either i) remain attached to the solid (usually solid or viscous liquid), ii) are fugitive (usually fluid liquid or gas) or iii) are a combination of i) and ii). These situations are illustrated schematically in Figure 1.

The corrosion rate is a function of many variables including temperature, refractory/liquid/interface composition and liquid density, viscosity, diffusivity and degree of agitation. If the reaction product is soluble or dissociates directly in the liquid slag then active corrosion may continue to destruction of the refractory. If, however, the reaction product is not completely soluble in the liquid slag it may form a barrier so that after its formation further attack is prevented, passive corrosion. In this case possible corrosion rate determining steps are chemical reaction forming the layer, diffusion through the layer or diffusion through the slag. Examples of passive corrosion include the formation of a dense MgO layer in MgO-graphite refractories, of a $MgAl_2O_4$ spinel layer in the corrosion of alumina refractories by MgO containing slags and of a C_2S layer on MgO-dolomite refractories attacked by silica containing slags. Selective corrosion may also occur in

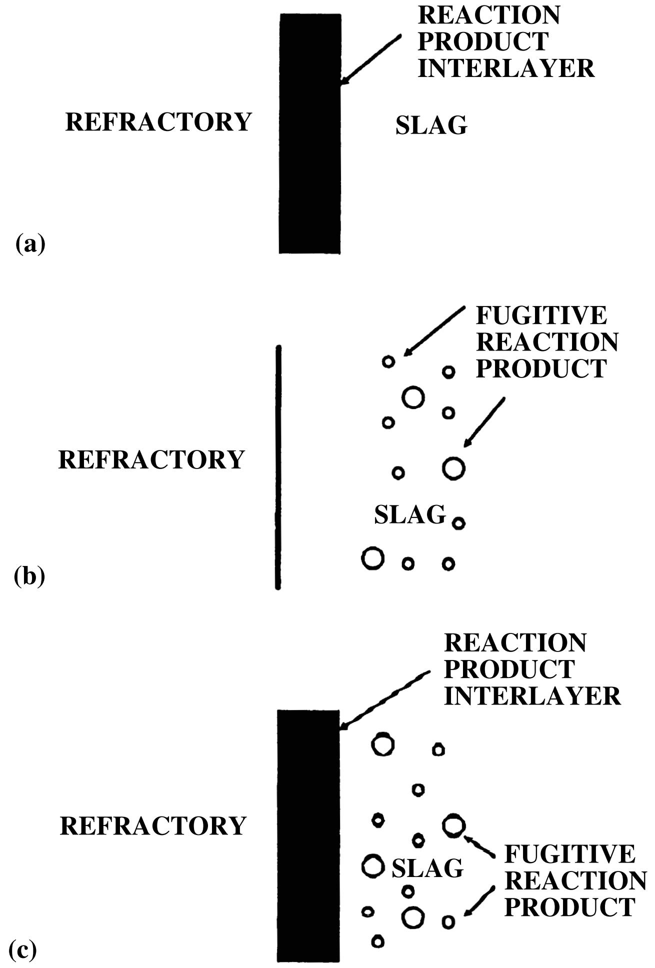

Figure 1. Reaction products can, a) remain attached to solid, b) be fugitive or c) be a combination of a) and b)

which only certain phases in the solid are attacked. A good example of this is the decarburization of carbon-containing refractories which occurs by several mechanisms including dissolution of C into the molten steel. Once the carbon has been removed the refractory is able to be wetted by the slag so that penetration and spalling of the decarburized layer can occur.

Dissolution at refractory/slag interfaces is governed by (a) chemical-reaction (or solution) at the interface or (b) transport (or diffusion) of reacting species through the liquid.[2] The rate determining step is used to define the types of dissolution which are termed reaction or interface controlled for the former and transport or diffusion controlled for the latter. Phases of dissimilar chemical nature tend to react at high temperature so that, in general, to limit the extent of dissolution the refractory and liquid in contact should be of similar nature. SiO_2 (B_2O_3, P_2O_5 and V_2O_5) are acidic so that high silica refractories are used with acid liquids (some steelmaking, coal gasifiers and glass melts). MgO and CaO are basic and so are used in contact with basic melts (e.g. Basic Oxygen Steelmaking, cement production). Some refractories e.g. $MgCr_2O_4$ and carbon are neutral resisting acid and basic slags to a similar degree. The optical basicity scale[3] for slags is useful in this regard being the equivalent of the pH scale for acid/base aqueous liquids as well as indicating the ability of the slag to hold solutes such as phosphates and sulphides in solution[4].

In direct, congruent or homogeneous dissolution[5] atoms from the solid dissolve directly into the liquid melt. Direct dissolution can be reaction or interface controlled when the diffusivity of reaction products is faster than the rate of chemical reaction at the interface or *t*ransport or diffusion controlled if it is slower. In the former case the dissolution process is then directly controlled by the reaction whose initial rate can be expressed by,

$$J = K(A_c / A_o)C_m \qquad [3]$$

where J is the dissolution rate (gcm^{-1}sec^{-1}), K is the rate constant, A_c is the actual area of refractory (cm^2), A_o is the apparent area of refractory (cm^2), and C_m is the concentration of reactant in the melt (gcm^{-3}). Surface irregularities such as grooves and porosity which increase the ratio of A_c to A_o in Equation [3] have a significant effect while other microstructural features such as crystal orientation, grain boundary phases and grain shape are neglected. For this simple treatment stirring of the melt has no apparent effect on dissolution rate. For direct dissolution to continue the atoms diffuse away from the interface at a rate proportional to $t^{1/2}$ as reactants are depleted and dissolved species build up in the absence of liquid convection or stirring.[6]

In a situation where the rate of removal of reaction products by diffusion is slower than the rate of chemical reaction, a solute-rich boundary layer builds up, whose interface with the refractory is saturated with reaction products. The diffusion of reactants to, or the products away from, the interface through the boundary layer then govern the dissolution process. If the boundary layer leads to formation of a solid interlayer this is termed indirect, incongruent or heterogeneous dissolution[5] and the rate of corrosion can be expressed in terms of the Nernst equation,

$$J = D(C_s / C_m)/\delta \qquad [4]$$

where D is the diffusion coefficient (in cm^{2}s^{-1}), C_s is the saturation concentration of refractory in the melt (gcm^{-3}), and δ is the effective boundary layer thickness (cm) which is defined as,

$$\delta = (C_s - C_m)/(dc/dx) \qquad [5]$$

where dc/dx is the concentration gradient over the interface. The saturation concentration of the refractory components in the melt is important but the saturation of liquid in the solid may also be important. If the solid is unsaturated with

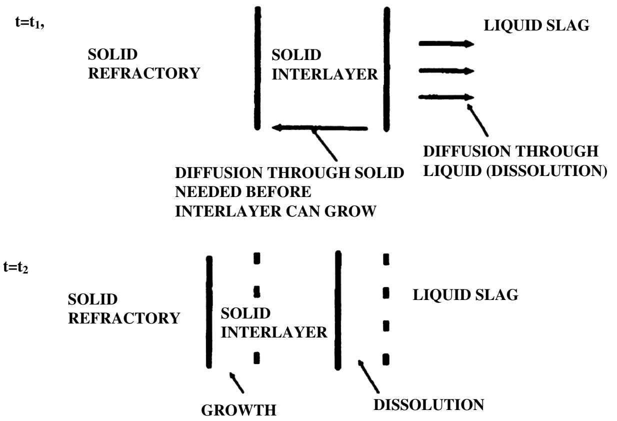

Figure 2. Growth of solid interlayed between refractory and slag leading to indirect dissolution; $t_1<t_2$

respect to at least one component of the liquid then solid solution reaction may occur. For diffusion controlled direct dissolution liquid phase diffusion of the product through the melt boundary layer is considered. However, once saturation occurs and a solid interlayer has precipitated between the melt and the refractory this is the diffusion-controlled indirect process and solid state diffusion of the reaction species from the melt through the solid interlayer must be considered (Figure 2).

