

Role of Salt Fluxes in Aluminium Refining: A Review

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Abstract: With the consideration of several industries and numerous governments with the increasing energy efficiency and reducing greenhouse gas emission, the production of aluminium in a sustainable method has received huge focus recently. Aluminium recycling is crucial as it preserves 95 percentage of energy and the emissions associated with producing the alloy from the ore. In addition to that, it saves the capital expenditures and decreases the land space requirements. Recycling of aluminium is an established process and encourages the recycling of other metals and alloys. Currently, the refining of aluminium is restricted to removal of alkali or alkali earth metals, non-metallic inclusions and hydrogen. Technologies for removal of these types are commercially mature and there is a need for focus on the removal of other undesirable or tramp elements such as copper, silicon, iron, iron or zinc from the aluminium melt and application of chlorine must be discouraged due to their toxic nature. Considering these problems, a review has been conducted to evaluate the current industrial practice in the refining of aluminium alloys using solid fluxes. The study has been extended to focus on the current techniques available for the extraction of aluminium from the drosses generated during aluminium melting by the application of solid fluxes.

Keywords: Aluminium, degassing, dross, grain refining, recycling, solid flux.

I. Introduction

Aluminium is a silvery white metal that is currently having diverse applications in numerous fields of science and engineering due to their unique properties. The metal is known for its high strength to weight ratio. This encourages consumers to apply aluminium in several sectors like medical, aerospace, automobile, and electrical and electronics are profoundly replacing aluminium over steel. In addition to that, this super metal encompasses several other immense properties like low density, thermal and electrical conductivity, corrosion resistance, magnetic neutrality, ductility and malleability. The aluminium family has been classified into Cast alloys and Wrought alloys. In the first type, the components are manufactured directly through casting the molten metal by three techniques: Sand casting, Gravity die casting, Pressure die casting. The latter includes casting into ingots or billets followed by subsequent hot working and cold working operations to produce wires, plates, rods etc. There are several classes like 2XXX, 3XXX, 5XXX, 6XXX, 7XXX series alloys that includes heat treatable and non- heat treatable alloys having different alloy compositions based on the requirements of application[1,2,3].

In order to reduce the wastage and the manufacturing costs the world is moving towards sustainable method of production. Recycling of aluminium requires only about 3-5 of input energy to produce primary aluminium. Currently, around 50-60% of aluminium alloys are recycled at the end of its life[4]. Aluminium recycling process is extensively capitalised during the World War II. Brazil recycles about 98% of its can production every year. Brazil has been ranked among first in the aluminium recycling countries[5]. Recycled aluminium reduces the emission of greenhouse gases. For growth in a competitive world, industries have to focus on recycling to reduce the production cost. There are two types of aluminium scraps available: New scraps and Old scraps[6]. The new scraps comes directly from the manufactures and are therefore easy to recycle and could be 100% re-melted with minor processing. However, the old scraps require significant processing. Newly improved aluminium recycling process are more efficient and the aluminium scraps are almost recycled to about higher percentages[7].

Porosity is a major problem during metal casting and that plays a major role in affecting the mechanical properties, pressure tightness and corrosion resistance of aluminium castings. Porosity mostly occurs when solidification rate is improper that leads to due to dissolution of gases in the aluminium melt. Hydrogen is the only gas that would be soluble in aluminium melt in the liquid state. Therefore, the removal of hydrogen gas from the molten aluminium is vital for the production of high quality aluminium castings. Therefore, in order to overcome this issue, several degassing techniques are currently applied to remove the hydrogen from the molten metal. Some of the degassing techniques include rotary impeller degassing, spray degassing, vacuum degassing and ultrasonic degassing, gas degassing[8].

However, these techniques have several parameters to be considered to reduce the porosity in the aluminium castings. In gas degassing parameters like Rotor speed, Gas pressure and Degassing time must be

accounted to reduce the porosity. The castings could be quality checked with several testing techniques like chemistry, density, hardness, tensile, porosity, inclusion, XRD, PODFA, AlspecQ, K-mould test, SEM, Optical microscopy etc. This paper presents the current technologies available for the refining of aluminium melt using solid fluxes as it is economical. A brief review on the extraction of aluminium from drosses has also been performed.

