AlF₃ reactive Al₂O₃ foam filter for the removal of dissolved impurities from molten aluminum: Preliminary results

Lucas Nana Wiredu Damoah a,b, Lifeng Zhang a,*

a Department of Material Sciences and Engineering, Missouri University of Science and Technology (Missouri S&T), 223 McNutt Hall, Rolla, MO 65409-0330, USA
b Department of Materials Science and Engineering, University of Ghana, Ghana

Received 24 May 2010; received in revised form 25 September 2010; accepted 28 September 2010
Available online 8 November 2010

Abstract

Filters coated with AlF₃ can be used to filter molten aluminum to simultaneously remove nonmetallic inclusions and dissolved alkali and alkaline earth metal impurities. Coating experiments were carried out in which anhydrous HF gas was generated from reactions involving NaF or CaF₂ and concentrated H₂SO₄, and used in a reaction with Al₂O₃ ceramic foam filter to produce a layer of AlF₃ coating on the surface of the Al₂O₃ filter. Samples from these experiments were studied by X-ray diffraction, scanning electron microscopy and electron probe microanalysis. Preliminary results of the coating experiments showed that it is possible to coat Al₂O₃ filters with AlF₃ by this method. Increasing the pressure of HF gas increased the yield of AlF₃ in the filter. Theoretical evaluation of the removal efficiency of dissolve impurity elements showed that dissolved calcium can be removed up to 99.8% within 30 s of contact time between the filter material and the molten aluminum.

© 2010 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

Keywords: AlF₃ reactive filter; Filtration; Aluminum; Inclusions; Dissolved impurities

1. Introduction

The expanding use of aluminum alloys for making critical components in castings, extrusions and rolling for the aerospace, automotive and other industries makes concerns on melt quality inevitable. This means that more companies will have to invest heavily in state-of-the-art casthouse technologies. Furthermore, there will be a strong drive from downstream companies for further improvements and new developments in the upstream processes leading to quality products. Two major classes of impurities can be distinguished in molten aluminum as dissolved elements and suspended particles, which may be nonmetallic or intermetallic in character. Sources of these impurities can be traced back to the electrolysis process, melt processing operations, and interactions between the molten metal and refractory materials and also the environment. Essentially, melt quality can be controlled by the removal of alkali and alkaline earth trace elements, hydrogen and inclusions [1,2]. Various technologies, such as in-line spinning nozzle units, furnace fluxing and packed bed, and rigid media ceramic foam filters, are used to control impurity levels. To make sure melt quality standards are met, these processes must be monitored to allow statistical control [2]. Impurities in the aluminum melt are a major cause of product failure during both processing and use. However, nonmetallic inclusions may play an important role in facilitating the crystal nucleation process and other primary phases [3], since they are usually present as solid particles in aluminum melt during solidification. They also help in precipitating Fe-intermetallic metallic phases, which are a major problem to the properties of aluminum. Various methods, such as filtration, sedimentation and bubble flotation, are already employed to remove nonmetallic inclusions from molten aluminum.
Common dissolved unwanted impurities usually found in molten aluminum from the electrolysis cell are Na, Li, Ca, Fe and H₂. Hydrogen is the only known gas with appreciable solubility in molten aluminum. Dissolved alkali and alkaline earth elements originate from the presence of fluoride salts such as NaF, LiF and CaF₂ in the electrolyte used during the Hall–Heroult process. Due to their relatively high vapor pressure, Na and H are regarded as volatile elements. Impurities such as Ca and Li can be removed by adding a variety of chemicals to the melt, and may therefore be referred to as reactive elements. Elements such as Fe and Si may be referred to as non-reactive because they are very difficult to remove from aluminum by ordinary fluxing processes. Na and Li can cause edge cracking during hot rolling by forming low melting point phases at the grain boundaries. For most products Na levels are kept below 10 ppm. Extrusion defects are also linked to higher Na levels. However, some researchers see no concern in Na levels significantly in excess of 10 ppm for common alloy extrusions [4]. H₂ causes porosity due to its low solubility in solid aluminum; it comes out of solution during solidification. The porosity can cause blisters in extrusions or during hot rolling of sheet metal. Na causes hot shortness in alloys which contain magnesium. Li creates an undesirable black film on foil products. Due to these unwanted properties, both elements must be reduced to very low levels.

Refining of aluminum typically involves fluxing out dissolved alkali impurities using Cl₂ or salts of chlorine or fluorine, argon degassing for H₂ removal and, finally, flotation/settling/filtration operations for the removal of solid inclusions [5]. Due to their better pollution control and superior results compared to gas fluxing, powder and granular particle injection into molten aluminum are employed in the removal of dissolved impurities [6–8]. Optimization of these techniques enhances the removal rates with respect to H, alkali and alkaline earth metals, and inclusions. Furthermore, the consumption of refining agents, which strongly depends on thermodynamics and kinetics, needs to be optimized. Besides the cost of the refining agent and its environmental impact, any excess of it will be involved in further reactions with the alloy. These reaction products will act as impurities which have to be removed later [9].

AlF₃ can be employed for the removal of dissolved alkali and alkaline earth metals from molten aluminum through three main methods: (1) powder injection [10]; (2) deep bed filtration [11,12]; and (3) ceramic foam filtration.

