

PURIFICATION OF ALUMINUM THROUGH $\text{Al}_2\text{O}_3 - \text{AlF}_3$ ACTIVE FILTRATION

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ABSTRACT

Filtration is the most cost effective method to purify aluminum. In this paper, filtration experiments have been carried out using both AlF_3 slurry coated, and uncoated Al_2O_3 ceramic foam filter (CFF) to study the removal of both nonmetallic inclusions and impurity elements. The results showed that the 30 ppi CFF removed up to 85% inclusions from aluminum. The contributing mechanisms for the removal of nonmetallic inclusions in the deep bed filtration mode are proposed: (1) collision with walls and interception effect; and (2) the formation of both intermetallic and nonmetallic inclusion bridges during filtration. Fluid dynamics modeling of inclusions attachment to the filter walls showed that most inclusions, especially those with larger sizes, are entrapped at the upper part of the filter while smaller inclusions dispersed well throughout the filter. The active filter could [Mg] remove impurity elements up to 86 %.

1. INTRODUCTION

Aluminum is a metal with applications in every technological industry in the world today. Sources of raw materials and methods of extraction and refining of the metal lead to the introduction of impurities into the metal, which are detrimental to its properties and performance reliability. Purification of aluminum refers to minimizing contaminants such as dissolved gasses (especially hydrogen), non-metallic inclusions (such as oxides, carbides, nitrides), a variety of intermetallic compounds, and alkali and alkaline-earth elements such as sodium, lithium and calcium. These contaminants enter the molten aluminum through the ore and raw materials used in the extractive metallurgical processes, from refractory materials and the

atmosphere during production of aluminum and even through the refining processes. The common types of inclusions in aluminum have been reported to be: oxides, nitrides, carbides, fluorides and borides.[1] Extensive research has resulted in a significant improvement in our present understanding of the various aspects of these contaminants, and in many foundries, melt-cleaning practices have been established and are routinely used. However with the ever-increasing demand for improved metal properties, the requirements for molten metal cleanliness have become extremely stringent. Various methods such as sedimentation, flow transport, bubble flotation, filtration, and electromagnetic force are being used for the removal of inclusions from molten aluminum. Investments in filtration systems are relatively cheap and hence every effort at making them even more efficient must be explored.

AlF_3 is used to purify the molten aluminum by removing dissolved impurities such as Na and Ca through powder fluxing [2-3] and granular bed filtration [4]. It was reported that ~98% Na and Ca were removed from aluminum through AlF_3 granular bed filtration[4-5]. The use and the evaluation of the efficiency of ceramic foam filters (CFFs) in the removal of non-metallic inclusions from molten aluminum have been widely studied in the literatures [6-14]. Reports from these studies indicated that CFFs are capable of achieving high aluminum filtration efficiencies and the formation of bridge-like structures of inclusions at the top area of the filter contributes to the high efficiencies. It is well known that CFFs also remove inclusions smaller than the pore size of the filter in a deep bed filtration mode.

However there is inadequate information to explain the removal mechanism of smaller particles within the filters. Furthermore, using the existing Al_2O_3 CFFs coated with AlF_3 to purify molten aluminum has the potential to remove both dissolved impurities and non-metallic inclusions simultaneously.

This study experimentally investigates the removal of nonmetallic inclusions and, the removal of unwanted impurity elements from the molten aluminum using regular uncoated 30 ppi Al_2O_3 CFF, and 30 ppi Al_2O_3 CFF coated with AlF_3 . Fluid dynamic calculations and other theoretical modeling have been made to explain the underlying purification mechanism.

2. EXPERIMENT

Schematic experimental set up, and scheme used for filtration are shown in **Figure 1** and **Table 1**. The experimental furnace used was an induction furnace. In the experimental set-up the crucible, fitted with the filter was placed in the induction coils of the furnace and a graphite tray positioned at the bottom of the furnace, directly under the molten metal outlet of the crucible to collect the filtered metal. Aluminum scraps cut into small lumps were charged into the crucible until an appreciable molten metal volume was reached. The compositions of the two forms of scraps used in the filtration experiments are described in **Table 1**.

Metal and filter samples from the experiments were taken for inclusion observation in the SEM with EDX capability to identify and count nonmetallic inclusions, and GDMS was used to analyze the concentration of impurity elements. Samples from the un-melted scraps were taken before filtration experiments for analysis.