Stirring the melt or rotating the refractory sample, enhances the rate of indirect dissolution (or effectively converts it to direct dissolution) by reducing the thickness of any liquid boundary layer (or breaking up any solid layer). In the case of a flat slab held vertically in the melt, the rate depends upon the boundary layer thickness which is limited by such variables as the degree of convective flow caused by thermal and density gradients, the liquid viscosity, the mean diffusion coefficient and the container size. Wagner[7] first used an equation taking into account these variables on dissolving a thin plate and the rate of dissolution under natural convection is

$$J = 0.5D\left(C_s - C_m\right)\left(\Delta\rho g / D\eta\right)^{1/4} x^{-1/4} \qquad [6]$$

where $\Delta\rho$ is the density differences between saturated and bulk melt (gcm^{-3}), η is the dynamic viscosity (poise), g is the gravitational constant ($cm^{-1}s^{-2}$), and x is the distance from the leading edge of the slab (cm).

Under forced convection where the melt is agitated, the fluid velocity U replaces $\Delta\rho$ as a variable. The dissolution rate can then be rearranged as,

$$J = D\left(C_s - C_m\right) / 3.09(U / vx)^{1/2}(v / D)^{1/3} \qquad [7]$$

and the effective boundary layer thickness $\delta = 3.09(vx/U)^{1/2}(D/v)^{1/3}$. U is the bulk velocity of the fluid (cms^{-1}) and v its kinematic viscosity (cm^2s^{-1}). It is clear that the value of (C_s-C_m) has a great influence on the dissolution rate. If the refractory oxide in the bulk slag has been saturated, then J = 0. Naturally, to minimize the dissolution rate (C_s-C_m) must be minimized. For example, increased MgO content in slag decreases the corrosion of periclase, the primary phase in many basic refractories. If $C_m = 0$, then the value of (C_s-C_m) reaches a maximum and thus, so does the dissolution rate. Consequently, the solubility of refractory oxides in molten slag and the saturation concentration at the interface between refractory and slag are very important in refractories corrosion.

Slag viscosity has significant effects on both the slag penetration and the refractories dissolution. A more fluid slag will be more penetrating and more likely to dissolve the solid refractory. Furthermore, if dissolving the refractory in the liquid leads to increased viscosity then mass transport through the melt layer next to it will be slower so that the melt layer becomes progressively saturated giving rise to diffusion control i.e. indirect dissolution. On the other hand if the viscosity of the melt layer is decreased then diffusion through it becomes more rapid, no saturated layer forms and reaction control or direct dissolution occurs. Raising temperature to give a more fluid slag can then lead to a change from indirect to direct dissolution.

Corrosion testing of refractories

Many different methods have been used to attempt to simulate the environment a refractory is exposed to during commercial service. Each has benefits and limitations and they can be categorized as either static where there is no attempt to simulate motion of the corroding fluid or dynamic where the fluid moves relative to the refractory. These tests are shown schematically in Figure 3. In all of them changes will occur in the slag during the test due to different oxidation states (especially Fe), preferential penetration of specific elements into the brick and dissolution of brick into the slag. These tests are essentially comparative but as discussed by Lee and Zhang[1] still useful for assessing the corrosion mechanisms.

All of the static tests suffer from the drawback of the corroding medium (usually slag) rapidly becoming saturated with products of reaction with the solid: a scenario unlikely when slag is moving relative to the refractory and being refreshed with slag free of corrosion products. In the *button or sessile drop* test (Figure 3a) shaped slag is placed on a refractory substrate, heated to temperature and held for a fixed time to allow the slag to wet and react with the refractory. The sessile drop technique is used to measure interface and surface energies in systems where the liquid is fluid and does not react with the solid but becomes more complicated when reactions occur such as when hot viscous slag is on a refractory solid. In the *dipping, immersion or finger* test (Figure 3b) one or more cylindrical or square-pillar shaped refractory samples are held in the corrosive slag for a certain period in an electric or induction furnace. In this method the atmosphere is easily controlled and the composition variation of the slag, associated with rapid saturation with reaction products, can be minimized by using a large volume of slag relative to the size of the samples. However, as in the button test no temperature gradient exists in the refractories; they are isothermal i.e. at the same temperature throughout their volume. This is not the case in commercial practice where a temperature gradient between the hot face of the contact lining and the cold face or safety lining exists. Any slag flow in this test arises from the thermal convection in the slag and so is small. In the *crucible, cavity, cup or brick* test (Figure 3c) a cored-out refractory brick is filled with slag and exposed to high temperature to promote slag-refractory interaction. This method is popular since it is simple and many samples can be tested in a short time. However, it suffers from the drawbacks associated with static tests i.e. no temperature gradient, rapid saturation of slag composition with reaction products (often all slag is absorbed into the brick) and no slag flow. In *the induction* furnace test (Figure 3d), refractory samples are set in the shape of a polygonal crucible in an induction furnace. Since the contents need to conduct electricity metal and slag are placed in the crucible and melted by induction heating. In this method a temperature gradient can be established, atmosphere and temperature are easily controlled, and rapid and vigorous corrosion can occur at the melt/slag line since the less dense slag floats on the metal. An induction furnace test induces some motion of the metal and slag upon heating and so has some dynamic aspect. The results of such a test can therefore effectively simulate the situation in a practical furnace except that flow is uncontrolled.

