Treatment of Aluminum for Improved Foundry Products

Description of Oxide Formation

Aluminum is an extremely reactive metal. Molten aluminum oxidizes rapidly in air or even relatively pure inert gasses as long as some oxygen is present. Aluminum oxide is slightly more dense than Aluminum. In the absence of surface tension and trapped gasses the oxide would sink to the bottom of the furnace and continue until all of the metal was oxidized. Fortunately the oxide layer is stable due to surface tension and will remain on the surface protecting the metal from further oxidation. In time some oxygen will diffuse through the oxide thickening the oxide layer. According to one author some aluminum atoms can propagate through the larger Al_2O_3 molecule and oxidize on the top surface. In any case when the oxide thickens it will break or "mudcake" exposing the liquid metal and creating more oxides.

Each tine the surface is disturbed fresh metal is exposed and more oxides are formed. The oxides are folded up and broken by force of burners, by mechanical stirring, and by dipping in foundry applications. Some of the disturbed oxides go into a dispersion in the metal while most of the oxide remains floating on the surface.

Skim, when folded back on itself, is porous and will therefore accumulate metal beads in the interstices between layers until the metal may be several times the weight of the skim. The metal may be released from the oxide by use of fluxes. If the skim is allowed to accumulate it will attach to the furnace walls. Finally the metal accumulated in the oxide layers further oxidizes until a solid dense shelf is formed at the metal line. While there is still some porous nature to the oxide it is possible to soften the oxide with fluxes so that they may be removed by scraping. After several days the accumulated material becomes hard and firmly attached so it is necessary to chip it away with a chisel like tool.

Furnace Problems without Fluxing

When no flux is used in the furnace the cleaning operation requires much more force which results in damaged brick. If the furnace is not well cleaned the oxides and spinels will build up on the furnace walls, particularly at the metal line. The longer the oxides and spinels stay attached to the brick, the more firmly attached they become, until cleaning is very difficult. At this point the furnace must be either hot c1eaned or cooled to allow mechanical cleaning with jack hammers. Both of these operations are damaging to the brick and result in lost production. One foundry reported only twelve months of brick life using only mechanical cleaning without flux. His furnace re-builder would only guarantee the lining if he followed a regular fluxing and cleaning schedule.

Without fluxing the metal is contaminated with oxides more severely and the product suffers poorer quality. Alcan presented a paper stating that a particular salt flux containing $MgCl_2$ was as good as chlorine for cleaning the metal in a holder, without the pollution control problems or hazards of chlorine handling. They did not claim equivalent degassing but rather argued that most applications which require low gas levels are using spinning nozzle degassers. There is little point in trying to degas to very low levels in the holding furnace when a spinning nozzle is used downstream of the holder.

Furnace Fluxing

Fluxing takes several forms. Ideally the flux is injected under the metal surface where it melts and floats to the surface carrying oxides with it. It then forms a semi-liquid layer on the molten metal which is effective in preventing further oxide contamination and reduces hydrogen pick-up in the melt. At the same time the liquid salts soften the oxides on the walls of the furnace and reduce the bonding of the oxide at the walls. Finally the liquid flux in contact with the skim layer wets the metal particles so they will coalesce and fall back into the melt. Flux applied in this manner is most effective in a holding furnace operation.

For melting furnaces the flux is frequently charged with the solid metal so that it melts as the metal melts and some salts will wet the surface and reduce oxidation during the melting cycle.

Another application method is to broadcast the flux on the surface of the skim where it melts and works its way down through the skim. This is the most effective method for separating metal from the oxide skim layer. The flux will chill the skim which is a good insulator so the flux will melt very slowly unless the brick have been heated with a firing cycle before the addition. If the flux is broadcast during the firing cycle it will vaporize making a heavy smoke. The flux is wasted since it is not retained in the furnace.

Finally, operators apply the flux to the walls to soften the oxides and spinels so they can be easily scraped during the cleaning operation. Again it is best to heat the refractories before the flux operation since the flux is generally more effective at higher temperatures. Cleaning should be done it the end of a firing cycle. The same principles apply to crucible fluxing except, that the flux may be added during the firing cycle as long is there is no direct flame impingement on the flux.

Fluxes are useful because they coat the oxide particles in the melt as well as oxides in the dross - The two liquids, flux and aluminum, are immiscible much like oil in water. As a result the metal is free to coalesce and run though the dross back into the melt once the oxides are wet. In the same manner, oxides that are wet beneath the surface are free to float if the combined density of the particle and flux is less than that of the surrounding metal.