3. $\text{Al}_2\text{O}_3 - \text{AlF}_3$ CFF ACTIVE FILTRATION OF ALUMINUM

3.1 Removal of Nonmetallic Inclusions

Figure 2(a) shows that the microstructure of the Alloys before melting and filtration. Both alloy-1 and alloy-2 contained many inclusions

before they were melted and filtered as shown in **Fig. 2. (a)** and **(d)** respectively. However, after filtration using both uncoated CFF (**Fig. 2.(b)**) and AlF_3 slurry coated CFF (**Fig. 2.(c)**) for alloy-1 and coated filter for alloy-2 (**Fig. 2.(e)**), there were no visible non-metallic inclusions with particle size $\geq 3\mu\text{m}$ observed.

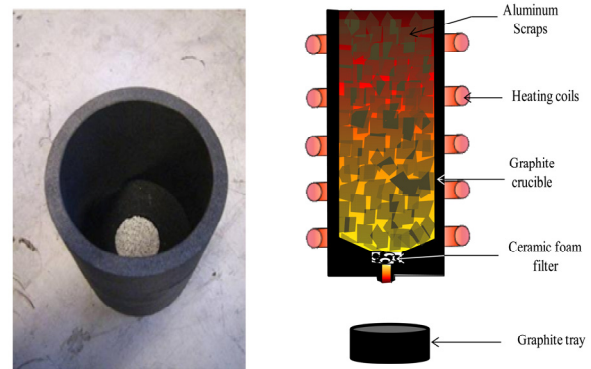


Fig. 1. Filtration crucible fitted with filter at the bottom and schematic filtration experimental set-up.

Table 1 Filtration experiments parameters

Experiments #	E1	E2	E3
Aluminum sample	Alloy-1	Alloy-1	Alloy-2
Filter	Uncoated	Slurry coated	Slurry coated
Molten metal mass (g)	2350	2431	2780
Maximum temperature/ °C	1010	970	900
Mass filtered (g)	1932	1780	1581
Filtration time (s)	602	361	705
Average mass flow rate (kg/s)	3.21×10^{-3}	4.93×10^{-3}	2.24×10^{-3}
Alloy-1: Si ~0.10 wt%, Mg ~0.01 wt%, Fe~0.275 wt%, others <0.05wt%			
Alloy-2: Si ~ 1 wt%, Mg ~0.45 wt%, Fe – 0.20 wt%, others < 0.1 wt%			

This is an indication of the effectiveness of the 30 ppi CFF filtration process. Several clusters of fine precipitates of light – colored features, identified to be Fe-rich intermetallics, were observed within the microstructure both before and after the filtration process. Iron (Fe) has unlimited solubility in molten aluminum but in solid aluminum, it is soluble only up to 0.04%. This explains why the Fe-rich precipitates are present in the metal both before and after filtration.

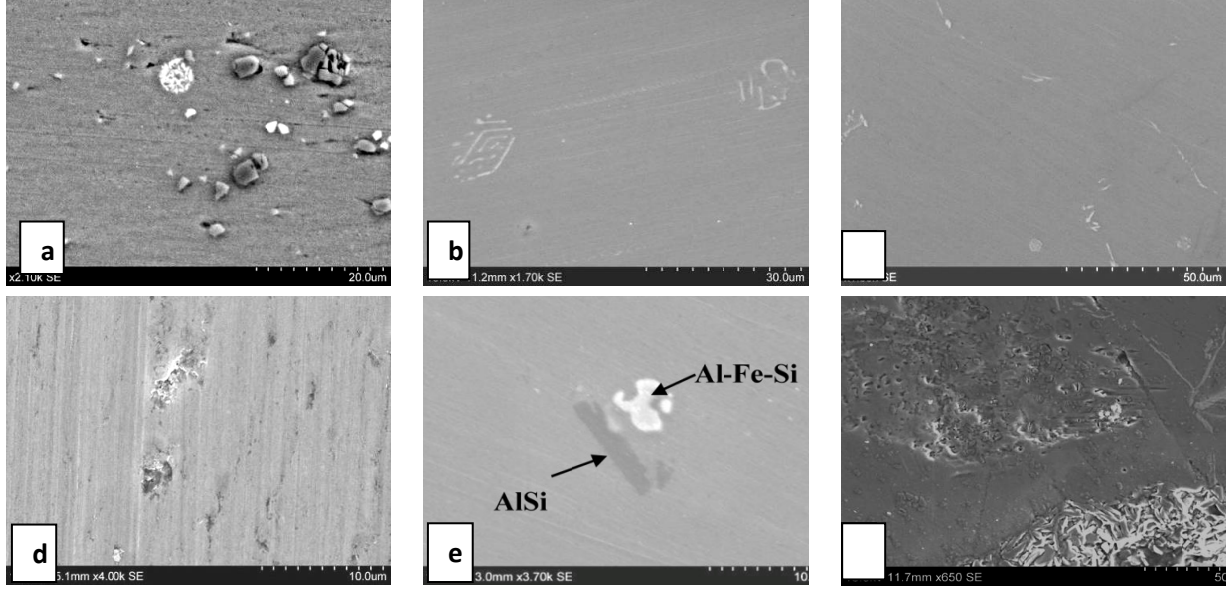
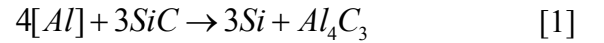