Relative motion of liquid slag and solid refractory is particularly important in systems where indirect dissolution occurs. The motion can remove the boundary layer and increase any active corrosion process so that dynamic tests are needed to simulate such behaviour. In fact, ignoring erosive effects this is a good test of whether dissolution is indirect (in which case corrosion rate increases with motion) or direct (in which case motion has no effect). The

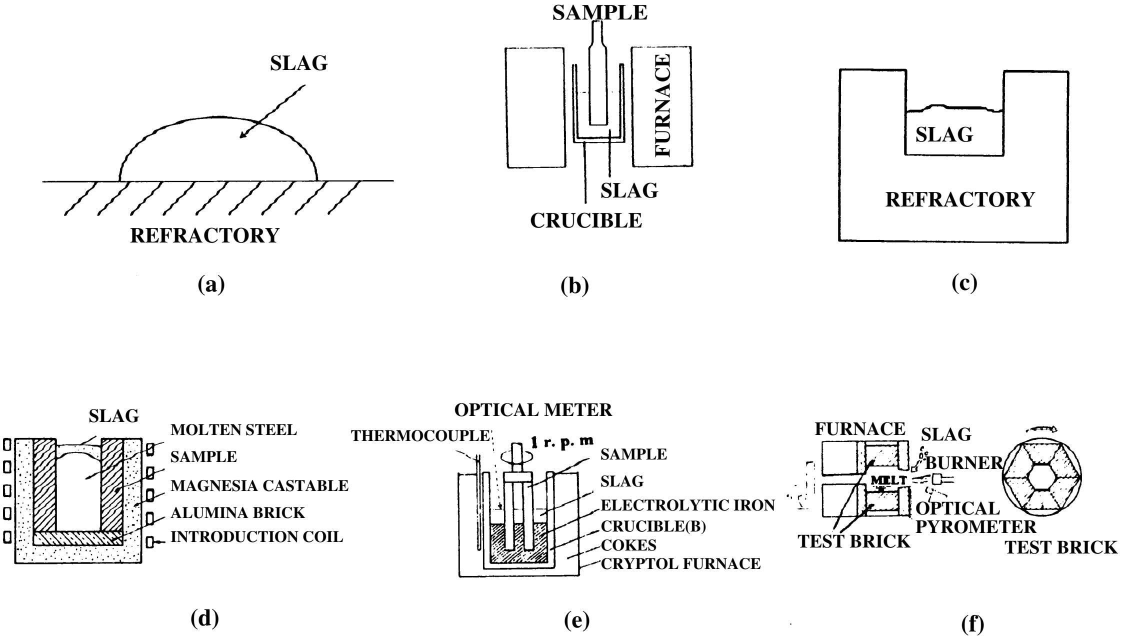

Figure 3. Common laboratory corrosion tests

dipping test can be made dynamic by rotating the samples in the molten slag, a *rotating finger* test (Figure 3e). Fahrbach *et al.*[8] compared the rotating finger and brick tests for slag attack of aluminosilicate refractories determining that the former gave a better indication of the extent and speed of penetration. Perhaps the most popular corrosion test procedure is the *rotary slag* test (Figure 3f) in which the slag is melted with an oxypropane flame in a cylindrical drum lined with sections of refractory and rotating about a horizontal axis. The slag is refreshed at periods throughout the test by tilting to remove old slag, returning to horizontal and adding new slag. The advantages of this method include the fact that many samples can be compared in a single test, a temperature gradient can be established, and the composition and fluidity of the slag is partially controlled although during the test the slag composition (especially the oxidation state of iron oxide) may change. However, since this is what happens during practical steelmaking procedures it is not necessarily a disadvantage. Nonetheless the purpose of refreshing the slag is to keep it as constant in composition as possible. Clearer drawbacks are that temperature is difficult to control and that the reproducibility of the results is not very good.

All of these methods along with other less well known tests such as the *mixing* test (in which powdered slag and refractory are reacted together) and the slag *dripping test* (in which molten slag is dripped on to the refractory) have been reviewed by Kobayashi *et al.*[9] Kii *et al.*[10] recently developed a new test for slag corrosion at high temperature which uses an electric resistance furnace combined with an X-ray transmission apparatus. This allows observation of corrosion phenomena as they occur during the test enabling valuable information for clarifying the mechanism and revealing the main factors affecting the corrosion. Another major advantage of such a test is that the corrosion rate of localized wear at different boundary conditions can be determined.

In situ refractories

The function of the slag in metal winning operations is to provide a vehicle for impurity removal from the original ores and later the molten metal. Where possible it should be designed to give minimum corrosion of the refractory lining; recent developments such as slag splashing in BOS vessels even use the slag as an *in situ* refractory. Lee and Moore[11] and Lee *et al.*[12] developed the concept of *in situ* refractories to include a range of types categorized as Types I-IV. Type I *in situ* refractories are those arising due to reactions solely within the components of the brick or monolith without any external contribution. 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 vapour) furnace contents. Type III includes those refractories that react with the furnace contents generating a protective interlayer between the refractory and furnace contents. Often the interlayer forms as a result of indirect corrosion of the refractory solid by penetrating liquid. 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 BOS vessel walls.

While the composition of the bulk liquid is important the composition of the liquid at the point of penetration is critical to the corrosion mechanism. A different local composition may arise for several reasons. Firstly, some species present in a molten liquid at high temperature can diffuse more quickly than others. In steelmaking slags Fe, Mn and Ca diffuse particularly rapidly and so tend to congregate at the most penetrated parts of the refractory. Secondly, some phases present in the refractory microstructure may be capable of taking these cations into solid solution and so negate their (often corrosive) effects. Fe and Mn in particular lead to a fluid and penetrating slag. Thirdly, phases in the refractory may dissolve in the local liquid altering its composition compared to bulk liquid.

Studies of refractories corrosion

Predominantly single-phase oxides

To achieve an understanding of chemical attack of complex multiphase refractories requires an understanding of the corrosion mechanisms of the individual phases present in their microstructures before the synergistic effects when they are combined in a complex phase assemblage can be considered. Lee and Zhang[1] reviewed studies of liquid attack of single crystal or dense polycrystalline oxide ceramics since such materials are often the grain phase in a refractory system. A few examples will be used here to illustrate the main findings of this earlier review[1]. Most attack of MgO appears to be indirect with formation of a magnesiowustite boundary layer in Fe-rich slags and a spinel layer in alumina- or chromia-rich slags. Indirect dissolution also occurs in general for Al_2O_3 in CAS slags controlled initially by diffusion of alumina through a liquid boundary layer at the alumina/slag interface. With continued dissolution one or more solid phases (such as CA_2, CA_6 and C_2AS) form at this interface complicating the indirect process with CA_6 opening up the interface allowing further penetration. In MgO-containing CAS slags indirect dissolution again occurs with formation of a MA spinel layer which, with enough MgO present, is complete and may passivate the corrosion process[13]. A protective spinel layer appears to form in a similar fashion in solid MgO corroded by high Al_2O_3 slags[14] and in solid Al_2O_3 corroded by high MgO slags. Since spinel forms on reaction of Al_2O_3 with MgO-containing slags and itself is slow to corrode it is often used as a grain phase in refractories needing to resist basic slags. Oh *et al.*[15] compared CAS slag penetration into polycrystalline spinel and alumina immersed in slag at 1400–1570°C. Iron from the slag diffused into spinel grains as well as along grain boundaries. The slag penetrating the spinel was thus a different composition from that of the slag penetrating the grain boundaries of the alumina specimens even though the original slag was the same. This emphasises the important concept of *local* liquid composition. Clearly at the boundary of the slag and the solid surface reactions occur changing the liquid composition but it is also possible that as liquid penetrates (say along grain boundaries) its composition changes and is quite different from the liquid at the bulk solid-liquid interface. If this change of liquid composition acts to increase its viscosity it can be beneficial in that it hinders penetration.

