Metal Entrapment in Slag during the Aluminium Recycling Process in Tilting Rotary Furnace

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Abstract

Contaminated aluminium scraps are often recycled in Tilting Rotary Furnaces under a salt flux. The salt flux has three main functions: protect the metal surface against oxidation, promote the coalescence and remove the impurities (mainly oxides) from the metal bath. The last aim leads to an evolution of the salt flux during the recycling process: the oxide content continually increases, the salt flux is therefore changed into a salt slag and the salt properties are altered.

This paper focuses on coalescence of aluminium chips in salt slag in TRF and the influence of cryolite. Different salt slags were synthetized from salt and non-metallic solid residue from the recycling of salt slag. The experiments were conducted in a lab-scale tilting rotary furnace and several salt slag compositions were considered. It was shown that the coalescence is linked to oxide and cryolite content of the salt slag.

1 Introduction

Metal losses are due to two main reasons during an aluminium recycling process in Tilting Rotary Furnace with salt use: oxidation and metal entrapment in the salt slag. The oxidized metal cannot be recovered again, which is not the case of entrapped metal: the droplets have to settle down through the salt slag in order to get back to the metal bath. The settling is accelerated by coagulation of the metal droplets, according to Newton's second law. The coalescence is essential to minimize the metal losses due to entrapment in the salt slag.

2   Background

One of the functions of salt flux is to remove the oxide film on the aluminium surface in order to let the coalescence between aluminium droplets happen. Indeed, aluminium alloys are always covered by an oxide layer; this layer is about 4,5 nm thick at room temperature [1] and can reach 100 nm at 550°C.

The removal of the oxide layer can be described in two steps:

•   Crack of the oxide layer on the metal

•   Detachment of the oxides and entrapment in the salt

The cracks in the oxide layer are developed by chemical and mechanical phenomena. An addition of fluoride to the salt flux causes a limited dissolution of alumina which can reach up to 2 wt% in the case of AlF3 [2]. Besides, the longer the salt is in contact with the oxide layer, the more advanced the dissolution reaction is [3]. The split of the oxide layer is also promoted by the phase transformation of alumina: the initial gamma alumina film transforms itself in alpha alumina, which has another density; this can therefore weaken and crack the layer. This transition normally occurs around 1100°C but the presence of fluorides in the melt decrease the transition temperature [4]. Finally, the movement of the furnace accelerates the cracks formation as the scraps undergo shocks.

In order to enable the coagulation of metal droplets, the oxide layer has to be completely removed from the metal surface. This action is not spontaneous but requires only a small amount of energy. The contact angle between metal and oxide in the salt flux has to be maximized so the wettability of the oxide by salt is minimized [5]. The detachment of the oxide layer is due of the formation of tension-active elements, coming from a reaction between the salt flux and the metal. These elements dramatically decrease the surface tension of the metal when they are absorbed on its surface. The tension-active elements formation is promoted by the presence of fluorides in the salt flux [6] and with magnesium as alloying element [7].

The aluminium droplets are able to coalesce when the oxide layer is removed. Several authors conducted coalescence experiments in a salt flux in order to determine the best salt flux composition to have an optimized coalescence, i.e. the largest metal droplets. According to the results of the different authors, it seems that Na3AlF6 and NaF bring the best results [8] [9] [10] [6].

However, the different coalescence experiments were conducted in a salt flux, which corresponds to the beginning of a recycling process, when the salt is still clean and has not turned into a salt slag. Indeed, the salt slag composition is constantly being modified during a recycling cycle because of the gathering process of impurities. The oxide content in final salt slag can reach until 60 wt% from the total composition in some cases [11]. The properties of the salt slag are modified compared to the initial salt flux and it influences the coalescence. Alumina and spinel have a higher density than molten salt, so the salt slag density is increased by the oxide content. The viscosity of the slag is

likewise increased by non-metallic particles: 2 wt% of oxides in the slag multiplies the initial salt flux viscosity by 10, 10 wt% by 1000 [12]. This modification of density and viscosity leads to a more difficult metal/slag separation and the droplets settling is restricted or inhibited by the oxides from the slag.

3 Coalescence experiments

Objective

The coalescence is a key point for the recovery of metal droplets entrapped in salt slag as the gathering of droplets eases the separation of the metal from the slag by settling. The objective of the following coalescence experiments is to study the influence of oxides in the salt slag and determine the coalescence degree depending on the slag composition. Only one type of fluoride is used, cryolite, and a further goal of the experiments is to figure out if a maximized coalescence is obtained by the same percentage of cryolite whatever the oxide content in the slag.