With respect to option (1) above, AlF₃ is injected into the molten metal in the treatment crucible and the melt is stirred simultaneously. The application of AlF₃ in industrial refining of molten aluminum is economically advantageous compared to chlorine gas and chloride salts in spite of its higher market price. However, analysis of this process with respect to kinetics has shown that AlF₃ is utilized in an inefficient manner [13]. Furthermore, crucible treatment with AlF₃ results in reaction products that require further processes to be removed and long crucible treatment times are required in order to maximize the efficiency of the fluxing process. The latter usually leads to the oxidation of the metal leading to the formation of more nonmetallic inclusions and increased metal losses.

Contact area per time of molten aluminum exposure to AlF₃ in the granular bed filter could be increased considerably. Such a filter containing AlF₃ as a filter medium could actively remove alkali from the melt and at the same time retain the reaction products. Eqs. (1)-(3) are the reactions involved in the purification process. Some of these products such as NaF or KF act as surfactants, which is suggested to possibly reduce surface tension and enhance alkali removal and/or particle capture [14].

The following chemical reactions give the mechanism by which AlF₃ removes dissolved alkali and alkaline earth impurities from the molten aluminum through filtration.

\[
[\text{Ca}] + \frac{2}{3} \text{AlF}_3 = \text{CaF}_2 + \frac{2}{3} [\text{Al}], \quad \Delta G^\circ(T) = -230,687 + 3.31T J/mol \quad (1)
\]

\[
[\text{Mg}] + \frac{2}{3} \text{AlF}_3 = \text{MgF}_2 + \frac{2}{3} [\text{Al}], \quad \Delta G^\circ(T) = -116,195 - 0.604T J/mol \quad (2)
\]

\[
3[\text{Na}] + \text{AlF}_3 = 3\text{NaF} + 3[\text{Al}], \quad \Delta G^\circ(T) = -230,086 + 42.37T J/mol \quad (3)
\]

In the deep bed filtration method the molten metal flows through the packed bed and interacts with the AlF₃ particles according to the above reactions. However, this method is not being applied by the aluminum industry at the moment.

High efficiency of up to 98% was reported for AlF₃ to remove dissolved impurities such as Na and Ca from aluminum through granular bed filtration [13,14]. The use and the evaluation of the efficiency of ceramic foam filters (CFFs) in the removal of nonmetallic inclusions from molten aluminum through filtration have been widely studied in the literature [15–19]. Therefore, using the existing Al₂O₃ CFF material coated with AlF₃ to filter molten aluminum has the potential to remove dissolved alkali and alkaline earth metal impurities and nonmetallic inclusions simultaneously.

There are three main methods by which AlF₃ can be employed in ceramic foam filtration. First, Al₂O₃ CFF can be immersed with AlF₃ slurry and sintered for use as filtration material [20]. There have been several patents about the coating of CFF filters with other materials [21–23], such as soda silicate [21,22] and silicon carbide [23], which have a softening point at the temperature of molten aluminum. The coated filters were supposed to be used for the removal of inclusions and dissolved alkali elements from the molten metal. Second, AlF₃ CFF can be produced for molten aluminum filtration by infiltrating polyurethane foam with AlF₃ slurry followed by firing to AlF₃ sintering.
temperature. This may also be done by casting AlF₃ slurry mixed with appropriate sizes and amount of polymeric particles into a box, as shown in Fig. 1. The cast product is then pyrolyzed to remove the polymer, and sintered to form AlF₃ ceramic foam filter. The third method, which is the subject of the present article, is by reacting Al₂O₃ with HF gas to form AlF₃ on and within the Al₂O₃ CFF.

There have been several patents on the production of AlF₃ by the reaction between HF gas and solid Al₂O₃ [24–28], some of which are from as far back as 1971 [24]. In Eisele’s patent [28], it was explained in detail how to react CaF₂ with H₂SO₄ acid to generate HF gas at ~200 °C, which can then react with solid alumina to form AlF₃. In Blake’s report [24], it was suggested that waste HF acid could be used to produce an AlF₃ filter for aluminum purification. However, Al₂O₃ CFFs coated with AlF₃ are not currently employed in industrial aluminum purification despite their obvious advantages. This is due to the lack of a clear-cut industrial filter-making process to facilitate economic and environmentally friendly Al₂O₃ CFFs coated with AlF₃ for the aluminum industry.

The present article preliminarily explores the coating of alumina CFF with AlF₃ through a method by which Al₂O₃ was reacted with anhydrous HF in a high-temperature furnace. Samples from the coating experiments were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) with electron dispersive X-ray (EDX) capabilities, and electron probe microanalysis (EPMA).

2. Experiments

2.1. Trial experiments

A method of coating an Al₂O₃ CFF with AlF₃ by dipping into slurry prepared using AlF₃ of 94% purity followed by sintering has been explored [20]. However, the slurry blocked some of the pores of the original filter. In the current study, the reaction of alumina foam filters with aqueous HF in an attempt to form a layer of AlF₃ on alumina was unsuccessful, as the aqueous HF (48% and 24%) dissolved the alumina too rapidly.