The open cubic crystal structure of $MgAl_2O_4$ and other spinels mean that they are able to accommodate nonstoichiometry and many impurity cations which can be preferentially taken up from liquid slags. Spinel can accommodate substantial excess Al_2O_3 but not as much MgO. While single phase MgO-rich spinels are theoretically achievable commercial MgO-rich spinel grain usually contains small periclase particles; bringing the associated problem of poor hydration resistance. Consequently, it is more likely that single-phase spinel is alumina rich. Al_2O_3-rich spinels contain an excess of charge compensating cation vacancies on octahedral sites so that it is easy for cations in the slag to find their way to these sites forming complex spinels i.e. $(Mg,Mn,Fe)O.(Fe,Al)_2O_3$ although the mechanism by which this occurs is not clear. The more rapidly diffusing species such as Fe and Mn will preferentially be taken up leading to high silica (and more viscous) slags adjacent to the spinel so limiting slag penetration and corrosion.

Mullite has an orthorhombic crystal structure containing oxygen vacancies which accommodate nonstoichiometry so that its average composition may range from $3Al_2O_3.2SiO_2$ to $3Al_2O_3.SiO_2$. Like spinel it is also able to accommodate many impurity cations such as Ti, Cr, Mg, Mn and Fe. Mullite is able, therefore, to absorb many cations from a slag (in particular iron oxides) so changing the composition and viscosity of the remaining liquid. It has excellent resistance to acid and neutral slags and mullite bricks find application in various parts of iron and steelmaking furnaces although never as a single phase. Samaddar *et al.*[16] investigated the dissolution of mullite in CAS slags. They suggested that the dissolution is diffusion-controlled and after reaction at 1500°C observed anorthite needles at the mullite-slag interface which quenching experiments indicated formed on cooling rather than at temperature. Aiba *et al.*[17] examined the reaction between mullite and molten steel and slag. They found that mullite is decomposed by Mn from the molten steel and CaO from the slag. Mn and CaO react with SiO_2 from the mullite to form low melting compounds. This dissociation of mullite by a fluxed composition is predicted by phase diagrams and often results in the appearance of corundum crystals.

Corrosion of predominantly two-phase oxide refractories

Influence of microstructure

Corrosion when more than one phase is present in a microstructure is initially complicated by the potential for differing solubilities of each phase in the starting liquid present during simultaneous dissolution reactions. Once these reactions have occurred a variation in local liquid composition may occur adjacent to each phase (Figure 4). The nature of each phase in the microstructure (grain size, shape and adjacent porosity level) also affects its corrodability. Invariably it is the porous bond or matrix that is initially attacked. Each of the products of initial reaction may then react with the melt pushing the reaction in unexpected directions. Often veins of penetrating liquid spread through the porous matrix. Post mortem examination of corroded refractories often reveals several boundary layers or zones of attack (Figure 5). These can be defined as:

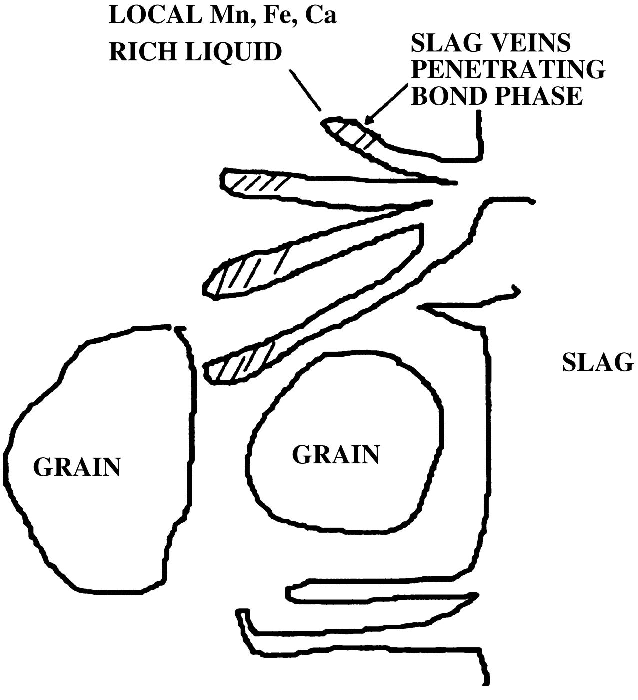

Figure 4. Local slag composition in penetrated body (shaded) may be quite different from that of bulk slag

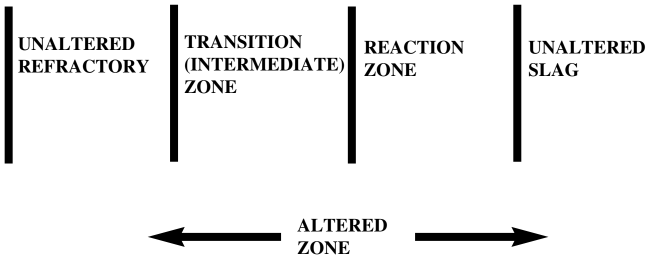

Figure 5. Various zones in corroded refractory

(1.) Unaltered slag,
(2.) Reaction zone (with massive changes in phase content compared to the original refractory)
(3.) Transition or intermediate zone (with some penetration and minor reaction)
(4.) Unaltered refractory.

Zones 2 and 3 together are termed the altered zone. Characterization of the nature of these zones gives insight into the reaction mechanism. They arise because the more rapidly diffusing slag species such as Mn, Fe and Ca penetrate the refractory forming product phases in the reaction zone while regions ahead or behind are denuded in them. Unaltered refractory means how it would be after exposure to the same temperature/time profile as in the corrosion test without penetrating melt. Often this control experiment is neglected in corrosion studies.

The composition of the bond in refractories is critical. Many refractories are prone to slag attack through the bond. MgO grain in magnesia and MgO-C bricks are held together by e.g. CMS (monticellite) or M_2S or C_2S through which the slag can penetrate and separate the MgO crystallites. Most of a refractories porosity is in the bond making this region most prone to penetration and attack. Minimizing the level of porosity and the pore size is a common aim of refractory processing requiring careful control of raw material particle size distributions. Sections 4.2.2 uses MgO- and alumina-spinel systems to illustrate corrosion mechanisms in two-phase refractories and highlight how to control them.

