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ScienceDirect
Acta Materialia 59 (2011) 896–913
Acta MATERIALIA
www.elsevier.com/locate/actamat

AlF_3 reactive Al_2O_3 foam filter for the removal of dissolved impurities from molten aluminum: Preliminary results

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

Abstract

Filters coated with AlF_3 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 CaF_2 and concentrated H_2SO_4, and used in a reaction with Al_2O_3 ceramic foam filter to produce a layer of AlF_3 coating on the surface of the Al_2O_3 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 Al_2O_3 filters with AlF_3 by this method. Increasing the pressure of HF gas increased the yield of AlF_3 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.

Keywords: AlF_3 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 floatation, are already employed to remove nonmetallic inclusions from molten aluminum.

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1359-6454/$36.00
doi:10.1016/j.actamat.2010.09.064

Common dissolved unwanted impurities usually found in molten aluminum from the electrolysis cell are Na, Li, Ca, Fe and H_2. 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 CaF_2 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]. H_2 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 Cl_2 or salts of chlorine or fluorine, argon degassing for H_2 removal and, finally, floatation/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].

AlF_3 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, AlF_3 is injected into the molten metal in the treatment crucible and the melt is stirred simultaneously. The application of AlF_3 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 AlF_3 is utilized in an inefficient manner [13]. Furthermore, crucible treatment with AlF_3 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 AlF_3 in the granular bed filter could be increased considerably. Such a filter containing AlF_3 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 AlF_3 removes dissolved alkali and alkaline earth impurities from the molten aluminum through filtration.

$$[\mathrm{Ca}] + \frac{2}{3}\mathrm{AlF_3} = \mathrm{CaF_2} + \frac{2}{3}[\mathrm{Al}], \quad \Delta G^o(T) = -230,687 + 3.31T \text{ J/mol} \tag{1}$$

$$[\mathrm{Mg}] + \frac{2}{3}\mathrm{AlF_3} = \mathrm{MgF_2} + \frac{2}{3}[\mathrm{Al}], \quad \Delta G^o(T) = -116,195 - 0.604T \text{ J/mol} \tag{2}$$

$$3[\mathrm{Na}] + \mathrm{AlF_3} = 3\mathrm{NaF} + [\mathrm{Al}], \quad \Delta G^o(T) = -230,086 + 42.37T \text{ J/mol} \tag{3}$$

In the deep bed filtration method the molten metal flows through the packed bed and interacts with the AlF_3 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 AlF_3 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 Al_2O_3 CFF material coated with AlF_3 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 AlF_3 can be employed in ceramic foam filtration. First, Al_2O_3 CFF can be immersed with AlF_3 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, AlF_3 CFF can be produced for molten aluminum filtration by infiltrating polyurethane foam with AlF_3 slurry followed by firing to AlF_3 sintering