Fluxes are generally based on a mixture of chlorides and fluorides which may be more or less effective in releasing the metal depending on their composition. Generally fluorides are more active than chlorides in reacting with aluminum. The affinity for halide salts to aluminum increases in the following order: $BaCl_2 < KCl < CaF_2 < CaCl_2 < BaF_2 < NaCl < MgF_2 < NaF < KF < MgCl_2$.

The flux not only must react with aluminum but it must also have the proper fluidity when molten at normal furnace temperatures. If it is not fluid enough it will set on top of the skim with no reaction. A flux that is too fluid results in difficulty for the operator in removing the skim. The flux and oxides simply flow around the flux rake and stay in the furnace. For this reason fluxes generally contain a mixture of salts which will have a lower melting point combined with some solids to give the skim a mushy character so that it will skim easily.

Fluorides are generally blended to increase activity and to improve fluxing action with some moisture. Fluoride concentration may be kept low for environmental reasons. Some salts are fluidizers which improve fluidity while others are thickeners which tend to make the salt less fluid and stick together better for skimming. The density of the molten salt is also important so that it will float free and skim easily without producing salt inclusions in the parts.

Economics of fluxing

Fluxing with molten salts is generally a cost saving operation. Initially much of the metal is released from the skim by fluxing which saves the cost of transporting and processing excess metal. The dross processors would rather have more metal in the dross and argue that the metal is returned. From the furnace operator's standpoint there is always a considerable loss both in metal units and in tolling charges for excess metal in the skim. The cost of the flux is made up easily by the reduction in "melt loss". An additional bonus is the improved metal cleanliness and the improved furnace cleaning without damaging the brick as well as saving the cost of re-melting the metal.

Classification of Fluxes by Use

There are basically four functions which fluxes provide: Drossing, which is the separation of metal from dross; Cleaning, which is the separation of oxides dispersed in the melt; Wall Cleaning, which is removal of the oxides attached to the wall at the metal line; and Cover Flux, which provides a liquid cover to prevent further oxidation of the melt.

Drossing Fluxes

The fresh oxide with trapped gasses is light in weight as was pointed out in the introduction and will trap molten metal particularly during the metal cleaning and degassing operations. The metal appears as fine beads of molten aluminum between the oxide layers. It is not unusual for the skim to contain much more than an equal weight of metal since the skim itself is light in weight. Like wet snow the skim which has a high metal content will take on a wet appearance and will feel heavy when it is held. Dry skim like dry snow is powdery and has a dry appearance. Dry skim is light in weight and falls apart easily. When the furnace is skimmed any metal remaining in the skim is lost to the furnace operator. At best he will receive partial value for the metal from a dross treatment facility. The better option is to treat the dross in the furnace to release the metal directly back into the furnace, saving the metal value and the heat content in the furnace. This operation is termed drossing.

Metal Cleaning Fluxes

The mechanism for cleaning the metal is to wet the oxides with flux so that they will either float or sink but will not stay suspended in the melt. Metal cleaning fluxes work best when injected. Injection consists of entraining the flux in a carrier gas which is directed by hoses and pipe under the surface preferably near the bottom of the furnace. Generally the carrier gas is either nitrogen or argon which will attach small bubbles to the oxides and float them to the surface. The combination of gas injection with flux reaction is also effective for removing hydrogen from the melt. Alternatively if the flux is rabbled into the melt it is possible to have a cleaning effect several inches below the surface. With enough stirring it is 'theoretically possible' to clean a high percentage of the metal. In practice, the rabbeling technique is much less effective than the injection technique.

Wall Cleaners

Wall cleaners wet the oxides with salts which soften the oxides and allows the operator to easily scrape them from the brick. If scraping after using wall cleaners is done regularly the furnace walls will stay clean. A solid dense shelf builds on the furnace wall if it is not cleaned. Eventually pieces of this dense shelf break off and sink to the bottom of the furnace. In time the furnace capacity will be reduced to the point where it is necessary to shut down the furnace and mechanically remove the oxides from the bottom and walls. This operation may require a considerable effort if the furnace is not cleaned regularly. Wall cleaners only soften the oxides and do not remove them from the furnace walls. Simply throwing wall cleaner into the furnace without scraping will result in oxide build up and will not clean the furnace. Scraping without wall cleaner generally results in brick damage and dirty furnace operation. Dirty furnaces produce dirty metal and result in more downstream problems in the products.