2.2. Reacting an Al₂O₃ filter with anhydrous HF gas

The experimental set-up consists of three reactors, as shown in Fig. 2, with three major reactions occurring – HF gas generation, AlF₃ coating and excess HF gas neutralization reactions. The experimental furnace was water cooled and controlled with a proportional–integral–derivative temperature controller. The target reaction occurs in reactor (2) of a quartz tube furnace, leading to the formation of the AlF₃ coating on the Al₂O₃ filter. The feasibility of generating HF from a reaction between sulfuric acid and NaF has been studied [29]. The following reactions are involved in the respective reactor processes during the experiments:

\[
\begin{align*}
2\text{NaF}_{(s)} + \text{H}_2\text{SO}_4_{(conc)} &= \text{Na}_2\text{SO}_4_{(s)} + 2\text{HF}_{(g)} \quad (4) \\
\text{Al}_2\text{O}_3_{(s)} + 6\text{HF} &= 2\text{AlF}_3_{(s)} + 3\text{H}_2\text{O}_{(g)} \quad (5) \\
\text{NaOH}_{(aq)} + \text{HF}_{(g)} &= \text{NaF}_{(liq)} + \text{H}_2\text{O}_{(liq)} \quad (6)
\end{align*}
\]

Powdered CaF₂ was also used here in place of NaF to react with sulfuric acid to generate HF gas in an experiment according to Eq. (7). The use of CaF₂ to produce
HF gas is a well-known process. Using CaF₂, and not NaF, prevents the evaporation of sodium into the filter materials during the experiment.

\[
\text{CaF}_2(\text{solid}) + \text{H}_2\text{SO}_4(\text{conc}) \rightarrow \text{CaSO}_4(\text{solid}) + 2\text{HF}(\text{gas})
\]  

The selection of material for the construction of the experimental set-up was an important factor for consideration, given the severe corrosiveness and poisonous nature of HF. The reactor vessels were thus selected from quartz material and connected to each other by Teflon tubes. The joints and fittings were adequately sealed with the help of Teflon tapes to avoid leakage of the HF gas. Quartz has an appreciable resistance to HF under the prevailing experimental conditions [30]. A quartz filter of 90 μm pore size was fitted within the furnace to be a platform for the filter sample and to also maintain a certain HF gas pressure within the reacting filter. The furnace was controlled by heating to 700 °C at a rate of 200 °C h⁻¹ and holding at this temperature for a specific time before cooling at the same rate.

According to the reaction stoichiometry, a minimum of 1 mol of anhydrous HF is required to produce 28.0 g of AlF₃. This formed the basis for the choice of quantities of the reagents for Eq. (4), where HF is generated for use in Eq. (5). Thus 1 mol of NaF and 0.5 mol of sulfuric acid were required to produce 28 g of AlF₃. The strength of the sulfuric acid used was 97%. Five experiments were conducted using NaF, and one experiment used CaF₂. Table 1 gives information about the various experiments. The yield of HF gas from Eq. (4) is below 100% and has been reported not to depend on the strength of the sulfuric acid [29], as 80% and 96.5% sulfuric acid were found to give approximately 80% yield. However, excess sulfuric acid above the required stoichiometric amount is reported to decrease the yield of HF, while higher temperatures increase it.

The set-up was purged with nitrogen gas until the final temperature of 700 °C was reached in the furnace and reactor (1) had attained a preheating temperature of about 120 °C. This purging helps to minimize corrosion in the reactors. The flow of nitrogen gas was discontinued before Eq. (4) was initiated by opening the valve to let concentrated sulfuric acid into reactor (1). After a reaction time of 5 min, the nitrogen flow was resumed to drive the generated HF gas from reactor vessel (1) to the furnace to initiate Eq. (5). This process continued until the furnace cooled down to 25 °C. Excess HF gas was absorbed in a 30% (15.75 M) NaOH solution, as shown in Eq. (6). To ensure that only negligible amounts of HF gas were released into the atmosphere, 5.5 l of NaOH solution (far in excess of the required volume) was used to neutralize the excess HF gas.

Coated filter samples were cut to approximately 1 mm × 2 mm, embedded in epoxy, ground on various grades of SiC paper and then polished for observation by SEM and analysis by EPMA. XRD samples were ground to fine powders averaging 2 μm in grain size with the help of an alumina mortar and pestle. Due to the high sensitivity of XRD to impurities and contaminants, the mortar and pestle were thoroughly washed with water, rinsed with ethanol and dried before successive samples were prepared.

### 3. Results and discussion

#### 3.1. Comparison between Al₂O₃ filters coated with AlF₃ slurry and coating by reacting with HF gas

Fig. 3 shows the distribution of pores within the filters coated by AlF₃ slurry and gaseous HF. The slurry-coated CFF showed less porosity than the HF gas-coated CFF material because the AlF₃ slurry blocked part of the pores. Visual examination indicated that the HF gas-coated filters had the same porosity as the original uncoated Al₂O₃ CFF. When touched, the AlF₃ coating on the filter coated by the slurry method appeared to fall off, indicating weaker adhesion strength of the AlF₃ coating to the Al₂O₃ base material. Distribution of fluoride within the walls of the slurry-coated and HF gas-coated filters are showed in Fig. 4. While fluoride was detected throughout the wall thickness of the base material in the HF gas-coated filter,
Fluoride in the slurry-coated filter appeared as an additional layer into the pores of the filter. This increased the wall thickness of the filter material from the slurry-coated process, thus reducing porosity.