Fig. 2. Contribution of filtration to inclusion removal from molten aluminum: (a) cluster of Al_2O_3 , SiC and Al_4C_3 inclusions in aluminum matrix before filtration; (b) cleaned aluminum matrix after filtration (experiment E1); (c) cleaned aluminum matrix after filtration (experiment E2), showing clusters of precipitated Fe-rich intermetallics; (d) cluster of Al_2O_3 and SiC inclusions in the matrix of Alloy-2 before filtration (experiment E3); (e) cleaned aluminum matrix after slurry coated filtration, showing flakes of precipitated Al-Fe-Si (white) and AlSi (dark lakes) phases; (f) evidence of nonmetallic inclusions trapped within filter window.

The Fe-rich intermetallics observed are secondary precipitates with low melting temperatures according to their composition (92.62 atom% Al and 7.38 atom% Fe) and the Al-Fe phase diagram [15]. Their melting point is $\sim 637^\circ\text{C}$, which is lower than the filtration temperature of 900°C . The effect of [Fe] on the properties of most aluminum alloys is negative.

Flakes of AlSi intermetallics and some large sized Al_4C_3 particles were also observed after filtration of alloy-2, which was not made for alloy-1. This may be attributed the higher Silicon content of, and the presence of more SiC particles in alloy-2 than in alloy-1. This resulted in a reaction between molten aluminum and SiC, as in Eq. [1] [16-17]. This reaction might have resulted in local [Si] concentration increases leading to the precipitation of the AlSi upon cooling. The likelihood of [1] suggests that great caution should be exhibited during processing of Al – SiC composites because it has the tendency to derail the entire inclusion removal process producing

Al_4C_3 particles and may also change the composition of the metal.



Studies conducted on used filter samples in the SEM showed many trapped Al_2O_3 , SiC, and Al_4C_3 particles within the windows of the filter during the filtration process as shown in **Fig. 2.(f)**. The filtration efficiency, E was calculated using Eq.[2].

$$E = \frac{N_i - N_o}{N_i} \times 100\% \quad [2]$$

where N_i and N_o are the average number of inclusions measured per square millimeter of aluminum matrix before and after filtration respectively. Filtration efficiencies of 84.4, 81.3 and 85.2 % were recorded for experiments E1, E2, and E3 respectively. The effect of flow rate on the filtration efficiency is clearly seen in the calculated values. Experiments E2 had the highest estimated flow rate of $4.93 \times 10^{-3} \text{ kg/s}$, followed by E1 with $3.21 \times 10^{-3} \text{ kg/s}$ and then E3 with a flow rate of $2.24 \times 10^{-3} \text{ kg/s}$. The filtration efficiency increased with decreasing flow rate.

3.2 Filtration mechanisms

Two main contributions to the removal of inclusions in the deep bed filtration mode are discussed as follows.

Collision with walls and Interception Effect

Since the pore size of the 30 ppi CFF is larger than the size of inclusions, deep bed filtration mechanism, in which inclusions attach to the filter wall, is one of the main filtration mechanisms. Inclusion capture in deep bed filtration is considered to be the result of two sequential events: transport of the particles from the bulk melt to inner parts of the filter pores, and attachment of the particles to the pore walls. The first step is controlled by different mechanisms such as collision with walls, interception (fluid flow transport), sedimentation (gravity), diffusion (or Brownian motion) for very small inclusions, turbulent fluctuation, and hydrodynamic effects. The pore size affects filtration efficiency very much. Inclusions will be removed more if with smaller pore filters. However, small pores are easy to be blocked by inclusions. Thus, the size of the filter pore should be optimized for any filtration process. Three-dimensional turbulent fluid flow and inclusion motion in a number of filter

channels are calculated, as shown in **Fig. 3. (a)**. Most of inclusions are entrapped at the upper part of the filter, which matches well with the experimental observation. The attachment locations of the large inclusions are more likely around the intersection between pores, and small inclusions disperse well on the whole wall of a pore.

