Refractory Considerations for Aluminum Melting and Holding Furnaces

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The Aluminum Industry, is a major consumer of refractories. In the United States, it is the second largest metal producer following steel. Because aluminum melts at a relatively low temperature (Figure 1) the refractory selection for use in secondary aluminum furnaces is often considered to be an easy application compared to that of other processes, but as anybody who has worked in the area can attest, it presents its own challenges.

To complicate matters, the refractories in the melting/holding furnaces are increasingly subjected to more 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 ever greater amounts of recycled Al metal used.

The combination of these events have led to an increase in furnace temperatures and more Mg bearing alloys to be melted creating a more aggressive environment for the furnaces. At the same time many new refractory choices to line the furnaces have come on the market. This work will present the reasons for refractory wear/damage, discuss some of the refractory choices available and provide considerations for deciding what to use.

Refractory Wear

Aluminum melting/holding furnaces can be thought of as consisting of several distinct zones based on their exposure environment: the upper zone which has the burners and contains the hot furnace atmosphere and the lower zone which is in contact with the molten aluminum. The lower zone’s upper boundary, the so-called bellyband, bridges these two areas and is exposed to a combination of molten aluminum-dross/flux-atmosphere representing the most difficult environment.

Most furnaces are lined with alumino-silicate based materials due to their ease of availability and cost advantages. Generally, different qualities are used for the upper and lower furnace areas so as to best address their distinct requirements. In broad terms the refractory in contact with the metal, the lower area, wears as a result of chemical reaction(s) of the aluminum 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 areas are exposed to higher temperatures, alkalies and thermal shock resulting from opening the furnace door. The belly band refractories have to withstand all of the above because of the changing metal level and, in addition, may have intermittent and localized high 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 the refractories and the molten aluminum. Reactions between the alumino-silicate and metal leads to the formation of corundum. Although corundum is the mineral name for Al2O3 in this context it is a mixture of Al2O3 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 and is very difficult to remove because it strongly attaches itself to the refractory filling its porosity. Cleaning of the walls of the furnace is imperative to maintain its capacity and because the formation of corundum negatively affects the thermal properties of the refractories.

Figure 1: Temperature for various industrial applications

Figure 2 is a schematic of the corundum formation and Figure 3 shows actual examples of build-up.
In order to determine the likelihood of the metal reacting with the various mineral components that make up a refractory one can use thermodynamics. Figure 4 is the Ellingham diagram for aluminum in contact with several refractory raw materials showing that all silica can be reduced by molten aluminum regardless if it is present as pure silica or in a mineral like mullite.

The formation of corundum is driven by the reduction of SiO₂ according to the following reaction

\[
3\text{SiO}_2(s) + 4\text{Al}(l) \rightarrow 2\text{Al}_2\text{O}_3(s) + 3\text{Si}(l) \quad (1)
\]

To complicate matters, if the aluminum is a magnesium bearing alloy, then the Mg can reduce the SiO₂ leading to the formation of either magnesia

\[
\text{SiO}_2(s) + 2\text{Mg}(l) \rightarrow 2\text{MgO}(s) + \text{Si}(l) \quad (2)
\]

or react with the Al₂O₃ to form a spinel:

\[
4\text{Al}_2\text{O}_3(s) + 3\text{Mg}(g) \rightarrow 3\text{MgAl}_2\text{O}_4(s) + 2\text{Al}(l) \quad (3)
\]

Depending on the amount of Mg in the Al-alloy either MgO, MgAl₂O₄ or both, can form.

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

\[
6\text{Al}(l) + 3\text{O}_2(g) \rightarrow 3\text{Al}_2\text{O}_3(s) \quad (4)
\]

Figure 5 is a schematic of the reaction mechanism for the formation and growth of alumina, magnesia and spinel in a refractory in contact with an aluminum alloy. 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, TiO₂, etc., are also reduced by molten aluminum.

**Control of Aluminum Penetration**

Several approaches are available to counter the ability of the aluminum to wet and subsequently penetrate and interact with the refractory. Their purpose is to retard or inhibit its ability to reduce 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 aluminum is one of the more common approaches, 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 sulfate, different types of fluorides (AlF₃, CaF₂, etc.)*10,11,12 and others. Studies carried out to determine the mechanism for protection of the refractory by adding barium sulfate 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 fluorides are thought to react and fill in pores. Anti-wetting additions decompose at differing temperatures and once it 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. When used in monolithics it aids in the formation of a refractory bond between new and used refractories, which is particularly important when carrying out a repair.

The use of sol-gel binders, in particular colloidal silica, lead to sufficiently small pores so as to hinder aluminum penetration, thereby not requiring or minimizing the need for the addition of a non-wetting component*9.

The latest development is the use of special raw materials or binders which have low wettability with respect to aluminum, and contain...
only lime and alumina, like calcium hexaluminate or bonite. Microscopy of bonite based refractory test samples showed no metal penetration after exposure to molten aluminum (Figure 6). Some of the commercial castables also have built-in insulating properties due to the nature of the aggregate used.

Testing of Refractories

An accepted mode for evaluating the merits of a new refractory for use in contact with aluminum is for it to undergo testing to simulate actual use conditions. Several major aluminum 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, 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. 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 refractory and the new one.

The refractory in the belly band area is additionally stressed by exposure to fluorides. These are materials manufactured by combining several different types and amounts of alkali salts, fluorides and chlorides, which have low melting points and consequently will penetrate the refractory. To determine the additional effect fluorides have on the refractory integrity and, its components, laboratory studies involving cup tests to simulate belly band conditions are carried out. They expose refractories to aluminum alloys covered with individual or a combination of salts, KCl, CaCl₂, NaCl, CaF₂, NaF, cryolite (Na₃AlF₆), etc. while at high temperatures (Figure 7). 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.

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. Initially phosphate bonded, fired brick were used, but this has generally been superseded with the advent of low and ultra-low cement castables. The disadvantage of using brick was that their installation required bricklayers, not always available and 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 most of the refractories were controlled during manufacture and did not depend on field conditions.

The use of mouldables (plastics) is not as prevalent as castables, but there is technically no reason for not using 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.

Although each type of refractory was considered by itself, they can be used in combination, and often are, so as to obtain the best lining from a cost, availability and longevity standpoint.
In summary there are many different types of refractories available to line aluminum melting/holding furnaces. Their selection should consider the quality of the available refractory choices, the abilities of the personnel that will carry out the refractory installation, equipment available for dry-out/burn in, total time available, etc.

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