Refractory considerations

Wear reasons and material choices of refractories for aluminium melting and holding furnaces.

By Ruth Engel*

The aluminium industry is a major consumer of refractories even though its processes take place at a comparatively low temperature (**Fig 1**). This leads to the expectation that refractory selection for use in secondary aluminium furnaces entails few challenges, but that is misleading.

The hot face refractories in melting/holding furnaces are subjected to increasingly demanding environments with the concurrent expectations of less time required for maintenance and higher efficiencies. The changes in throughput expectations can be observed in the type of fluxes used, in the furnace cleaning practices, the replacement of gas burners with oxy-fuel ones and in the use of ever greater amounts of recycled Al metal[2]. These factors result in higher furnace temperatures and the increased production of Mg bearing alloys both detrimental to the refractories.

This work will present the reasons for hot face refractory wear/damage, discuss the refractory choices and provide suggestions for deciding what to use.

Refractory considerations

The lining usually consists of layers. The innermost one, the working lining, has to contain and be in contact with molten metal, withstand the interaction and attack of flux/salts and dross and, be inert to an alkali bearing atmosphere. Behind these refractories, a back-up layer, an insulating layer or both, may be installed. The appropriate refractory design, together with good operating practices, minimises the system's heat losses and provides maximum energy availability to the load (**Fig 2**).

Refractory wear

Aluminium melting/holding furnaces consist of several distinct zones: The upper zone has the burners and the hot furnace atmosphere and, the lower zone contains the molten aluminium. Between them is the belly band which has to withstand a combination of molten aluminium/dross -flux/atmosphere and represents the most difficult environment.

Most furnaces are lined with alumino-silicate based materials due to their ease of availability and cost advantages. Often, different qualities are used for the upper and lower furnace zones so as to best address their distinct requirements. Generally, the refractory in contact with the metal wears as a result of chemical reaction(s) of the aluminium with the lining components, mechanical damage resulting from cleaning to remove the dross from the walls/bottom of the furnace and thermal shock plus mechanical damage due to the charging practice while the upper zone is exposed to high temperatures, alkalies and thermal shock resulting from opening the furnace door. The belly band is part of the lower zone refractories although it has to withstand all of the above challenges and, additionally, intermittent and localized extreme temperatures due to thermiting.

Reaction(s) of refractory in contact with metal

Much research has been carried out to understand the reactions and wear mechanisms between refractories and molten aluminium. Reactions between the alumino-silicate and metal leads to the formation of corundum. Although corundum is the mineral name for pure Al_2O_3, in this context, it is a mixture of Al_2O_3 with unreacted refractory pieces, plus Si and Al. This alteration product often starts below the belly band and grows upwards disrupting the integrity of the lining. It is very difficult to remove because it strongly attaches itself to the refractory by filling its porosity. Cleaning of the walls of the furnace is imperative to maintain its capacity and because corundum adversely affects the thermal properties of the refractories.

Fig 3 is a schematic of the corundum formation and **Fig 4** shows actual examples of build-up.

In order to determine the likelihood of the metal reacting with the various mineral components of a refractory one can use thermodynamics. **Fig 5** is the Ellingham diagram for aluminium in contact with several refractory raw materials showing that all silica can be reduced by molten aluminium regardless if it is present as pure silica or in a mineral like mullite.