Effect of Inclusion Bridges on Filtration

Inclusions firstly approach filter walls, growing into a large network (bridge) of inclusions which prevent and blocks any moving particle that comes its way. The attraction of inclusions toward each other may lead to a “mushy zone” of inclusions, which act as nucleation sites for forced or premature precipitation of Fe-rich phases even at a higher temperature, as shown in **Fig. 3. (b)**. Precipitated Fe-rich phases reinforce particles in the “mushy zone” to form bridges of inclusions. These bridges trap more inclusions that come their way. In this case, small channels between the inclusion bridge and the filter wall may become way of escape for small sized inclusions. Another contribution is the formation of large clusters of Fe-rich phases, which form “semi bridges” to trap inclusions.

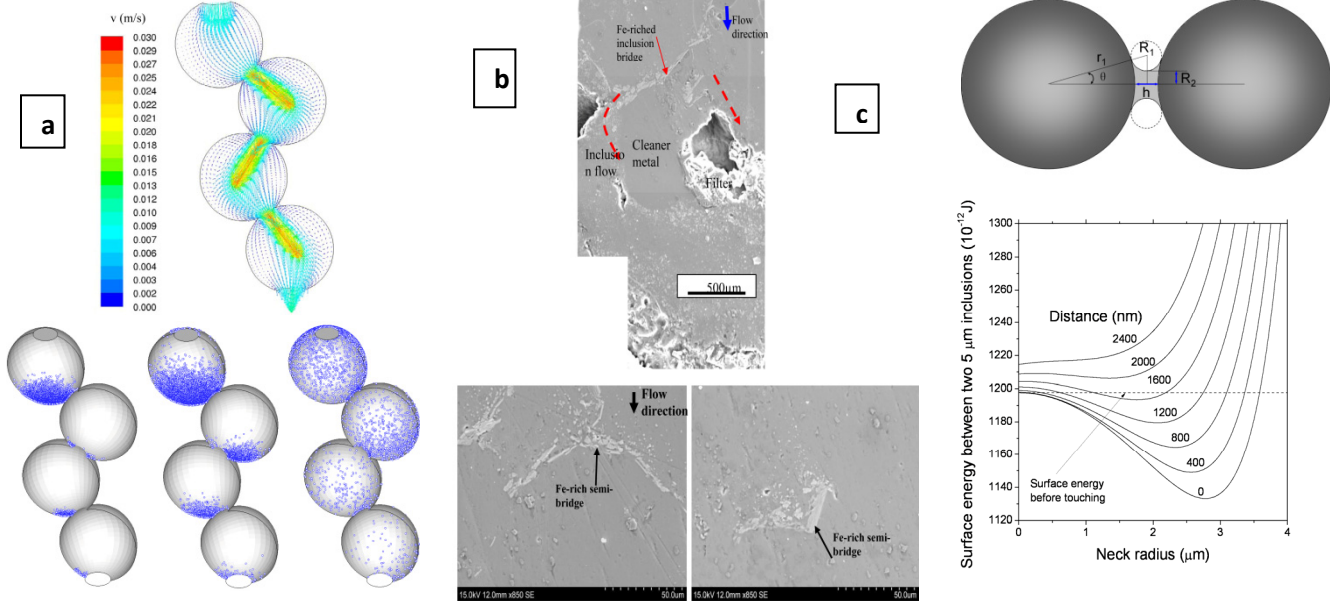


Fig. 3.(a) Calculated fluid flow velocity (m/s) and the respective attachment locations to filter walls of 100 μm, 50 μm and 10 μm inclusions. (b) Contributions of inclusions bridges to effective filtration and (c) Calculated surface energy between two 5 μm collided particles.

Interfacial Energy between Two Collided Inclusions

Interfacial forces at the three interfaces between melt and filter material, melt and inclusions, and inclusions and filter play an important role in an efficient filtration process. As an example, two spherical solid particles with size of $5\mu\text{m}$ collide with each other. After reaching steady touching state, there will be a vacuum film generated between the two particles, as shown in **Fig. 3 (c)**. The calculated surface energy as function of neck radius R_2 and distance h is shown in **Fig. 3.(c)**. For a given distance h , the collision between two particles needs an initiated energy E_a , and then can finally steadily stay together with the energy of E_s .