Fig. 4. Comparison between (a) HF gas-coated filter and (b) slurry-coated filter in the distribution of fluoride in filter walls. The slurry-coated filter bears solidified aluminum after a filtration experiment. It shows an extra $\text{AlF}_3$ layer, which extends into the pores of the filter, thereby reducing its porosity.
Fig. 5 shows the microstructure of the filters. There was significant difference in the microstructures of the uncoated filter (Fig. 5a) and the filter coated by the HF gas process (Fig. 5b). Fig. 5c shows the microstructure of the filter immersed in an aqueous HF solution. The wall thickness of the filter decreased until it was very thin as a result of dissolution of the alumina by the aqueous fluoride solution, and no AlF$_3$ layer remained on the filter. The remaining Al$_2$O$_3$ material was very fragile and is therefore not suitable for use by the metal industry for filtration purposes. Fig. 5d shows that the wall thickness of the filter coated by the AlF$_3$ slurry process increased, with an extra layer of fluoride. An important observation is the grain boundary (surface misfit) between the layers of the filter and the AlF$_3$ coating on the filter walls. This is probably the reason for the weak adhesion of the AlF$_3$ coating to the base material that we observed.

Fig. 6 presents the EDX results of elemental compositions of the filters after the various HF gas-coating experiments. The first set of columns (experiment number zero) represents the uncoated filter, while the last set (experiment number seven) represents the filter from the aqueous HF experiment. For the conditions of the different experiments, see Table 1.

![Fig. 5. Microstructure of various filters: (a) uncoated filter, (b) HF gas-coated, (c) aqueous HF coated and (d) slurry-coated filter, with an additional layer (fluoride layer).](image)

![Fig. 6. Compositions of various elements detected in the filters after the various experiments. The last columns represent the filter from the aqueous HF experiment. For the conditions of the different experiments, see Table 1.](image)

![Fig. 7. The dependence of fluoride yield in the filter on the HF gas pressure. This result does not include points from experiments 3 and 6 because they were under different conditions.](image)
experiment. Various elements, such as silicon (Si), sodium (Na) and phosphorus (P), were detected, along with oxygen (O), aluminum (Al) and fluorine (F). The uncoated filter contained O, Al and P. Aluminum phosphate is a binder/sintering aid used in the manufacturing of the Al₂O₃ filter. It can be seen from the figure that fluoride was successfully introduced into the filters in all the HF gas-coating experiments. Traces of elements other than fluorine were also detected in the filters from certain experiments. Sodium was detected in the filters from experiments 1, 3, 5 and 6. Silicon was detected after experiments 2 and 5 and 6. According to the EDX results, the filter material coated in experiment 4 did not contain traces of sodium and silicon. The base filter material is phosphate-bonded alumina.

The relationship between the fluoride yield in the filter and the amount of HF gas supplied is shown in Fig. 7, where the fractional increase in the quantity of reagents relative to experiment 1 is plotted against the respective fluoride yield in the filter. This indicates that increasing the pressure of HF gas has the tendency of increasing the yield of fluoride within the filter.

The chemical compositions of the filters were confirmed by EPMA, as shown in Figs. 8–11. Figs. 10 and 11 are XRD spectra of the filters coated by the slurry method and by HF gas method respectively, showing the compounds formed within the filters during the coating process.

3.2. Evaluation of the HF gas-coating process

The EDX results of the filter walls shown in Fig. 6 indicate that the concentration of fluoride within the walls of the CFF increased with increasing amount of HF generated from Eq. (4). The highest average fluoride concentration within the filter walls was measured for experiment 5 to be 37.35 wt.%, followed by experiment 4, with 29.17 wt.% of fluoride. Experiment 3 gave the least fluoride yield in the filter, with a fluoride concentration of 5.28 wt.%, followed by experiment 1, with 8.77 wt.% fluoride. These results were expected because more HF was expected to yield from Eq. (4) as the stoichiometric concentration of NaF and concentrated H₂SO₄ increased. Therefore, the fluoride yield from experiment 5 was expected to be highest, followed by that from experiment 4 and so on. However, less HF gas yield was recorded for experiment 3 according to the amount of fluoride within the filter material. The HF yield from Eq. (4) is reported to be dramatically reduced when the quantity of H₂SO₄ is in excess of stoichiometric requirements [29]. This is probably the reason for the low HF gas yield in this experiment, leading
Fig. 9. Mapping of elements in filter after coating experiments 1 (a), 2 (b), 3 (c), 4 (d) and 5 (e).
Fig. 9 (continued)
Fig. 10. XRD results of slurry AlF₃-coated alumina CFF.
Fig. 11. XRD spectra of AlF₃-coated filter, coated by the HF gas method in experiments 1 (a) and 2 (b).
Fig. 12. Elemental maps of HF-coated filter from experiment 6.
Dynamic calculations were taken from Ref. [31]. The concentration difference between the fluoride in the filters from experiments 1 and 2 is over 130% of the concentration of fluoride in the filter from experiment 1 even though the increase in HF yield reagents (i.e. NaF and concentrated H$_2$SO$_4$) from experiment 1 to experiment 2 is only about 50% (see Table 1). Thus the fluoride yield in the CFF may be improved by the supply of more HF to the filter. This result was observed throughout the experiments, from experiment 1 to experiment 5, as shown in Figs. 6 and 7. Experiment 5 was performed at a temperature of 650°C, the lowest holding temperature among all the experiments. After heating to, and holding for 30 min at, 700°C, the furnace was allowed to cool down to a temperature of 650°C before HF gas from Eq. (4) was introduced into the furnace. The holding time of the furnace at 650°C was 15 min, after which the cooling schedule was resumed until a temperature of 25°C was reached. Thus the success of experiment 5 is an indication that the process could be performed at a temperature lower than 700°C. The calculated standard molar Gibbs energy of Eq. (5), shown in Eq. (8), indicates that the reaction can occur at temperatures below 820°C. All data for thermodynamic calculations were taken from Ref. [31].

$$\Delta G_m^o(T) = -430, 700 + 394T$$  \hspace{1cm} (8)

The thermodynamics suggest that the reaction possesses greater energy at lower temperatures and that coating results would be better at temperatures far below around 25°C. Therefore, the process can be undertaken at room temperature. The temperature of 700°C was arrived at after a review of the literature.