II. Degassing the Melt

Fluxing is done to remove alkali metals, alkali earth metals, impurities, non-metallic inclusions, dissolved, hydrogen and excess magnesium as they affect the final properties of the product. The commonly used salt fluxes are NaCl-KCl, -KCl with additions of fluorides, chlorides, carbonates [9,10,11,12]. The salt fluxes must have a low melting point as they fuse with aluminium oxides at lower temperatures and increase the viscosity of the slags and thereby enabling removal through setting up a chemical reaction or by means of physical separation[13]. The chemical composition and the amount of salt are crucial factors determining the metal yield and economics of the process. Pirker et al [10] have demonstrated the effect of KCl in the NaCl-KCl mixture. KCl is an expensive salt. A limited reduction of KCl in the mixture does not affect the metal loss. Also reducing the KCl content in the flux reduces emissions. It is also reported that the activity NaCl is greater than KCl. But the increased reduction in KCl increases the melting point of the slag and thereby affecting metal recovery. Therefore decreasing the amount of KCl to an optimum level is economically and environmentally effective. Sometimes, for refining of low-grade scraps, the refiners use liquid flux. The scraps are dipped in the liquid flux before they are charged into the furnace. However, the composition of the liquid flux must be carefully monitored. The flux must not thicken up as the impurities are absorbed. Therefore, some quantities of fluorides are introduced in the flux. In the case of high silicon alloys, sodium salts such as sodium fluorides are employed. But if iron and manganese content exceed more than 1%, the modification is prevented. In the case of high magnesium alloys, Magnesium Chloride is used for fluxing. The magnesium chloride on reaction with the magnesium oxide in the metal forms magnesium oxychloride which is absorbed in the slag. But as Magnesium Chloride is hygroscopic, it is used along with the salts. This reduces the risk of moisture absorption. It has been reported that a mixture of one-third of sodium chloride, potassium chloride, and magnesium chloride is most successful. If the magnesium is present as an impurity in the alloy, they can be removed by degassing techniques employing chlorine gas, hydrochloric acid gas, silico-fluoride gas, boro-fluoride gas and the compounds formed are taken into the slag. The temperature required for this process is above 800°C[11,13].

Jun et al [14] investigated the effects on purification, microstructure and properties in A00 melt with C_2Cl_6 and several other fluxes. In the melt sheared with C_2Cl_6 several cracks and porosities existed in the surface oxide film which led to increased melting loss. In addition to that the slag mainly composed of pure aluminium and aluminium oxide. The size of the inclusion ranged under 10 μm and the size of the grains ranged from 100-150 μm extended along the radius. These smaller sized inclusions had no adverse effects on the strength but on the elongation.

Zhao et al[8] studied the behaviour of gas bubbles in aluminium alloys during the re-melting process by observation with X-ray micro focus radiography. The experimental observation depicts that the re-melting has caused a significant effect on degassing. In addition to that it is also benefitted by decreasing the inclusion percentage in the casting. The fundamental theory behind this experiment is that the surface of the melt remains calm unlike being agitated in the degassing process. Therefore, the oxides present in the surface could not be entrained into the melt. However the author failed to address the energy, cost, time and environmental effects that would be costing during the re-melting process.

Utigard et al[15] projected the role played by solid and gaseous fluxes in the removal of inclusions, gases and magnesium in the aluminium alloys and in the drosses generated during melting. In addition to that thermodynamic analysis of aluminium melting was performed. The function of the flux and the temperature to be applied must be considered before accounting a flux to be incorporated in the aluminium melt. In addition to that, the alloy in which it is added should also be accounted. Sodium or fluoride fluxes must not be incorporated into aluminium-magnesium alloys. From a thermodynamic view, fluoride salts are stable than chlorides, sulphide and oxides. Hence, a fluoride salt incorporated to mixture of chlorine and magnesium, it would stabilise the magnesium present in the salt. Application of C_2Cl_6 tablets decomposes the melt generating $AlCl_3$ bubbles of gas which collects the hydrogen present in the melt. In addition to the salts also contains salt fluxes which wets the inclusion of oxides and thereby enabling the removal of hydrogen entrapped in the inclusions. For effectiveness, the tablets are plunged inside the melt and stirred and stationed allowing the bubbles to subside.

Westberg et al[16] studied the environmental effects of application of C_2Cl_6 in the aluminium melt refining with particular focus on the emission of Organo chlorine compounds in the atmosphere. Figure 1 shown

below depicts the emissions of octachlorosty- rene (OCS), hexachloroethane (HCE), hexachlorobenzene (HCB), carbon monoxide (CO), total hydrocarbons (THC) and hydrogen chloride (HCl).