Furnace

The coalescence experiments were conducted in a lab-scale tilting rotary furnace. The Mini TRF is a resistance furnace, which owns two specific properties:

-        The stainless steel frame of the furnace can be continuously tilted from 0° (vertical position) to 65°; the tilted furnace is shown on the left picture of Figure 1

-        The inner graphite crucible (Figure 1 right) rotates from 0 to 40 RPM.

Setting the position and rotation of the crucible does not interrupt the heating process. Argon is injected in the furnace through the lid in order to prevent the metal oxidation. Experiments were conducted in alumina crucibles inserted in the graphite outer crucible in order to facilitate the experimental setup and avoid the reaction between the graphite and the input material.
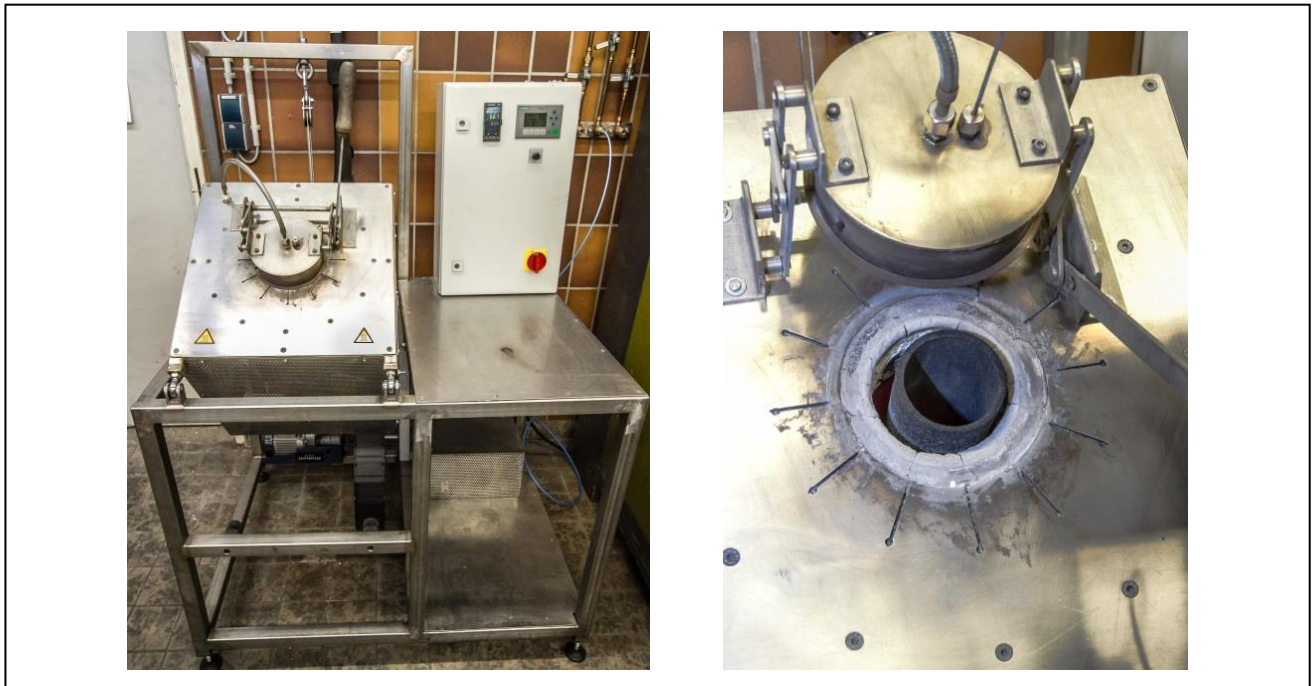
Figure 1: Mini TRF (left: overview, right: rotating graphite crucible)

Input material & experimental setup

Aluminium chips from a 3104 alloy were used for the coalescence trials. The chips were preoxidized in a resistance furnace in order to have a thicker oxide layer on the metal. This pretreatment highlights the effect of fluoride addition concerning the removal of the oxide layer. Chips before and after pretreatment are presented on Figure 2.

Figure 2: Aluminium chips (left: before pretreatment; right: after pretreatment)