The formation of corundum is driven by the reduction of SiO_2 according to the following reaction
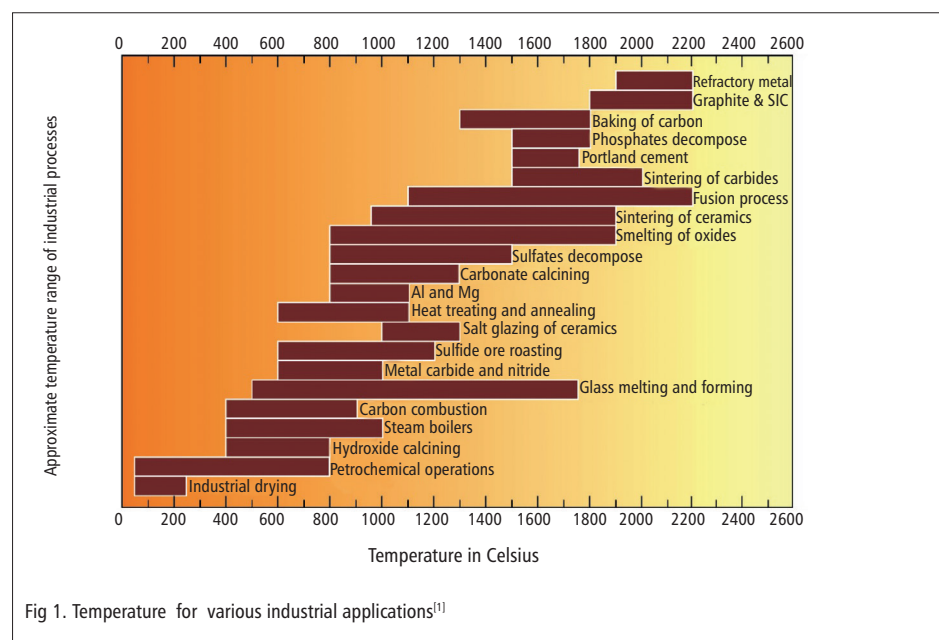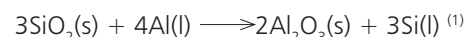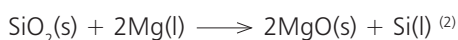
$$3SiO_2(s) + 4Al(l) \longrightarrow 2Al_2O_3(s) + 3Si(l) \quad {}^{(1)}$$
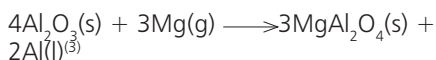

Fig 1. Temperature for various industrial applications[1]

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To complicate matters, if the aluminum is a magnesium bearing alloy, then the Mg can reduce the SiO_2 leading to the formation of either magnesia

$$SiO_2(s) + 2Mg(l) \longrightarrow 2MgO(s) + Si(l) \quad (2)$$

or react with the Al_2O_3 to form a spinel:

$$4Al_2O_3(s) + 3Mg(g) \longrightarrow 3MgAl_2O_4(s) + 2Al(l) (3)$$

Depending on the amount of Mg in the Al-alloy either MgO, $MgAl_2O_4$ or both, can form.

In addition, the oxidation of the aluminium will occur any time there is oxygen available:

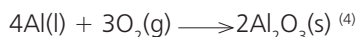$$4Al(l) + 3O_2(g) \longrightarrow 2Al_2O_3(s) \quad (4)$$

Fig 6 is a schematic of the reaction mechanism for the formation and growth of alumina, magnesia and spinel in a refractory in contact with an aluminium alloy and **Fig 7** shows a refractory microstructure supporting these reactions. A more complete discussion can be found in several papers[7,8,9]

Although these reactions have garnered most attention other oxides frequently found in refractories, like Fe oxide, TiO_2, etc., are also reduced by molten aluminium.

Control of aluminium penetration

Several approaches are available to counter the ability of the aluminium to wet and subsequently penetrate and interact with the refractory. Their purpose is to retard or inhibit the reduction of the refractory components thereby avoiding the initiation of reactions 1 through 3. Much development work has been carried out to deal with this and below is a listing of available technologies.

The use of anti-wetting additions to refractories in contact with molten aluminium is a common approach, specially for calcium aluminate containing castables. Many different materials have been used for this purpose and their addition is considered proprietary in nature. Consequently, the mechanism(s) by which they work are not always known. Additives commonly mentioned in the literature are barium sulphate, different types of fluorides (AlF_3, CaF_2, etc.)[10,11,12] and others. Studies carried out to determine the mechanism for protection of the refractory by adding barium sulphate showed that it most likely is the result of the formation of a celsian[10] at 1000°C which acts as a barrier to Al corrosion, while the flourides are thought to fill in pores with reaction products. Anti-wetting additions decompose at differing temperatures and once this is exceeded the refractory loses their protection.