Fig. 7 shows clearly that the fluoride yield in the filter material increases linearly with increasing HF gas pressure. It is noteworthy that, even though the best fluoride yield was achieved by experiment 5, it also produced the second-highest Na concentration in the filter as detected by EDX, after experiment 3 (Fig. 6). Fig. 8 shows elemental maps of the Al$_2$O$_3$ CFF before the coating experiments. It shows moderate traces of sodium (∼1 wt.%) within the filter before coating. This could be the result of atmospheric contamination. However, there is no doubt that the coating experiments introduced sodium into the filter, as can be seen from Fig. 9. Unlike the EDX results, the EPMA maps show that the filter with the highest Na concentration was from experiment 5 (Fig. 9e), while experiment 3 also gave very high traces of Na within the filter. The reason why the highest Na concentration in the filter was from experiment 5 is not readily known. It is suspected that the preheating processes might have evaporated some Na into the filter material. According to Fig. 9d, experiment 4 showed no traces of Na. We therefore consider this experiment to be the most successful of the experiments involving NaF.

Since sodium is not wanted in the filter, the chemical forms of the filters were investigated by XRD. Figs. 10 and 11 show the XRD spectra of the filter materials. The results show that sodium was present in the form of NaF in the filter from experiment 1. Another form, (Na$_2$O)$_{1.52}$A$_1$SiO$_2$(SiO$_2$)$_{65}$H$_2$O (sodium aluminum silicate hydrate), was detected in samples from other experiments. The distribution and intensities of fluoride within the walls of the filters compared to those of Na as shown in Fig. 8 indicate that more fluoride than Na was introduced into the filter. Fluoride in the filters was detected by XRD as AlF$_3$. A comparison between the filters coated by the slurry method and those coated by the HF gas method showed that more AlF$_3$ was detected in the slurry-coated filters than in the HF gas-coated filters. This is evident from the AlF$_3$ peaks of Figs. 10 and 11. However, the EPMA maps indicate that, for the HF gas-coated filters, not only is fluoride on the surface of the CFF, it is also throughout the entire CFF material. Therefore, under the appropriate HF gas pressure and temperature it is possible to convert the entire thickness of the filter wall into AlF$_3$ by this method. This means greater AlF$_3$ activity within the filter without significantly changing the porosity of the filter.

The worrying observation of NaF within the sample prompted an experiment using CaF$_2$ instead of NaF (as in experiment 6). Eq. (4) was then replaced by Eq. (9) in the process.

$$\text{CaF}_2 + \text{H}_2\text{SO}_4 = 2\text{HF} + \text{CaSO}_4$$  \hspace{1cm} (9)

$$\Delta G_m^o(T) = 62, 600 - 228.3T$$  \hspace{1cm} (10)

The thermodynamics of this reaction, Eq. (10), indicate that it is a spontaneous reaction at room temperature. There is therefore no need to preheat CaF$_2$ to a higher temperature. The concentration difference between the fluoride in the filter from experiment 1 to experiment 2 is only about 50% (see Table 1). Thus the fluoride yield in the CFF may be improved by the supply of more HF to the filter. This result was observed throughout the experiments, from experiment 1 to experiment 5, as shown in Figs. 6 and 7. Experiment 5 was performed at a temperature of 650°C, the lowest holding temperature among all the experiments. After heating to, and holding for 30 min at, 700°C, the furnace was allowed to cool down to a temperature of 650°C before HF gas from Eq. (4) was introduced into the furnace. The holding time of the furnace at 650°C was 15 min, after which the cooling schedule was resumed until a temperature of 25°C was reached. Thus the success of experiment 5 is an indication that the process could be performed at a temperature lower than 700°C. The calculated standard molar Gibbs energy of Eq. (5), shown in Eq. (8), indicates that the reaction can occur at temperatures below 820°C. All data for thermodynamic calculations were taken from Ref. [31].

$$\Delta G_m^o(T) = -430, 700 + 394T$$  \hspace{1cm} (8)

The thermodynamics suggest that the reaction possesses greater energy at lower temperatures and that coating results would be better at temperatures far below around 25°C. Therefore, the process can be undertaken at room temperature. The temperature of 700°C was arrived at after a review of the literature.

Fig. 7 shows clearly that the fluoride yield in the filter material increases linearly with increasing HF gas pressure. It is noteworthy that, even though the best fluoride yield was achieved by experiment 5, it also produced the second-highest Na concentration in the filter as detected by EDX, after experiment 3 (Fig. 6). Fig. 8 shows elemental maps of the Al$_2$O$_3$ CFF before the coating experiments. It shows moderate traces of sodium (∼1 wt.%) within the filter before coating. This could be the result of atmospheric contamination. However, there is no doubt that the coating experiments introduced sodium into the filter, as can be seen from Fig. 9. Unlike the EDX results, the EPMA maps show that the filter with the highest Na concentration was from experiment 5 (Fig. 9e), while experiment 3 also gave very high traces of Na within the filter. The reason why the highest Na concentration in the filter was from experiment 5 is not readily known. It is suspected that the preheating processes might have evaporated some Na into the filter material. According to Fig. 9d, experiment 4 showed no traces of Na. We therefore consider this experiment to be the most successful of the experiments involving NaF.