MgO-spinel and Al_2O_3-spinel

Refractories containing $MgAl_2O_4$ spinel have excellent thermal shock resistance and refractoriness and are being used increasingly in steelmaking and cement kilns, a trend driven in part by the need to replace Cr-containing linings. Commonly, they are used in castable systems based on calcium aluminate matrix cement and mixtures of Al_2O_3 and spinel grain or MgO and spinel grain and matrix spinel generated on processing or by *in situ* reaction.[18] Al_2O_3/spinel systems tend to be used in steelmaking while MgO/spinel systems are used in cement kilns although they are now also being used in secondary steelmaking ladles. MA spinel has a range of stoichiometry discernable by its phase field in the Al_2O_3-MgO binary phase diagram. Spinel powders are manufactured commercially by sintering or fusion. Fused spinel often contains significant quantities of Na_2O with the result that β-alumina can exist as a discrete phase. Sintered spinel is typically made with CaO-Fe_2O_3-SiO_2 additives which form a liquid phase often leaving calcium aluminates and silicates at grain boundaries and triple junctions.[19]

Nagai *et al.*[20] compared the slag penetration of alumina, spinel, and alumina-spinel castables. Castables with 20% spinel showed lowest penetration and corrosion explained by the alumina and spinel in the castable react with CaO, FeO, and MnO in the slag locally increasing its melting point and viscosity. Castables with 10-30% spinel showed good penetration and corrosion resistance. Other studies concluded that corrosion behaviour is a strong function of the spinel stoichiometry. Alumina-based refractories containing alumina-rich spinel show improved resistance to slag penetration against steelmaking slags. It has been suggested[21] that this behaviour arises from the defect structure of the nonstoichiometric spinel which contains an excess of charge compensating cation vacancies on octahedral sites. Consequently, it is easier for the rapidly diffusing cations in the slag to find their way into these vacancies forming complex spinels i.e. $(Mg,Mn,Fe)O.(Fe,Al)_2O_3$ in the refractory so that the increased viscosity and melting temperature of the local slag associated with higher SiO_2 content is achieved early in the corrosion process.

Recent studies have characterized corrosion mechanisms at the microstructural level. Goto *et al.*[22] investigated corrosion MgO-spinel bricks by CAS slag using a static brick test at 1400–1450°C. Thermodynamic calculations and post mortem examination of the corroded bricks enabled the mechanism to be determined. It involved initial dissolution of fine matrix MgO in the local slag reacting with alumina already present in the slag to form secondary spinel. Further solution of MgO in the slag and removal of Al_2O_3 via precipitation of secondary spinel leads to crystallization of CMS and C_3MS_2. Microstructural characterization revealed secondary spinel, CMS, C_3MS_2 and MgO forming in this sequence as the brick is penetrated highlighting the variation in composition at the refractory/slag interface. Korgul *et al.*[23] observed the microstructure change of Al_2O_3-spinel castables before and after a rotary slag test with a CMAS slag. Examination of the corroded refractories revealed the zones shown in Figure 6. The corrosion mechanism involved initial reaction of CaO in the slag with alumina fines in the refractory bond. The local slag then becomes saturated in CaO and Al_2O_3, and CA_2 is precipitated from it along with other calcium aluminosilicates. The spinel fines and grain in the refractory take up the $MnO/FeO/Fe_2O_3$ from the slag, which becomes silica-rich as CA_2 is precipitated and highly viscous. Further into the refractories CA_6 is formed, firstly crystallized with a tabular morphology in dense regions and then with a similar morphology in more porous regions. Deeper still in the refractory CA_6 had a whisker/needle morphology.

These studies highlight the complex interaction between take up of rapidly diffusing cations from the slag into solid phases (such as Fe and Mn into spinel) and dissolution of solid (initially fine, reactive matrix phases) into the slag altering its local composition. The liquid product of this interaction is the phase in contact with the solid phases of the refractory and responsible for the penetration and corrosion.

Corrosion of oxide-carbon composite refractories

Carbon-containing refractories are used throughout the steel industry. Benefits of carbon include its non-wettability by slag and its high thermal conductivity, which facilitates use of cooling systems and improves thermal shock resistance. Carbon is used in two forms. Pyrolytic carbon derived from pitch or resin binders which is located in the matrix and is fine and reactive or as graphite flakes which could be

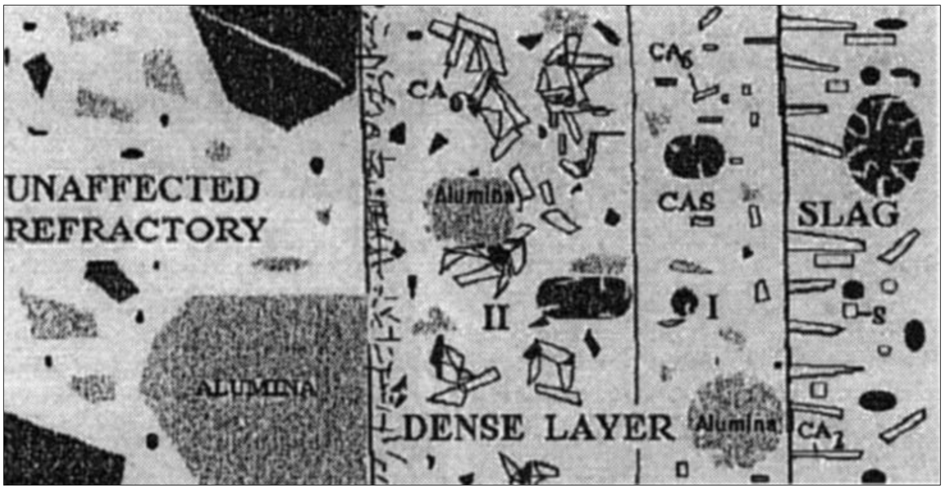

Figure 6. Zones of attack of Al_2O_3-spinel castable

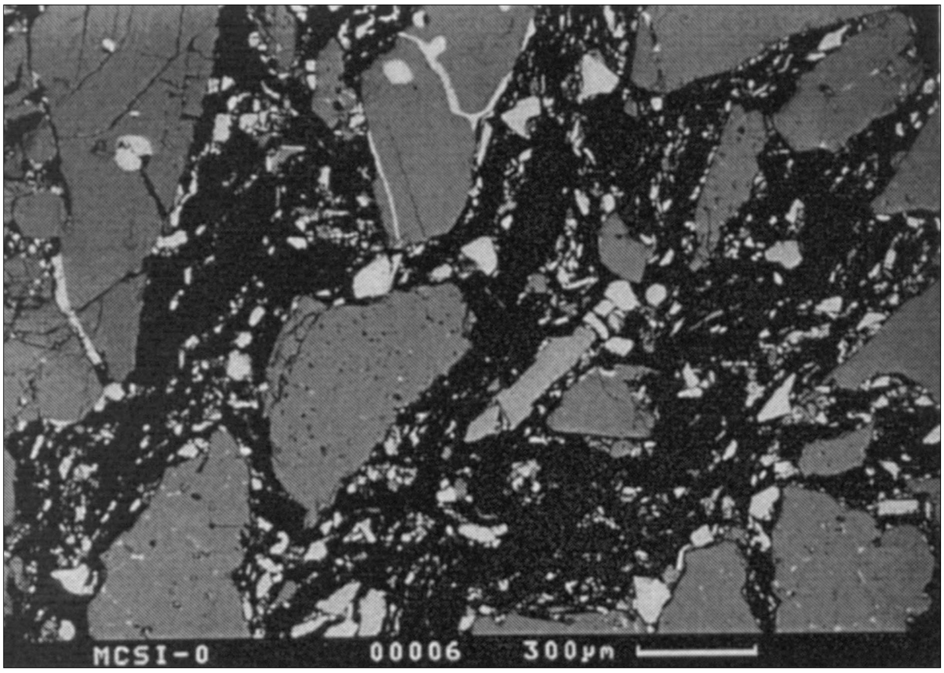

Figure 7. Unfired MgO showing fused and sintered MgO grain, graphite flakes and bright angular Si metal antioxidant

categorized as part of the aggregate system. Carbon in both forms is used with many refractory oxides such as Al_2O_3, SiO_2, ZrO_2 and MgO. A typical unfired microstructure (Figure 7) contains large sintered and fused MgO grains bonded to graphite flakes by a nanoscale carbon bond. Light antioxidant angular Si metal particles are the brighter phase in the matrix.

