Mechanisms in the Cleaning of Aluminium Melts with Flux Preparations

I. Impurities in the melt

Hydrogen and oxides are common impurities in an aluminium melt. Source is the water from the atmosphere, the reaction between the aluminium melt and the water is shown in the following picture:

The aluminium oxides can crystallize to very hard corundum with the following structure:
That means that as a rule, hydrogen and oxides are simultaneously present in the melt.

The law of Sievert describes the solubility of atomic hydrogen in aluminium. There is a significant drop of the solubility when the metal is solidifying. Due to this decrease the hydrogen atoms are recombining to molecules, and bubbles can develop.

\[ l = K \sqrt{p} e^{-\frac{1}{2} \frac{\Delta G}{RT}} \]

solubility \( l \) = function (pressure \( p_{H_2} \), temperature \( T \))

The graph above shows the solubility of hydrogen in pure aluminum.

The next pictures show the process of oxide formation and building up of hydrogen bubbles schematically. The water of the atmosphere is reacting with the aluminium melt, forming an oxide layer and atomic hydrogen on interstitial sites. The oxides will not stay only on the surface, some are moving into the melt, too, and when temperature decreases, due to the law of Sievert, molecular hydrogen bubbles build up close to those oxides.
During a casting process, the aluminium is surrounded by an oxide skin; some of the oxides will get into the melt, too. The oxides can have the shape of skins with a very high length to width ratio; some of the skins include or surround some aluminium drops, too.

The release of hydrogen, that means the building up of bubbles, takes place at interior defects in the melt and lattice of aluminium, oxides act as nuclei for the bubbles:

There is a critical radius for bubbles: Bubbles with a radius higher as 0,32 nm will grow, their surface tension is low, smaller ones can collapse, having a high surface tension and only a low inner pressure.
Oxide impurities can be removed by the use of flux preparations. Fluxes contain fluorides, those can bind the oxides. The interfacial tension between oxide and metal is significantly higher than the interfacial tension between oxide and fluoride.

\[
2 \text{Na}^+ \left[ \begin{array}{c} \text{F} \\ \text{Si} \\ \text{F} \\ \text{F} \end{array} \right]^{2-}
\]

sodium silicofluoride

Fluorides and oxides subsequently form mixing phases, because due to the lower energetic state the fluorides adhere to the oxides and coat them, aluminium is separated from the mixing phases.

The next pictures are showing the cleaning process schematically. The fluoride containing flux is introduced into the melt and distributed well, it covers the oxides, the oxides will crack at their weakest points, and the pieces can swim up, because the density of the mixing phases now is lower as the density of the melt. The density of the pure oxides is nearly equal to that of the melt, so there is no swimming up. At the end there is a low metal dross.
The cleaning process with fluxes can be combined very well with an impeller treatment. So an optimal degassing and removing of oxides combined with a low metal dross in guaranteed.
Without a flux, the impeller treatment is not so effective in removing all oxides, and the dross will be metal rich in the end.
Impeller treatment and fluxing can be combined very well. The process starts with a high rotation speed, there is the formation of a vertex to distribute the flux and generate a reaction with the impurities and the melt.
For the actual cleaning process the rotor rotates with a lower rotation speed. It rotates in the opposite direction as the melt. So the relative motion between melt and rotor is very high, the resulting bubbles are very small, and no vertex is created. Once the melt rotates in the same direction as the rotor, the rotor changes its direction (this happens 3 or 4 times per cleaning process).

For this highly effective impeller process no ceramic baffle is needed.

There is a big difference in the appearance and the metal content of dross without and with the use of flux preparations:

Without the use of a flux the metal content is very high, normally between 80 and 95 %. If a flux is used, the dross is fluffier, and the metal content between 20 and 35%:
So there is a saving potential by the use of a flux, because there is more metal available for the casting process. This metal is much more worth as the costs for the flux.

**Impurities on furnace and crucible walls**

The next pictures show the influence of the oxides on furnace and crucible walls resulting in some damage if no flux is used.
In the melt you can find some oxides, there are micro cracks in the wall. There is some sticking of the oxides at the wall, some oxides even diffuse into the micro cracks. Depending on time and temperature, some crystallization of the oxides to corundum takes place, at which the micro cracks are opened more. If the crystallization continues, some pieces of corundum can get into the melt, too.

In the worst case the corundum can be found in the castings:
This is a high pressure die casting with a very hard inclusion. During the machining process the tooling was destroyed by this. A metallographic examination could show some corundum and agglomerates of oxides in this area.

If a flux is used, the situation is much different:
The oxides are covered by the flux, as shown before. There is only a loose connection of them to the crucible wall, and the most important thing is, that there is NO crystallization to corundum. The loose adherences to the crucible wall can be removed very easily during taking away of the dross.

There is a special flux which can be used for furnaces, if corundum has built up:
For cleaning the furnace it should be almost empty, and heated up to high temperatures between 800 and 900 °C. The furnace cleaning agent is sprayed upon and around the affected areas, burners are switched off. By doing this the binding between the corundum and the furnace wall is weakened. After bringing up the furnace cleaner, the furnace door should be closed, still the burners are not switched on. After some time, 30 or 40 minutes, doors are opened again, some of the corundum might be already detached, and with a tool the residual can be removed much more easily as without the use of this special flux.
Best the furnace cleaner is sprayed on the walls.

III Basics of flux preparations

Flux preparations consist of cations and anions. Cations can be sodium, potassium, or calcium. For aluminium melts in a foundry, calcium should be avoided, sodium has lower cost as potassium, but there is the release of some sodium, which should be avoided in a few cases, for some alloys.

Anions are chloride, fluorides like aluminium fluoride or silico fluoride, carbonate. There is a special group of fluxes which use nitrates as anion, that is the group of exothermic fluxes.
There is an exothermic reaction between the nitrates and the aluminium, in which the aluminium is oxidized and locally very high temperatures up to 2000 °C are produced. Due to these high temperatures the viscosity of the aluminium in the dross will be very low and it can flow out of the dross. The disadvantage here is, that the low metal dross is reached here by increased oxide formation in the melt, that means there is no cleaning process at all.

The next pictures compare the effects of exothermic fluxes and fluoride containing ones:
Both types of fluxes are creating a low metal dross, but the exothermic ones do not remove the oxides from the melt, they even create new ones, and so increase the building up of corundum at the crucible walls.
Fluxes can be delivered as powder or compacted to flakes:

![powder](image1)
![flakes](image2)

The powder type is cheaper, but there is the formation of dust, the reaction is slower and more flux has to be used.

**IV. Impurities due to foreign metals**

There are some metals, which can be removed from aluminium melts. That are the alkaline and earth alkaline metals like Li, Na, Mg, Ca or Sr. Not removable are metals like Fe, P, Sb or Ti. If their content is too high, the only way will be to dilute the melt with pure metal without those elements.

The removal can be done by the use of chlorine gas, but this is very poisonous and prohibited very often. Alternatives are fluxes, either flux based on chlorides, or based on fluorides. The first group which is based on chlorides can develop some chlorine gas, too, and cause a bad smell in the air. Flux based on fluorides does not smell as bad if it is used.