Since sodium is not wanted in the filter, the chemical forms of the filters were investigated by XRD. Figs. 10 and 11 show the XRD spectra of the filter materials. The results show that sodium was present in the form of NaF in the filter from experiment 1. Another form, (Na$_2$O)$_{1.52}$A$_1$SiO$_2$(SiO$_2$)$_{65}$H$_2$O (sodium aluminum silicate hydrate), was detected in samples from other experiments. The distribution and intensities of fluoride within the walls of the filters compared to those of Na as shown in Fig. 8 indicate that more fluoride than Na was introduced into the filter. Fluoride in the filters was detected by XRD as AlF$_3$. A comparison between the filters coated by the slurry method and those coated by the HF gas method showed that more AlF$_3$ was detected in the slurry-coated filters than in the HF gas-coated filters. This is evident from the AlF$_3$ peaks of Figs. 10 and 11. However, the EPMA maps indicate that, for the HF gas-coated filters, not only is fluoride on the surface of the CFF, it is also throughout the entire CFF material. Therefore, under the appropriate HF gas pressure and temperature it is possible to convert the entire thickness of the filter wall into AlF$_3$ by this method. This means greater AlF$_3$ activity within the filter without significantly changing the porosity of the filter.

The worrying observation of NaF within the sample prompted an experiment using CaF$_2$ instead of NaF (as in experiment 6). Eq. (4) was then replaced by Eq. (9) in the process.

$$\text{CaF}_2 + \text{H}_2\text{SO}_4 = 2\text{HF} + \text{CaSO}_4$$  \hspace{1cm} (9)

$$\Delta G_m^o(T) = 62, 600 - 228.3T$$  \hspace{1cm} (10)

The thermodynamics of this reaction, Eq. (10), indicate that it is a spontaneous reaction at room temperature. There is therefore no need to preheat CaF$_2$ to a higher temperature.

<table>
<thead>
<tr>
<th>Pore size (ppi)</th>
<th>$\varepsilon$</th>
<th>$S_m$ (m$^2$ m$^{-3}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.878</td>
<td>$1.71 \times 10^4$</td>
</tr>
<tr>
<td>30</td>
<td>0.874</td>
<td>$3.37 \times 10^4$</td>
</tr>
<tr>
<td>45</td>
<td>0.802</td>
<td>$2.78 \times 10^4$</td>
</tr>
<tr>
<td>65</td>
<td>0.857</td>
<td>$6.84 \times 10^4$</td>
</tr>
</tbody>
</table>

Table 2
Data for various CFF pore sizes adopted from Ref. [34].
temperature. The results from this experiment are shown in Fig. 12. Even though there was preheating of CaF$_2$ to 140 °C before the reaction, there was no significant detection of Ca by EPMA. The results show a successful coating process with an even distribution of fluoride within the filter. However, more sodium was detected within the filter material after this experiment. It should be mentioned that the same experimental set-up was used for all six experiments. Therefore, the source of sodium in the filter material of experiment 6 is a result of evaporation and condensation of sodium compounds from within the Teflon tubes and the quartz stage of the filter. To eliminate the risk of introducing Ca into the filter, AlF$_3$ may be used instead. In that case, reaction (1) will proceed as follows:

$$2\text{AlF}_3 + 3\text{H}_2\text{SO}_4 = 6\text{HF} + \text{Al}_2(\text{SO}_4)_3$$

$$\Delta G_m^o(T) = 381,700 - 677.7T$$

The standard molar Gibbs energy of this reaction shows that AlF$_3$ requires preheating to temperatures >260 °C for the reaction to occur.

The reactor materials also have the ability to reduce the amount of HF available for the reaction with Al$_2$O$_3$ CFF. The amount of HF available to react with the CFF is reduced if the reactor materials are not inert to HF attack. Thus corrosion of the reactor material by HF can reduce the extent of reaction with Al$_2$O$_3$ CFF to produce AlF$_3$.

3.3. Theoretical analysis of [Ca] and [Mg] removal from molten Al

The AlF$_3$-coated CFF shows great potential for the successful removal of dissolved elemental impurities from molten aluminum simultaneously with the removal of inclusions. Filtration results using AlF$_3$ slurry-coated CFF showed that dissolved magnesium could be removed up to 87% through the following equation [32]:

$$[\text{Mg}] + \frac{2}{3}\text{AlF}_3 = \text{MgF}_2 + \frac{2}{3}[\text{Al}]$$

In the study, [Ca] and [Na] could not be removed further due to their initial low levels. Dissolved [Na] removal efficiency of up to 98% and 78% efficiency for the removal [Ca] using active granular bed filters coated with aluminum fluoride have been reported [13]. The efficiency of the filter in removing dissolved impurities may be evaluated by considering the reaction kinetics during the filtration process. If $M$ is the dissolved impurity alkaline earth element, the following reaction would be expected:

$$[M] + \frac{2}{3}\text{AlF}_3 \rightarrow \text{MF}_2 + \frac{2}{3}[\text{Al}]$$

Assuming the first-order reaction rate with respect to $M$, and assuming pure AlF$_3$ and only one dissolved impurity element in aluminum, the rate of reaction can be written as

$$R_M = kC_M$$

where $k$ is the rate constant and $C_M$ is the concentration of $[M]$ at the reaction interface. Fig. 13 is a schematic diagram of the reaction interface, showing the concentration profile of $[M]$. The mass flux of $[M]$ to the interface between the filter and molten aluminum can be written as follows:

$$J_M = h(C_{M,b} - C_M)$$

where $C_{M,b}$ is the concentration of $[M]$ at the boundary between the filter and molten aluminum.
where $h$ is the mass transfer coefficient and $C_{M,b}$ is the concentration of \([M]\) in the bulk of the molten metal.