Another approach is to add a phosphate as it imparts highly non-wetting properties to the refractory and does not decompose until temperatures >1500°C are reached[13]. In brick it was incorporated into the mix prior to firing, in castables it can be the bonding agent or supplement it and, in mouldables (plastics) it is the binder. In addition, the use of a phosphate as a component of the monolithic aids in bonding new and used refractories, which is particularly important when carrying out a repair.

The use of sol-gel binders, in particular colloidal silica, results in sufficiently small pores so as to hinder aluminium penetration, thereby not requiring or minimising the need for a non-wetting component[9].

The latest development is the use of special raw materials or binders which have low wettability with respect to aluminium, and contain only lime and alumina, like calcium hexaluminate or bonite[6,14,15]. Microscopy of bonite based refractory test samples showed no metal penetration after exposure to molten aluminium (**Fig 8**). Some of these castables also have built-in insulating properties due to the nature of their aggregate[17].

Testing of refractories

An accepted mode for evaluating the merits of a new refractory for use in
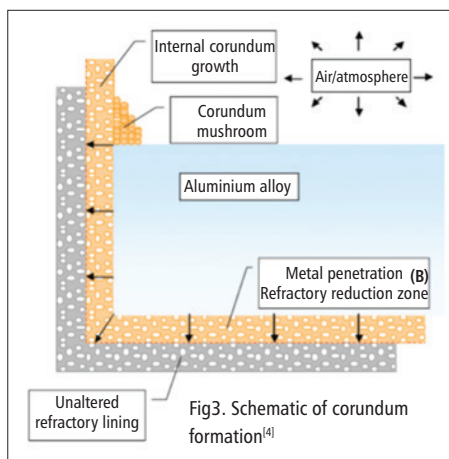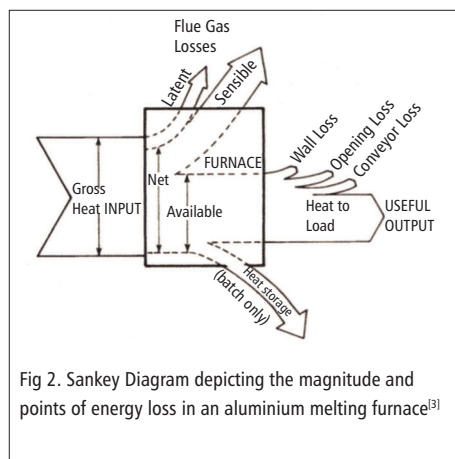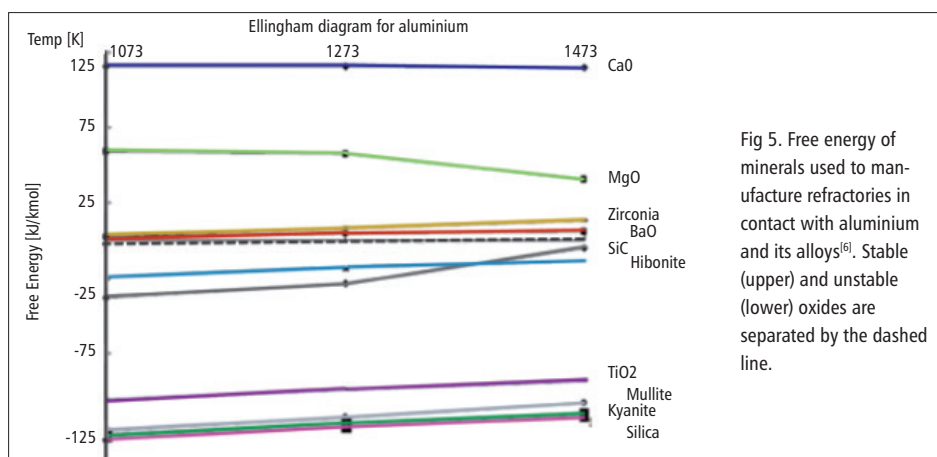

Fig 2. Sankey Diagram depicting the magnitude and points of energy loss in an aluminium melting furnace[3]

Fig3. Schematic of corundum formation[4]

Fig 4.Corundum: (A) build up on refractory sidewall, (B) piece removed from a surface[5]

Fig 5. Free energy of minerals used to manufacture refractories in contact with aluminium and its alloys[6]. Stable (upper) and unstable (lower) oxides are separated by the dashed line.