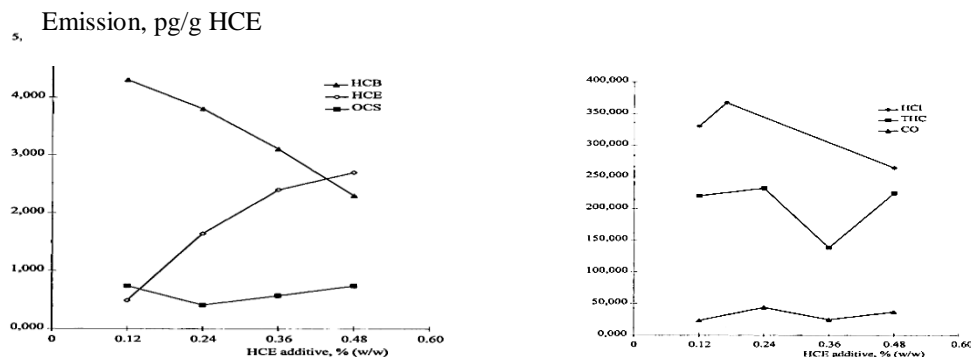


Figure 1: a) Emissions of octachlorosty- rene (OCS), hexachloroethane (HCE) and hexachlorobenzene (HCB); b) Emissions of carbon monoxide (CO), total hydrocarbons (THC) and hydrogen chloride (HCl)

III. Grain Refining

Metals solidify with a coarse columnar grain structure under natural conditions. Coarse grains affect the property of the castings. Coarsening phenomenon can be inhibited by carefully controlling solidification by restricting the columnar growth of the grains[17]. Several grain refining experiments were attempted in the past using Zr, Nb, W, V, B, Cr and Ta. Murty et al has stated that by increasing the number of nucleation sites, grain size can be reduced and also by increasing the undercooling temperature. The grain size is inversely proportional to the degree of undercooling. There are also other methods of grain refinement like melt agitation and vibration[18]. Grain refinement is an important function in the aluminium melts processing. The increasing interest in grain refinement arises from the fact that finer grains provide better properties to the castings. Addition of grain refining elements results in the achievement of fine equiaxed grain structure that enhances the yield strength, plastic strength, formability, ductility and toughness[19,20]. The most common practice used is the application of the grain refiner Al-5Ti-1B master alloy to the aluminium melt to attain the fine grain structure. It is produced by inoculation of halide salts such as K_2TiF_6 and KBF_4 in the aluminium melt. Several parameters like Ti/B ratio, reaction time, temperature, frequency of salt additions, stirring conditions contribute to the grain refining efficiency[18,17].

Han et al[20] discussed high-intensity ultrasound effect in the production and melting of Al-5Ti-1B master alloy on its grain refinement microstructure. The ultrasound enhances the distribution of Ti and the TiB_2 particles in the melt, makes the $TiAl_3$ phases more uniform, and changes the morphology of agglomerated TiB_2 into loose corals. The ultrasound makes the bulky $TiAl_3$ phase distribute evenly. In addition to that, the agglomerated TiB_2 disintegrates like loose spawn. The grain refining efficiency increases with the ultrasound.

Majidi et al[21] studied the effect of fluxing temperature in aluminium refining process. Increased temperature caused a loss of energy and produced fumes and gases. In addition to that it causes skimming and fluxing difficult and also it decreases the accuracy and refining efficiency. Majidi et al discovered the optimum temperature for fluxing as $740^\circ C$ as it does not pose any problems.

Murty et al[22] reported the influence of Si, Zr and Cr on the efficiency of grain refining by Al-5Ti-1B master alloy. It was determined that the poisoning effect ascends in the order of Si, Zr and Cr. It is due to the formation of borides, silicides, aluminides upon interaction of grain refining constituents' 5/1Ti/Al with alloying elements. This problem could be recuperated by increasing the proportion of grain refiner or by adding Mg in the case of Aluminium- Silicon alloy.