At steady state, the rate of consumption \([M]\) by the reaction is required to be equal to the mass flux of \([M]\) to the reaction interface. This can be expressed as

$$R_M = J_M$$  \hspace{1cm} (17)

leading to Eqs. (18) and (19):

$$C_M = \frac{h}{h+k} C_{M,b}$$  \hspace{1cm} (18)

$$R_M = \frac{C_{M,b}}{1/k + 1/h}$$  \hspace{1cm} (19)

For the high-temperature filtration system, the rate constant, which depends exponentially on the temperature, can be conveniently said to be far greater than the mass transfer coefficient (i.e. $k \gg h$) [33] and that

$$R_M = hC_{M,b}$$  \hspace{1cm} (20)

Since mass transfer of \([M]\) to the reaction interface includes diffusion through the bulk of the molten aluminum and the filter material, $h$ would be replaced by the total mass transfer coefficient, $h_t$, to include the diffusion coefficients. The rate of consumption of \([M]\) then depends on the mass transfer coefficient. Since the concentration of \([M]\) varies along the depth of the filter, it is important to define the concentration of \([M]\) over the depth of the filter. This can be achieved through a molar balance as follows:

$$\frac{Q C_{M,b}(z) - Q C_{M,b}(z + \Delta z)}{\Delta z} = R_M \cdot S_v \cdot A$$  \hspace{1cm} (21)

where $Q$ is the volumetric flow rate of molten aluminum (m$^3$ s$^{-1}$), $z$ is the depth of the filter (m), $S_v$ is the surface area per unit volume of AlF$_3$ active filter material (m$^2$ m$^{-3}$) and $A$ is the cross-sectional area of the filter (m$^2$). Substituting Eq. (20) in Eq. (21) and rearranging leads to Eq. (22):

$$\frac{dC_{M,b}}{C_{M,b}} = -\frac{h_t S_v A}{Q} dz$$  \hspace{1cm} (22)

The removal efficiency of dissolved \([M]\) by the coated filter can be defined by Eq. (23):

$$E = \frac{C_{M,b,\text{in}} - C_{M,b,\text{out}}}{C_{M,b,\text{in}}} = 1 - \left(\frac{1}{C_{M,b,\text{in}}}ight)$$  \hspace{1cm} (23)

The removal efficiency can then be related to the filter properties, as shown by Eq. (24):

$$\ln(1 - E) = -\frac{h_t S_v A z}{Q}$$  \hspace{1cm} (24)

$$E = 1 - \exp\left(-\frac{h_t S_v A z}{Q}\right)$$  \hspace{1cm} (25)

Fig. 15. Filtration results after the use of AlF$_3$ slurry-coated Al$_2$O$_3$ CFF. The figure shows solidified aluminum within the filter and reaction products between the AlF$_3$ coating and dissolved [Na] and [Mg] [20].
The cross-sectional area of the filter material $A$, and the volumetric flow rate of the molten metal, $Q$, can be related to the bulk volume of the filter, $V_b$, and the porosity of the filter, $e$, as follows:

$$A = V_b \left(1 - e\right)$$  \hspace{1cm} (26)

$$Q = \frac{V_b \cdot e}{t}$$  \hspace{1cm} (27)

where $t$ is the residence time of molten aluminum within the filter. The dissolved impurity elements removal efficiency can then be written as follows:

$$E = 1 - \exp\left(-ct\right)$$  \hspace{1cm} (28)

$$c = \frac{h \cdot S_v \cdot (1 - e)}{e}$$  \hspace{1cm} (29)

The total mass transfer coefficient for calcium at the molten aluminum filtration temperature is reported to be $4.15 \times 10^{-5}$ m s$^{-1}$ [14] and $1.23 \pm 0.15 \times 10^{-3}$ m s$^{-1}$ [13]. Table 2 gives information about the CFFs, compiled based on data from Ref. [34].

Fig. 14 shows the theoretical calculation of the removal efficiency of calcium by the filter for various parameters. It can be seen that the removal efficiency of the AlF$_3$-coated CFF depends exponentially on the residence time of the molten metal within the filter, the contact area of the filter by the molten metal and the mass transfer coefficient. Increases in the contact area (increasing ppi of the filter) of the filter increased the removal efficiency significantly. Similarly, increases in the mass transfer coefficient reduced the time required to obtain higher removal efficiency. This implies that dissolved elements with higher mass transfer coefficients in aluminum will be removed first and/or faster than those with relatively smaller mass transfer coefficients. Using $4.15 \times 10^{-5}$ m s$^{-1}$ as the mass transfer coefficient of [Ca] for a 30 ppi coated CFF, it can be seen from Fig. 14 that the reaction proceeds at a fast rate within the first 28 s, resulting in corresponding [Ca] removal efficiency of 99.65%, then slows down until after 61 s, when 100% Ca removal efficiency is recorded. The standard Gibbs energy of formation of CaF$_2$ and MgF$_2$ are approximately $-1080$ and $-950$ kJ mol$^{-1}$ [35], respectively. This indicates that,

![Fig. 14](image_url)

Fig. 16. EPMA maps of elements on granular bed filter after aluminum filtration [13]. The figure shows reaction products between AlF$_3$ and dissolved [Na] and [Ca].
thermodynamically, [Ca] will react with AlF3 preferentially to [Mg]. Magnesium might be an expensive addition in Al–Mg alloys, and therefore the AlF3-coated CFF might not be recommended, especially where the dissolved [Ca] content is low in the molten aluminum. The mass transfer coefficient of dissolved [Mg] in aluminum was calculated to be $1.15 \times 10^{-6}$ m s$^{-1}$ [32]. Therefore, both the thermodynamics and the kinetics favor removal of dissolved [Ca] from molten aluminum preferentially to [Mg].