Fig 6. Schematic representation of the Al and Mg reactions[8]

Fig 7. Microstructure of molten Al-5 wt. % Mg alloy, after oxidation, in air and at 1150°C. The layer between the alumina and aluminum areas is the primary $MgAl_2O_4$ spinel[8]
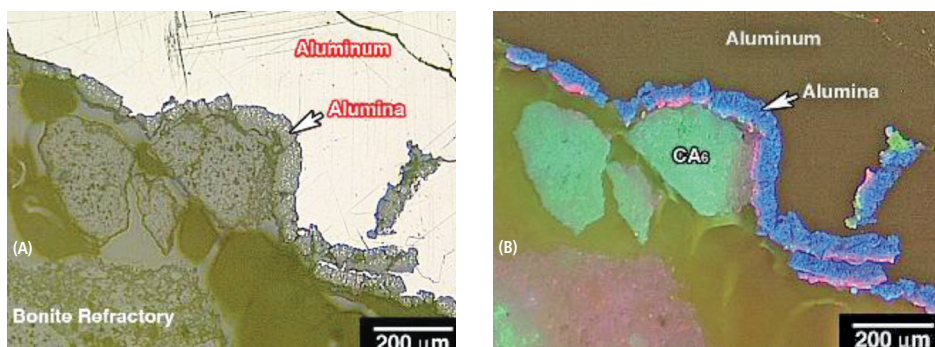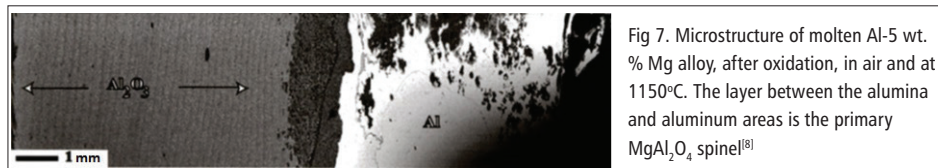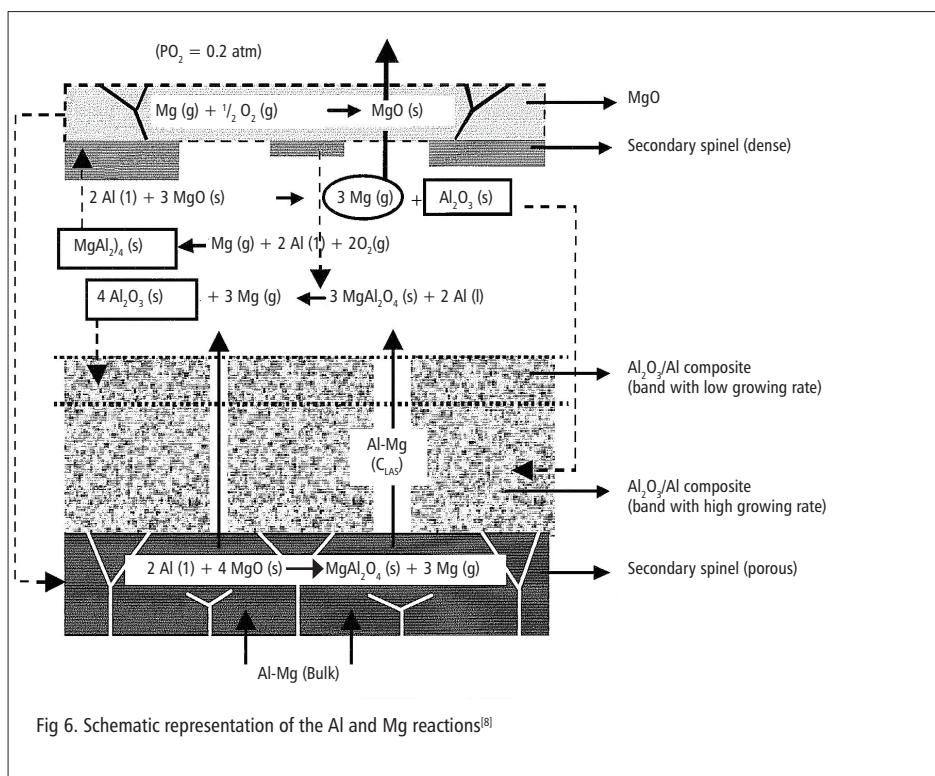