3.3 Removal of impurity Elements

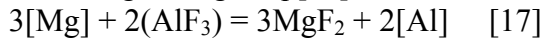
Glow discharge mass spectrometry (GDMS) was used to study the impurity elements removal capabilities of the two filters. The initial Mg levels were 90 ppm in Alloy-1 and 4500 ppm in Alloy-2. However, the initial levels of Ca and Na elements within the aluminum alloys used were too low to allow for appreciable reaction. In experiment E1, no reactive AlF_3 layer was used, thus the removal of the [Mg] can only be by evaporation followed by air oxidation, Eq.[3], and accounts for ~13% removal.



$$\Delta G_{\text{Reaction}}^o(900^\circ\text{C}) = -945.7 \text{ kJ/mol} \quad [18] \quad [4]$$

Due to the high vapor pressure of magnesium at 900°C , its oxidation might be occurring at the surface of the molten metal [18], followed by entrainment into the molten metal due to its higher density. Evidence of this was seen within the filter window, as a large cluster of MgO particles was observed.

The results showed that the coated filter removed 63-87% Mg through Eq.[17].



In the current study, [Ca] and [Na] could not be removed further due to their low initial concentrations. However, the results of Gorner *et al*, [19] showed [Na] removal efficiency of up to 98 % and 78 % efficiency for the removal of [Ca] for active granular bed filters coated with aluminum fluoride.

Figure 4 shows the calculated removal efficiencies of [Ca] and [Mg] by the AlF_3 -coated

filter. **Fig. 4.(a)** shows the calculated removal efficiencies for dissolved [Ca] by AlF_3 coated CFFs. It indicates that, if no other elements are present in the molten aluminum, within 30 s residence time of the molten aluminum in the filter, 99.8 % of [Ca] could be removed by the 30 ppi filter. Using data from experiment E3, the [Mg] removal efficiency can be calculated as shown in **Fig. 4.(b)** based on the calculated total mass transfer coefficient of $1.15 \times 10^{-6} \text{ m/s}$ towards the walls of the filter. A removal efficiency of 90.4 % within 7 min. (420 s) could be achieved by a 30 ppi AlF_3 coated filter. The standard Gibbs energy of formation of CaF_2 and MgF_2 are approximately -1080 and -950 kJ/mol respectively [20], which indicates that dissolved [Ca] will react preferentially with AlF_3 before [Mg]. This results indicate that for too long residence times (more than 60 s) of molten metal within coated filter, equilibrium state of reaction between dissolved [Ca] (and [Na]) and AlF_3 will be reached, thus [Mg] will be removed. This may result in challenges when purifying Al-Mg alloys because Magnesium, in this case, is an expensive addition.

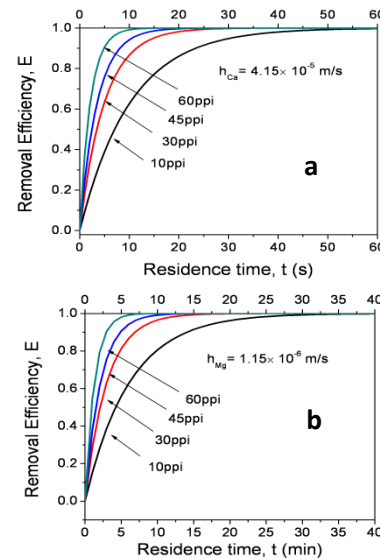


Fig. 4. Calculated impurity element removal by coated filter: (a) removal of [Ca] and (b) removal of [Mg].

4. CONCLUSIONS

Filtration of molten aluminum using regular uncoated 30 ppi Al_2O_3 and AlF_3 -coated Al_2O_3 CFF were undertaken to removing both dissolved

impurity elements and inclusions. The following conclusions are drawn from the study:

- Filtration with 30 ppi CFF is an effective method of removing inclusion from aluminum with filtration efficiencies > 81%.
- Fluid dynamics modeling of inclusions attachment to the filter walls showed that most inclusions, especially with larger size, are entrapped at the upper part of the filter while smaller inclusions dispersed well throughout the filter similar to observations made on spent filters from the experiments.
- Two main contributing filtration mechanisms are (1) collision with walls and interception effect and (2) the formation of both intermetallic and nonmetallic inclusion bridges during filtration.
- The interfacial energy between two collided inclusions was calculated, indicating that very strong attractive forces hold the particles together within the filter.
- The AlF_3 coated could remove dissolved Mg up to 87 %. Theoretical calculation showed that dissolved [Ca] in molten aluminum can be removed up to 99.8 % by the coated filter 30 s.

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