Different types of oxide-C refractories have emerged for use in different areas of iron and steelmaking and MgO-C refractories as used in BOS and EAF steelmaking furnace linings will be considered here. While carbon confers many of the desired properties on oxide-C refractories and means that slag penetration is usually limited it brings along the drawback of being highly vulnerable to oxidation. Consequently, lifetimes of carbon-containing refractories in oxygen-rich atmospheres depend, to a large extent, on their oxidation resistance. Furthermore, the weak nature of the C bond between the oxide and graphite leads to relatively low strengths. To inhibit oxidation and provide stronger (ceramic) matrix bonding at high temperatures, metallic or carbide powder additions are made and the thermochemical[24] and microstructural changes arising from their presence as a function of temperature are well known. Several mechanisms for the good slag resistance of C bonded doloma and MgO refractories have been proposed (summarized by Lee and Rainforth[25]). These include carbons non-wettability so that liquid penetration is limited, reduction by C of MgO to form Mg vapour which reoxidizes and deposits as a dense layer of secondary MgO at the slag-brick interface physically preventing penetration, reduction by C of iron oxides to Fe metal so that they do not attack the oxides forming low melting phases and formation of CO vapour by oxidation of C and/or Mg vapour (from reduction of MgO) which provides an overpressure resisting slag/metal ingress. Which of these mechanisms is the most significant is still unclear.

Corrosion of oxide-C refractories follows the scheme shown in Figure 8:

- *formation of a decarburised layer* due to oxidation of graphite/pyrolytic C mainly by FeO in the slag or oxygen in the furnace atmosphere (Figure 8a)
- *infiltration* of slag into the decarburized layer and erosion of the oxide grain by slag penetration aided by high temperature softening of any intragranular silicate bond and reaction and dissolution of the oxide grain into slag and molten steel (Figure 8b)
- *reduction of oxide grain* by high temperature (≈1600°C) reaction with carbon (in MgO systems this is termed the MgO-C reaction) resulting in its exposure and further erosion (Figure 8c).

The microstructures of oxide-C refractories (Figure 7) contain identical grain phases as those described in a previous section but with graphite and pyrolytic carbon present as well as various phases derived from the antioxidant additions. Simplistically it can be considered that once the C has gone the wear of grain phases will be similar to those discussed in the previous sections. However, this picture is complicated by the fact that the atmosphere may be reducing (although in some cases locally oxidizing) and the liquids may contain low levels of C. Furthermore, several reactions may occur leading to generation of vapour species. The thermodynamic situation is, thus, rather complex and may vary depending on location in the brick i.e. whether the hot (slag) face is being considered or the inside of the brick away from liquid penetration.

Many studies have indicated the beneficial protective effect of a secondary MgO dense layer formed at the hot face of MgO-C bricks first detected by Herron *et al.*[26] In both dolomite and MgO refractories this arises from reduction of MgO by C to Mg vapour which is transported to the hot face where it subsequently reoxidises to fine-grained, dense MgO helping to prevent slag/metal ingress. This dense layer does not always form and careful control of conditions both inside and outside the refractory are required to maintain it. For example, a high CaO/SiO_2 ratio slag is required which maintains the delicate balance between dense layer dissolution and formation by limiting

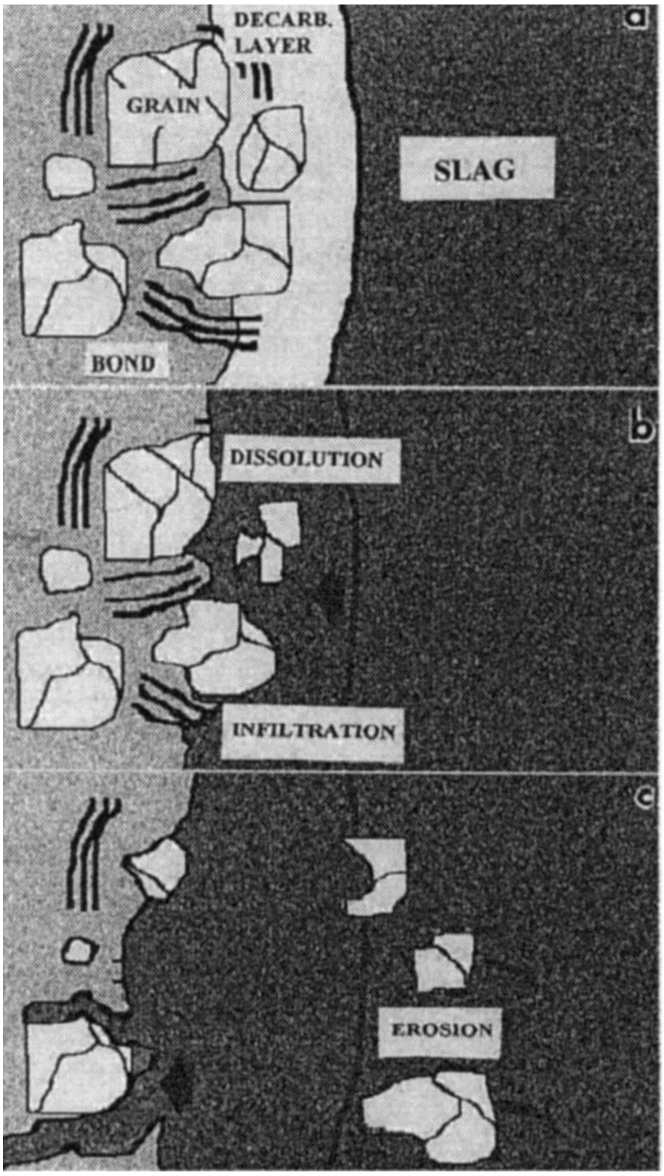

Figure 8. Schematic of general mechanism of corrosion of oxide-C refractories

the former.[27] Furthermore, the presence of iron oxide in the slag is beneficial as it diffuses into the MgO layer forming $MgFe_2O_4$ in contact with the slag, (Mg,Fe)O further in the refractory and Fe metal inside the brick. This observation suggests that oxygen is continuously supplied from the slag to the dense layer by reduction of iron oxides. Inside the brick the following reaction occurs

$$FeO_{(1)} + Mg_{(v)} \rightarrow Fe_{(s)} + MgO_s$$

helping the MgO dense layer to grow while causing precipitation of metallic Fe. It is now realised that dense layer formation can be promoted by metallic additions to the MgO-C brick.