Fig 8. Reflected light/Cathodoluminescence (CL) micrographs showing no metal penetration and minimal metal-refractory reaction for bonite based refractory. (A) reflected light, (B) same area but using CL. Blue CL alumina layer is due to oxidation of aluminum, not due to refractory reduction[16]

Fig 9. Castable molds showing different shaped cavities for use in testing[18]
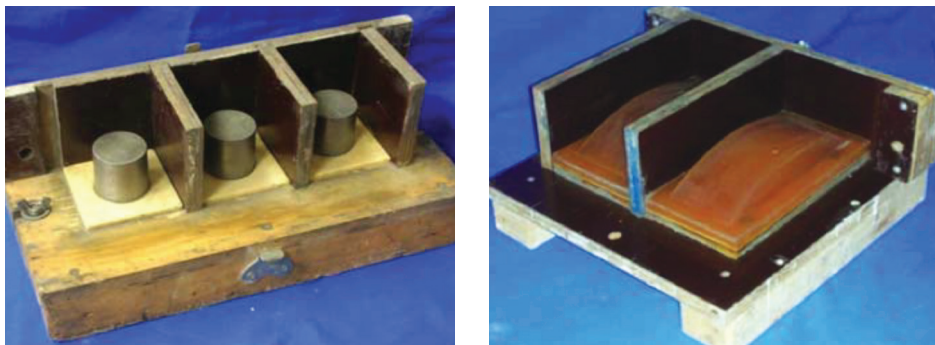
contact with aluminium is for it to undergo testing to simulate actual use conditions. Several major aluminium companies have developed their own "standard" tests that expose a refractory to molten metal for a selected length of time, at a pre-established temperature. The tests differ in the shape of the cavity which is to be filled with metal (**Fig 9**), the pre-fire temperature in the case of a monolithic and, the temperature and the length of exposure time at which the test is carried out, all of which can vary significantly and, will affect the results[18]. The refractory is then rated according to a pre-established criteria. This often consists of a visual comparison of the metal's penetration and degree of alteration between the currently used and a new refractory.

The refractory in the belly band is additionally stressed by exposure to fluxes. These are materials manufactured by combining several different types and amounts of alkali salts, fluorides and chlorides, which have low melting points and consequently penetrate the refractory. To determine the additional effect fluxes have on the refractory integrity and components, laboratory studies involving cup tests to simulate belly band conditions are carried out. They expose refractories to aluminium alloys covered with individual or a combination of salts, KCl, $CaCl_2$, NaCl, CaF_2, NaF, cryolite (Na_3AlF_6), etc. while at high temperatures (**Fig 10**). These tests have shown that fluorides are more aggressive towards refractory integrity than chlorides and that the use of cryolite leads to the greatest amount of damage[19].