Cover Fluxes

Cover fluxes generally form a liquid or semi-liquid layer to minimize oxidation and hydrogen absorption. Frequently the furnace operation requires multiple purpose fluxes so that a small amount of a multiple purpose flux is left on the surface as a cover flux. The requirement is that the flux is relatively fluid so that it covers the furnace surface with a continuous liquid layer. Many fluxes can he used successfully as cover fluxes.

Special Requirements for Fluxes

Sodium Free Fluxes

Magnesium containing alloys above 3% magnesium retain sodium at the grain boundaries. This phenomenon results in liquid grain boundaries at elevated temperatures. Hot working will result in cracking at the grain boundaries and may cause scrap parts in forging, extrusion, or rolling operations. When the charge material contains sodium or if sodium salts dissociate in the melt there can be serious problems in downstream fabrication operations. Some fluxing salts dissociate and increase sodium content in the melt. Since most metallurgists do not want to investigate flux chemistry or tailor processes to avoid sodium pick up, they specify no sodium in fluxes for magnesium alloys. There is a cost for this decision both in terms of price and effectiveness. The sodium salts are frequently replaced with less active salts from other sources. Properly formulated sodium free fluxes can be effective in all flux applications but are always more expensive products.

Since no definitive study has been conducted to show which sodium salts contribute to sodium pick up it is prudent for the metallurgist to specify “no sodium”. This becomes a serious problem when there are additional restrictions on fluorides. The flux must contain a low melting point mixture of salts to be active in the furnace. For this reason too many or unnecessary restrictions frequently result in ineffective and expensive fluxes which do not satisfy the requirements of the process.

Fluoride Free Fluxes

In some areas there are pollution control requirements for “no fluorides” in the process. This requirement is based on operations such as aluminum reduction cells where tons of fluorides can be spewed out into the atmosphere. Some regulatory agencies tend to take the view that if large quantities damage the environment then zero is the only acceptable level for emissions.

The flux manufacturers respond to the no fluoride requirement with no-fluoride fluxes. These fluxes are much more expensive and generally less effective so the process suffers. The “no sodium” requirement for high magnesium alloys may be specified so that there are more limitations on the products and a substantial degradation of the flux products. Most flux manufacturers substitute these products as equivalent to less restricted products and the customer is dissatisfied with the results. Since it is difficult for the small foundry to measure the effectiveness of a flux product it may be months or even years before the undesirable results of these changes become apparent.

Exothermic Fluxes

Fluxes generally have a high heat of fusion and high specific heat which results in a chilling effect when the flux is broadcast in the furnace. If temperature is high or the operation is flexible enough to allow addition of the flux after a heating cycle, the problems are not severe. When the flux is added to a furnace that has not fired for some time and the oxide layer is thick enough to be a good insulator the flux will chill the oxide surface and lay there without melting. An effective way to combat this problem is to create an exothermic reaction either within the flux or between the flux and the skim. This reaction can raise the temperature enough to melt the flux and produce the desired fluxing action. The most common method of generating heat is to add an oxidizer to the flux which will oxidize a small amount of metal in the skim to produce heat. Generally the amount of oxidizer required is small so the amount of metal consumed is negligible compared to the amount recovered with the drossing action of the flux.

High Temperature Fluxes

For some applications, particularly in foundries, fluxes are chosen to minimize smoking when they are charged into a very hot melt. In this case the fluxes are generally no more than three components and are selected for a relatively high fusion temperature. No oxidizers are added to these fluxes. Salts with relatively low vapor pressure at higher melting temperatures are chosen. It should be noted that no one flux is proper for all applications. Fluxes are not only tailored by alloy but also by local regulations and by furnace operational parameters

Demagging Fluxes

One of the most common scrap sources is aluminum cans. The can body is 1.5% magnesium while the lid is 4.5% magnesium. When the cans are melted the melt is usually at about 2%—2.5% magnesium. Many alloys do not need this much magnesium and so the magnesium content must be reduced. Occasionally, mixed scrap or miscalculations will produce a melt that exceeds the upper limit for magnesium. The most common method to reduce magnesium is to burn out the magnesium with chlorine. This procedure works where chlorine is acceptable. When restrictions are applied to chlorine use another material must be found. Flux manufacturers have found various products that are effective for reducing magnesium. Small percentages are easily adjusted however larger quantities burn out more slowly requiring at least a stoichiometric quantity of flux and enough time for a complete reaction Most recycler’s find that blending scrap is a preferable way to control composition.