3.4. Experimental results of molten aluminum purification with coated filter

Aluminum filtration experiments using AlF3-coated Al$_2$O$_3$ CFF by the HF gas method is yet to be conducted. However, to have an idea about the impurity elements removal efficiency of the AlF3 coated CFF, preliminary filtration experiments were carried out by the authors and published elsewhere [32], which tested the removal of dissolved magnesium from aluminum using the AlF3-slurry-coated 30 ppi Al$_2$O$_3$ filter. The results showed that the slurry-coated filter could remove dissolved [Mg] up to 87% in the filtration process without compromising the efficiency of the filter at removing nonmetallic inclusions. This result is in direct agreement with the prediction of the model for [Mg] removal. Fig. 15 shows the result from experiments using AlF3 slurry-coated CFF [20]. It shows that the AlF3 coating reacted with dissolved [Na] and [Mg] in the molten aluminum, leading to segregation of sodium and magnesium on the surface of the filter. It is observed that the filter retains the products of the reactions with the impurity elements. The coating removed sodium from the molten aluminum through Eq. (30):

$$3[Na] + AlF_3(s) = 3NaF(s) + [Al] \quad (30)$$

Fig. 16 shows the filtration results using an AlF3 granular bed filter, taken from Ref. [13]. It provides further evidence of the reactions that occur between the surface fluoride on the filter and dissolved [Na] and [Ca].

These filtration results indicate that AlF3-coated Al$_2$O$_3$ CFF or AlF3 CFF has a greater potential to remove dissolved alkali and alkaline earth impurity elements from the molten aluminum while removing inclusions from the metal.

4. Summary

Anhydrous HF gas was generated from a reaction between NaF/CaF$_2$ and H$_2$SO$_4$, which was used to react with Al$_2$O$_3$ ceramic foam filter to produce an AlF3 coating on the filter surface in our experiments. The coated filter is expected to be used to filter molten aluminum to remove both nonmetallic inclusions and dissolved alkali and alkaline earth dissolved impurities. Theoretical evaluation of the capability of the coated filter to remove dissolved impurity elements was also undertaken with a case study on dissolved [Ca]. The results indicated that:

- It is possible to coat Al$_2$O$_3$ filter with AlF3 by reacting it with anhydrous HF gas without compromising the filter’s porosity. HF gas could be generated from a reaction between NaF, CaF$_2$ or AlF3 and H$_2$SO$_4$. NaF and CaF$_2$ can react at room temperature, while AlF3 reacts at temperatures above 290 °C.
- Increasing the pressure of HF gas involved in the coating reaction increased the yield of AlF3 within the filter.
- The AlF3 coating produced by this method formed part of the original filter wall; therefore the porosity of the filter was retained.
- Na/NaF was introduced into the filter materials via evaporation and condensation. There was not significant detection of Ca in the filter when CaF$_2$ was used. The use of AlF3 is proposed to resolve the possible introduction of Na/Ca impurities into the filter.
- The theoretical calculations show that the removal efficiency of dissolved elements in aluminum by the AlF3-coated CFF depends exponentially on the residence time of the molten metal within the filter, the contact area of the filter with the molten metal and the mass transfer coefficient. Increasing the contact area of the filter increases the removal efficiency significantly. Similarly, increasing the mass transfer coefficient reduced the time required to obtain near-100% removal efficiency. Calculated examples show that it is possible to obtain well above 99% removal efficiency for dissolved [Ca] impurities by the use of AlF3-coated CFF for filtration within 30 s of residence time for 10–50 ppi filters.

5. Future work

- Coating experiments using AlF3 and sulfuric acid will be undertaken in addition to the determination of the optimal coating conditions.
- Further studies will be carried out using AlF3 in place of NaF and CaF$_2$. Optimum coating conditions will be determined and properties of the coated filters evaluated relative to the coating process parameters.
- The useful life of the AlF3 coating on the filter will be investigated.
- Active filtration of aluminum will be investigated using AlF3-coated Al$_2$O$_3$ CFFs, coated by reacting with anhydrous HF gas, to study their efficiency in removing dissolved alkali and alkaline earth metals.

Acknowledgements

This research is supported by the Research Board Grant, Laboratory of Green Process Metallurgy and Modeling (GPMM), Material Research Center (MRC), Intelligent Systems Center (ISC) at Missouri University of Science and Technology (Missouri S&T).
References


[28] Eisele D. Using an air jacket to capture the heat of reaction for waste heat recycle in the production of aluminium fluoride. USA patent No. 20060093548. USA, 2006.

[29] Sidkar SK, Moore JH. Process for producing fluorine compounds and amorphous silica. USA patent No. 4,308,244; 1981.