The upper zone conditions are strongly dependent on the furnace temperature, gas cleanliness and type(s) used and, any alkalies present as, at high temperatures the flux components decompose and can become gaseous. Once the flux components are part of the atmosphere they can penetrate the refractory and react with it. Alkali testing is used to determine if a new refractory formulation shows improved wear resistance in this environment before field installation takes place. It can be carried by forming a cavity in a brick like shape or setting refractory samples in an enclosed box. The cavity/box is filled with the alkali to be tested against, a lid is added to restrict the movement of the gaseous species and the assemblage is heated and kept at temperature for a predetermined length of time. The tested pieces are then analysed as to penetration and alteration. **Fig 11** shows the results of such a series of tests. In aluminum melting/holding furnaces the alkalies are assumed to react with silicates in the refractory forming a glass which seals the pores preventing further destruction.
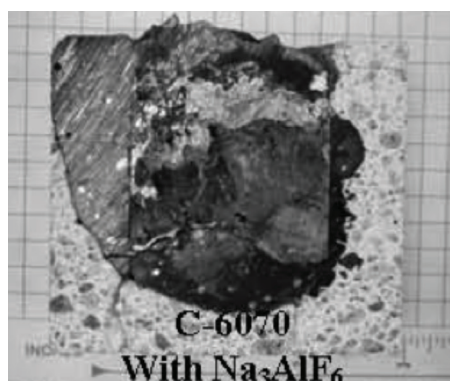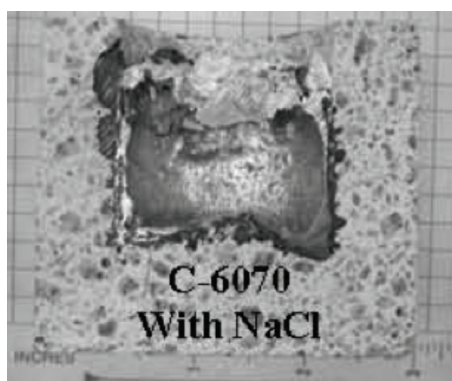
Fig 10. Cross section of cup test showing the effect of different salts on the same low cement castable (C-6070): ~30% SiO_2, ~57% Al_2O_3 with non-wetting addition[19]

Refractory choices

Refractories used to line aluminium melting/holding furnaces can be bricks, castables, mouldables (plastics) or, a combination of any of these.

Initially phosphate bonded, fired brick were used, but this has been superseded with the advent of low and ultra-low cement castables. The disadvantage of using brick was that their installation required bricklayers, which took considerable time. In addition, the mortar used between the brick could be a weak link of the installation. An advantage was that the properties of the refractories were controlled during their manufacture and did not depend on field conditions.

The early use of castables was restricted to precast and fired shapes, big block, while the current expectation is that they will be field installed[21]. Precast shapes can have the same advantages as brick but still have joints and need to be brought to use temperature, which can be a challenge. Field cast installations require less time than brick for relines and lead to a minimum number of joints for comparable performance. Their disadvantage is that they depend on the installation procedures being closely adhered to so the expected properties are achieved and for a proper dry-out/burn-in schedule to be followed before they come in contact with aluminium. The selection of a castable should consider the advantages of the different types of binder/raw material systems from a wear resistance, chemical compatibility, available equipment and personnel for installation, recommended speed of dry out and, cost.

Although the use of mouldables (plastics) is not as prevalent as castables there is no technical reason for avoiding them. Care needs to be taken to ensure proper installation procedures are followed to avoid laminations and, burn-in should take place soon after installation as the refractory may creep due to the binder being heat setting.

Even though each type of refractory was considered by itself, they can be used in combination, and often are.

In summary, there are many different types of refractories available to line aluminium melting/holding furnaces. Their selection should consider the locally available choices, the abilities of the personnel that will carry out the refractory installation, equipment available for dry-out/burn in, total time allowed for installation and heat up, cost, etc.

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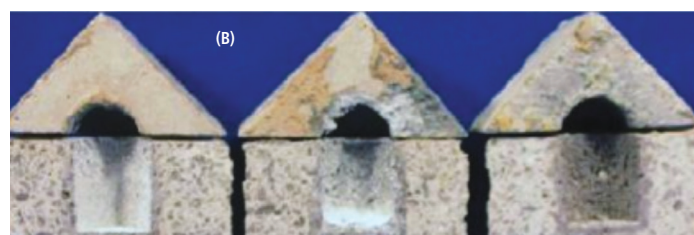
Fig 11. Condition of refractory material for aluminium melting furnace after alkali testing at 1100°C with K2CO3/Na2CO3: (A) refractory currently in use, (B) new formulation[20]

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