Particle Sizing for Specific Applications

Particle size limits require that many products are screened before they are blended to make the product. Flux injection machines frequently require a specific size range so that both the coarse and the fine particles must be screened out to make a usable product. Frequently the customer demands a particle size that is small enough to react quickly but large enough so that the product isn't pulled out of the furnace with the stack draft. Again the product must be sized for the customer. The residual salt may not be marketable in the size that is removed so the material .is disposed of as a waste. There are customers who require coarse products and customers who require fine products for a variety reasons.

Multiple Purpose Fluxes

Frequently a customer has more than one desired result so the f1ux must be blended to satisfy multiple requirements. One customer will want a cleaner-degasser while another will want a degasser-grain refiner. Still other customers want grain refiner and a cleaning flux in one product. The combinations add up to many fluxes that fall in the category of custom blending. Asbury does custom blending to customer specifications or will design a custom, flux based on customer requirements.

Measurement of oxides in Aluminum

Direct measurement of oxides is very difficult. A variety of devices and tests are employed but none are without difficulties. Foundries generally use notched bar tests, fluidity spirals, or, more recently, “Qualiflash”. More sophisticated foundries and many primary producers use PODFA or LAIS to look for oxides. Alcan has developed the LIMCA which operates like a Coulter Counter which counts oxides. Another class of measurements look at the downstream operations and infer metal quality from production results

The notched bar test consists of casting bars with a transverse ‘V’ notch in the casting. The bar is bent until it fractures at the notch. The fracture surface is then examined for oxides and other inclusions. This is a simple test which gives immediate feed back to the operators. The disadvantage is that the metal has to be extremely dirty for there to be a statistically significant number of oxides on the fracture surface

Fluidity spirals measure how far the metal flows before it stops flowing and freezes. When all other variables are held constant this can be an effective measurement of oxides. This is an indirect measurement so it is subject to a large number of variables. Generally metal temperature, alloy content, and mold temperature are obvious variables that are easily identified but difficult to control in practice. Gas content specific impurities and pouring rate are less obvious and equally difficult to measure. In practice operators are more likely to look at average numbers of defects from incomplete filling of thin sections.

Qualiflash consists of a funnel shaped container with a filter in the bottom. The metal flowing through the filter is collected in a mold until the filter plugs and the metal stops flowing. The amount of metal collected in the mold is inversely proportional to the density of inclusions in the metal. This is probably the newest and most easily performed test for the foundry operator. The disadvantage is that unless the metal is quite dirty the splashing of metal as it is poured into the funnel may create more oxides than were initially present in the melt. A well trained operator can minimize this variable

PODFA and LAIS are very similar tests. A measured amount of metal is drawn through a fine filter. The filter is then cross sectioned and the collected inclusions may be counted and identified by a skilled metallographer.

LIMCA performs a continuous measurement in a flowing channel of molten metal. The liquid metal is alternately drawn into a chamber and expelled through a small orifice. A constant current is maintained through the liquid metal in the orifice. Any nonconductor moving through the orifice will create a voltage spike which is analyzed and counted by a discriminator circuit. LIMCA is a very expensive machine which requires a well trained operator. Additionally gas bubbles in the metal are not easily distinguished from inclusions.

Many companies have developed their own measurement techniques. One company manufactures a large volume of the same part. They look at tool changes in the finishing operation to determine oxide content. Tools are dulled quickly by oxides; longer average tool life is related to cleaner metal, while shorter tool life is related to dirty metal. One wheel manufacturer counts defects on a painted surface on the wheel. He claims that oxide does not take paint the same as metal so he can relate defects on the painted surface to inclusions on the machined surface of the part. Anodize streaks are seen on sheet products. Wire breaks are related to inclusions in the wire drawing operation. Fractures in tensile test bars are examined for inclusions. Pin holes in foil are also related to inclusions and porosity. On-line X-ray and ultrasonic inspections are also used for finding large defects in critical parts. These last two methods offer the advantage of 100% part inspection but are generally more sensitive to voids than to inclusions

Conclusion

Everyone who works with molten aluminum should be concerned with inclusions. Measurement techniques are not developed to the point where we can guarantee defect free parts. Failures in critical parts are expensive. For critical parts we must start with the cleanest metal possible, maintain a clean furnace, use the best fluxing techniques available, filter the metal when appropriate, and handle the metal carefully to avoid generating oxides in the pouring operation.