Birol et al[19] studied the efficiency of grain refining with the stirring conditions. The stirring action had detrimental effect on grain refining of Al-Ti-B master alloy. However, the effect was not as it was observed in stirring while holding. However, the possible mixing of potassium aluminium fluoride with aluminium melt is responsible for the loss of efficiency of grain refining. The boride particles are wetted by the salts present in the molten alloy which acts as the nucleation sites and assists in the agglomeration

Kumar et al[17] investigated the grain refining efficiency of Al-Ti-C master alloy. Grain refinement could not be attained at increased addition of Al-Ti-C master alloys as TiC particles get agglomerated. In addition to that increased holding times causes fading of the grain size. However higher magnesium and finer TiC particle is required for better wetting behaviour of the master alloys and thereby reducing the agglomeration. Figure 1 shown below depicts the comparative grain size analysis of LM25 alloy a) grain refined using Al-5Ti-0.8C master alloy; b) Grain refined using different grain refiners at different Ti or B addition; c) Grain refining efficiency of Al-5Ti-1B at different holding times; d) Grain refining efficiency of Al-3B at

different holding times; e) Grain refining efficiency of Al-5Ti-1B at different holding times; f) Grain refined using Al-5Ti-1.2C master alloy.

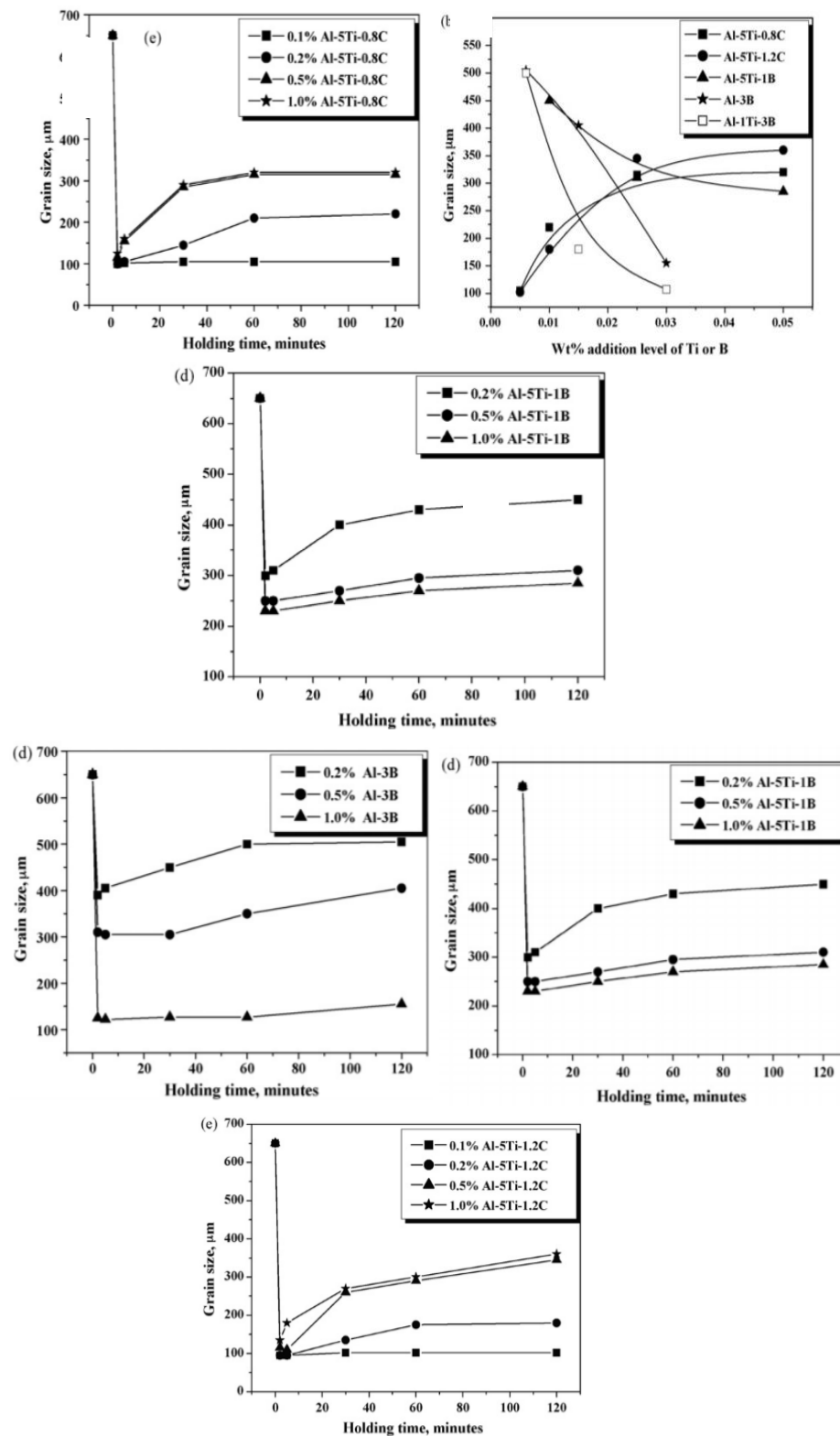


Figure 2: Comparative grain size analysis of LM25 alloy a) grain refined using Al-5Ti-0.8C master alloy; b) Grain refined using different grain refiners at different Ti or B addition; c) Grain refining efficiency of Al-5Ti-1B at different holding times; d) Grain refining efficiency of Al-3B at different holding times; e) Grain refining efficiency of Al-5Ti-1B at different holding times; f) Grain refined using Al-5Ti-1.2C master alloy[17]

IV. Dross Processing

Aluminium salt slag is produced during the melting of scraps in secondary aluminium production. These slags are heterogeneous by mass. It consists of metallic aluminium, aluminium oxides, salts such as NaCl, KCl, nitrides, phosphides, sulphides etc. depending upon the nature of the scrap and the type of salt used. There are two types of dross, Black dross and white dross. White drosses contain 20-45% of metallic aluminium and black drosses contain 10-20% of metallic aluminium. These slags are toxic and hazardous in nature which will lead to explosions, odorous gases, such as NH₃, CH₄, and H₂S etc. that pollutes the groundwater. Therefore, environmental regulations have been passed on the disposing of the drosses in specialized land filling sites. However, it increases the disposal cost and also aluminium and the salts within the slag have to be recovered[23]. Recycling of aluminium dross is an eco- friendly and economical process of waste utilization[24].

The most commonly used method is the B.U.S process. It consists of five steps:

- Manual hand separation, Eddy current separation[25]and Electrostatic separation[26]