MgO grain quality

The quality (i.e. purity, porosity, and crystallite size) of the oxide grain used in oxide-C refractories has significant effects on the corrosion resistance of the refractories. For example, MgO grain usually contains various second phases arising from impurities or deliberate additions (such as SiO_2, Al_2O_3, Fe_2O_3, Cr_2O_3, FeO and CaO) to provide a silicate bonding phase. To improve the refractories corrosion resistance the purity of the MgO grain must be enhanced, in particular, to determine C/S ratio which controls the compositions of these bond phases. Usually, the C/S is kept > 2 so that refractory C_2S and C_3S form in the matrix.[28] Among other impurities, B_2O_3 is the most critical because it fluxes the C_2S bond, lowering its melting point so that the refractories grains literally float apart at temperatures as low as 1200°C. Furthermore, its presence can accelerate the oxidation of carbon by MgO via the MgO-C reaction[29] decreasing corrosion resistance. SiO_2 also accelerates this reaction so it is more pronounced in low C/S bricks. Larger crystallite size within the magnesia grain means fewer secondary phase containing grain boundaries which can be penetrated by liquid leading to improved corrosion resistance.[30] The large crystallite size (typically over 100 μm) may also decrease the extent of the MgO-C reaction by limiting the surface area of contact. Fused magnesia grain has higher purity and larger grain size than sintered grain and, hence, fused grain MgO-C bricks show better corrosion resistance than those containing sintered MgO[31].

Carbon quality and type

Carbon in MgO-C refractories is present as graphite or pyrolysed carbon from pitch and resin. Detailed comparative studies on the reactivity of these forms of carbon with slags are still lacking and this should be a fruitful area for further study. However, some useful research has been reported. For example, Dietrichs *et al.*[32] found different wear profiles for pitch- and resin-bonded MgO-C refractories in a crucible test. This was explained by the lower oxygen partial pressures in resin-bonded refractories believed to result from higher carbon contents allowing formation of a dense MgO layer in direct contact with the slag whereas in pitch-bonded brick this layer is produced in the altered zone at a depth of about 3 mm. In resin-bonded brick the FeO from the slag was reduced to metallic iron at the slag front thereby decreasing the aggressiveness of the slag whereas in pitch-bonded refractories this occurs at the deepest part of the altered zone. The resulting slag penetration into the fine-grain matrix as well as diffusion into the coarse grains results in widened grain boundaries (veins) and disintegration of the pitch-bonded MgO grain. In resin-bonded bricks the dense layer was generally attacked only at the slag front. Purity and crystal size, therefore, had a stronger influence on corrosion resistance of pitch-bonded brick. Naefe *et al.*[33] also compared the corrosion resistance of pitch- and resin-bonded MgO-C bricks but at 10 wt% graphite loading they observed little difference between bricks made from the two types of binder. Clearly further study is necessary.

The influence of graphite content on corrosion of MgO-C bricks has also been extensively studied. Yoshino *et al.*[34] found that wear rate decreased with increasing graphite content from 10–35 wt% but increased above 35% presumably because the graphite flake content was so high that they were acting as flaws opening up the microstructure to penetration. However, Nakao *et al.*[35] investigated the effect of graphite content on corrosion of MgO-C in oxidizing atmosphere and found that the corrosion resistance of 10% C-containing MgO-C refractories was superior to those with 20% C although no explanation was offered.

Impurities in the ash remaining after graphite flakes have decomposed (especially SiO_2) react with MgO grains to form low melting phases which accelerate the MgO-C reaction[36] and thus decrease the corrosion resistance of MgO-C refractories. Consequently, the trend over the passed decade has been to increase graphite purity from levels of about 88% to 99% carbon.

Antioxidants

Two main types of additives are used in oxide-C refractories, metals/alloys (such as Al, Si, Mg and Al/Mg) and boron-based compounds (such as B, B_4C, CaB_6, ZrB_2, $Mg_3B_2O_6$ and SiB_6).[37] Historically, the emergence of these additives began in the 1970s with use of pure metal (Si, Al, Mg) powders, followed in the 1980s by development of alloys and in the 1990s by ceramic powders. These two additive types work in different ways. Metal/alloy additives act as CO reducing agents contributing to carbon oxidation inhibition and/or improving hot strength by forming high-temperature ceramic bonds. The ceramic phases forming are a strong function of the temperature and environment but e.g. Si may react to form SiO_2, Mg_2SiO_4, SiC or Si_3N_4 and Al to form Al_2O_3, $MgAl_2O_4$, Al_4C_3 or AlN as fine bonding phases which act to hold the microstructure together thus improving hot strength. Furthermore, metal additives have been observed to facilitate dense layer formation both at the slag-refractory interface and locally inside the brick leading to earlier in service protection. Local dense layers form e.g. around graphite flakes by deposition of MgO and Mg_2SiO_4 from Mg or SiO vapours derived from metal additives so preventing graphite oxidation.[38] Condensed species also deposit in pores helping to densify the microstructure limiting oxygen penetration.[39] Boron-based additives, on the other hand, act to block open pores to reduce the oxidation of carbon by formation of liquid phases. This has the drawback of lowering the hot strength and corrosion resistance.

SiC and Si_3N_4 have also been used to improve the corrosion resistance[40] with SiC additionally observed to retard carbon oxidation although the mechanism has not been specified. When the SiC content is below about 5% the wear rate of the bricks decreases with increasing SiC content but above about 5%, owing to excessive formation of SiO_2, the corrosion resistance begins to decrease. Conversely, Nagai *et al.*[168] indicated that addition of SiC always decreases the corrosion resistance of MgO-C bricks.

Slag composition

Slag composition also has a significant effect on the corrosion resistance of MgO-C refractories. In general, corrosion rate increases with increasing Cr_2O_3, iron oxide and MnO but decreases with increasing MgO or basicity in the slag.[1] The use of *in situ* slag coating techniques to protect the hot face has improved primary steelmaking vessels lives substantially. Watanabe *et al.*[41] determined that MgO-C brick texture degradation was greatly reduced by slag coating and inferred that the evaporation of Mg and CO vapour generated by the MgO-C reaction was suppressed. The resulting increase in brick internal pressure limited further reaction. The ideal composition of slag for use as an *in situ* protective coating needs further study.

Summary

This review has highlighted two types attack of refractories by silicate liquids: direct in which atoms of the solid dissolve directly into the liquid and indirect in which a boundary layer forms between the original solid and liquid. Direct attack is usually undesirable while indirect may be beneficial if the boundary layer leads to a lower rate of attack. The influence of the local liquid at the point of penetration into the refractory is seen to have a critical effect on the nature of attack. Its composition is influenced by the bulk liquid and/or the refractory. Rapidly diffusing species in the bulk liquid such as Mn and Fe migrate to the local liquid. The refractory may take up species from the local liquid or release its own, so altering the local composition and viscosity. Control of slag attack can be through the refractory whose composition is arranged to make the local liquid viscous by uptake or release of suitable species or by development of a tight texture and/or dense layers at the liquid/refractory interface. Alternatively, the slag composition can be controlled to minimize attack of the refractory by e.g. saturating it in the main refractory phases. In practice, passive, protective coatings can be generated by alternative process techniques such as slag splashing in BOF vessels or clinker coating in cement kilns. Challenges for the future are to:

- use current understanding of interactions between slags and refractories to develop more corrosion-resistant refractories e.g. by formation of controlled boundary layers or use of benign boundary layer phases in bulk refractories
- develop experimental corrosion tests which more nearly simulate practical conditions
- improve techniques for characterizing corrosion mechanisms as they occur in real situations
- attempt to develop a comprehensive theoretical model of high-temperature corrosion which includes calculations of solid/liquid/vapour equilibria and physical erosive liquid flow effects along with heat flow calculations via finite element methods into the predominantly chemical dissolution phenomena considered in this review.