- Leaching
- Solid-liquid separation
- Gas treatment
- Evaporation and Crystallization[27].

Alternative processes have also been proposed for black dross treatment: 1) Hydrometallurgical and 2) Pyrometallurgical processes[28]The usual approach is pulverizing the dross powder and screening them and the undersized drosses are landfilled. This method reduces the amount of dross, energy and salt cake generated at the end of the process[25]. The aluminium recovery from the dross by salt additions was studied by Tenorio et al[29]. Tenorio's initial analysis stated that the compositions of the drosses are mostly oxides and metallic aluminium. The initial washing with water dissolves sodium or potassium salts present in the dross[30]. The drosses were then treated with NaCl-KCl equimolar mix. The chloride due to their corrosive nature breaks down the oxide layer into fragments. The incorporation of fluorine salts such NaF, CaF enhances the fragmentation process. The segregated aluminium droplets then collage and sinks back into the bath. As we are aware that the drosses consist of other reactive metals and inclusions entrapped, the complex reactions that occur due to the salt additions were not considered by the author. Also, the viscosity of the slag was not considered which is a major factor for reaction kinetics[31].

V. Future Aspects

Although recycling of aluminium has been followed since its commercial production, the sector still demands growing concern of focus and research in many areas.

- Implementation of chlorine-free aluminium melt treatment
- Reduction of harmful impurities in the solid waste
- Reduction energy consumption
- Implementation of filtration techniques that focuses on the removal of large harmful particles
- Improved testing techniques for measuring entrapped oxides inclusions.
- On-line monitoring of melt quality which is still in the research stage must be commercialised.
- Lack of methods to remove undesirable or tramp elements: Zn, Cu, and Fe that are picked up in the supply chain.

VI. Conclusion

There is a growing consumption of recycled aluminium in the market. Recycling will certainly benefit the current situation of growing demand for aluminium products. The various techniques for refining of aluminium melt using solid fluxes that are currently available at the industrial scale and the lab scale have been discussed in this paper focusing on the technical, economic and environmental aspects. However, drastic improvements are still profoundly required in the areas of inclusion removal, studying the effects of trace elements in the castings, reduction of environmental damage, reduction of energy and cost. The future researches that appear in this field must be a life cycle analysis rather than a single stage development so that not only the useful resources can be recovered but also other materials harmful to the environment can be disposed of appropriately.

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