ReferencesS

1. LEE, W.E. AND ZHANG, S. *Int. Mater. Rev*. vol. 44, no. 3. 1999. pp. 77–104.
2. MCCALLUM, N. and BARRETT, L.R. *Trans. Brit. Ceram. Soc.* vol. 51, 1952. pp. 523–48.
3. DUFFY, J.A., INGRAM, M.D., and SOMERVILLE, I.D. *J. Chem. Soc. Faraday Trans.* vol. 14, 1978 pp. 1410–19.
4. YANG, Y.D. and SOMERVILLE, I.D. Phys. Chem. Glasses vol. 43C. 2002. pp. 362–71.
5. McCAULEY, R.A. '*Corrosion of Ceramics*', 1994, New York, Marcel Dekker.
6. COOPER, A.R. and KINGERY, W.D. in '*Kinetics of High-Temperature Processes*', (ed. W. D. Kingery) New York, Wiley. 1959. pp. 85–92.
7. WAGNER, C. *J. Phys. Colloid Chem.* vol. 53. 1949. pp. 1030–33.
8. FAHRBACH, D.O.E., HOWAT, D.D., and JOCHENS, P.R. *Trans. Brit. Ceram. Soc.* vol. 68. 1969. pp. 151–58.
9. KOBAYASHI, M., NISHI, M., and MIYAMOTO, A. *Taikabutsu Overseas*, vol. 2. 1982. pp. 5–13.
10. KII, T., HIRAGUSHI, K., YASUI H., and MUKAI K. *Proc. Unified International Technical Conference on Refractories* (UNITECR'95), Kyoto, Japan. 1995. pp. 379–386.
11. LEE, W.E. and MOORE, R.E. *J. Am. Ceram. Soc.,* vol. 81. 1998. pp. 1381–1407.
12. LEE, W.E., ZHANG, S., and SARPOOLAKY, H. *Ceramic Transactions* vol. 125. 2001. pp. 245–252.
13. SANDHAGE, K.H. and YUREK, G.J. *J. Am. Ceram. Soc.*, vol. 73. 1990. pp. 3643–49.
14. HERZOG, S.P. and SCAND. *J. Met.* vol. 5. 1976. pp. 145–150.
15. OH, T.-I., SHEN, L.N., URE, R.W.JR., and CUTLER, I.B. *Bull. Am. Ceram. Soc.* vol. 56. 1977. pp. 64–50.
16. SAMADDAR, B.N., KINGERY, W.D., and COOPER, A.R. Jr. *J. Am. Ceram. Soc.* vol. 47. 1964. pp. 249–254.
17. AIBA, Y., OKI, K., ARAKAWA, K., SUGIE, M., and WATANABE, T. *Taikabutsu*, vol. 37. 1985. pp. 434–440.
18. FUHRER, M., HEY A., and LEE, W.E. *J. Euro. Ceram. Soc.*, vol. 18. 1998. pp. 813–820.
19. WILSON, D.R., EVANS, R.M., WADSWORTH, I., and CAWLEY J. *Proc. Conf. UNITECR'93*, 1993, pp. 749–760.
20. NAGAI, B., MATSUMOTO, O., ISOBE T., and NISHIUMI Y. *Taikabutsu*, vol. 42. 1990. pp. 418–426.
21. MATSUMOTO, O., ISOBE, T., NISHITANI, T., and GENBA, T. US Patent 4990475, 1991.
22. GOTO, K., ARGENT, B.B., and LEE, W.E. *J. Am. Ceram. Soc.* vol. 80. 1997. pp. 461–71.
23. KORGUL, P., WILSON, D.R., and LEE, W.E. *J. Euro. Ceram. Soc.* vol. 17. 1997. pp. 77–84.
24. YAMAGUCHI, A. Taikabutsu Overseas vol. 4. 1984. pp. 32–37.
25. LEE, W.E. and RAINFORTH, W.M. Ceramic Microstructures, Property Control by Processing, London, Chapman and Hall, 1994.
26. HERRON, R.H., BEECHAN, C.R., and PADFIELD, R.C. *Bull. Am. Ceram. Soc.* vol. 46. 1967. pp.1163–68.
27. KIM, S-M., NICHOLSON, P. S., and LU, W.-K. *Bull. Am. Ceram. Soc.* vol. 57. 1978. pp. 652–656.
28. WHITE, J. High Temperature Oxides, Part 1: Magnesia, Lime and Chrome Refractories, (ed. A. M. Alper). New York, *Academic Press*, 1970, pp. 77–141.

29. ISHIBASHI, T., MATSUMURA, T., HOSOKAWA, K., and MATSUMOTO, K. *Taikabutsu* vol. 35. 1983. pp. 473–448.

30. ISHIBASHI, T., MATSUMURA, T., and NOMIYAMA, S. *Taikabutsu* vol. 36. 1984. pp. 519–522.

31. ARAKI, S. and FUJII, K. *Taikabutsu* vol. 32. 1980. pp. 579–583.

32. DIETRICHS, P., DHUPIA, G.S., and KRONERT W. *Interceram Special Issue* 1985. pp. 84-87.

33. NAEFE, H., SEEGER, M., and STUSSER, D. *Interceram Special Issue* 1985. pp. 37–40.

34. YOSHINO, S., KYODEN, H., NISHIO, H., MATSUMOTO T., and WATANABE J. *Taikabutsu Overseas* vol. 3. 1983. pp. 21–23.

35. NAKAO, J., ISHII A., and ASANO K. *Taikabutsu* vol. 44. 1992. pp. 114–121.

36. COOPER, C.F. *Refractories J.* vol. 6. 1980. pp. 11–21.

37. CHAN, C.F., ARGENT, B.B., and LEE, W.E. *J. Am. Ceram. Soc.* vol. 81 1998. pp. 3177–88.

38. ARTIR, R., LEE, W.E., ARGENT, B.B., and LARSEN, P.H. *High Temperature & Mater. Science* vol. 34. 1995. pp. 69–103.

39. SEMLER, C.E. AND BREZNY, R. in *Proc. 1st Conf. on Refractories*, Tokyo, Japan. 1983. pp. 171–183.

40. NARUSE, Y., FUJIMOTO, S., KAMATA, Y., and YOSHITOMI J. *Taikabutsu*, vol. 35. 1983. pp. 455–459.

41. WATANABE, A., TAKAHASHI, H., SAEKI, G., NANBA S., and NISHIKAWA Y. *Taikabutsu*, vol. 34. 1982. pp. 339–341.