The salt slag was synthetized from equimolar NaCl-KCl salt and non-metallic particles (NMP), both coming from the recycling process of salt slag which is described on the diagram on Figure 3. Cryolite is mixed to the NMP and the salt based on the needs.
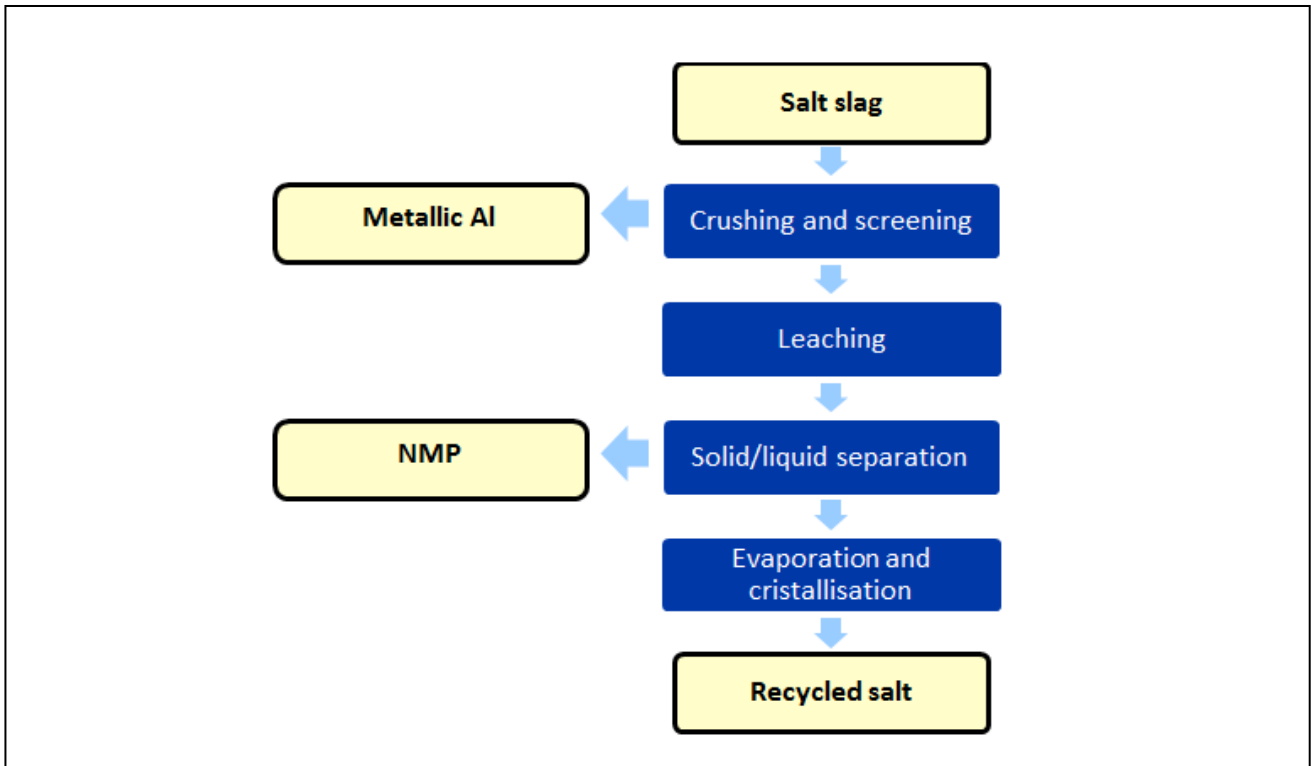

Figure 3:   Recycling process of salt slag [13]

The experiments took place at 750°C in an alumina crucible in Mini TRF with a rotation speed about 20 RPM and an inclination angle of 40° (from the vertical position). The salt slag components were mixed to the chips in the furnace and after a defined time, the inner crucible was taken out of the furnace and quickly cooled down in a water cooling system. The crucible content was in a second time lixiviated with water in order to separate the metal droplets from the synthetized slag. Finally, the droplets were classified by size and the coalescence efficiency was calculated with the following formula:

$$Coalescence\ Efficiency = \frac{Weight\ of\ droplets\ with\ a\ \emptyset > 3,15\ mm}{Total\ weight\ of\ recovered\ droplets}$$

4 Results

Determination of an adapted experimental duration

The first trials campaign consisted in testing different experimental times in order to determine which duration was the most adapted to see the coalescence evolution with the oxide content in the salt slag. The cryolite addition was fixed to 2 wt% from the salt content; time and oxide content were used as variable.

The results are shown on Figure 4. Whatever the oxide concentration in the salt slag, an increase of the duration of the experiment leads to a better coalescence. Indeed, a longer trial gives more time to the aluminium chips to melt and coalesce together, i.e. the molten aluminium droplets can settle on a longer distance and have more chance to coagulate together. The settling and the meeting of molten aluminium droplets progress with the time.

Besides, an enhancement of the oxide concentration in the slag leads to a sharp decrease of the coalescence efficiency. The salt slag properties strongly depend on the oxide concentration in the slag. As the oxide particles are solid in the salt slag, the viscosity of the flux is heightened and the movement of the metallic droplets in the slag is slowed. Moreover, the density of the oxides is higher than the one of the salt, so the oxides tend to settle also in the salt, and the metal/slag separation is tougher.

Seven minutes is the best experimental duration in order to distinguish an evolution of the coalescence depending on the oxide content of the salt slag. A longer time leads to an advanced coalescence, no difference is observed for oxides concentrations between 0 and 30 wt%. A shorter duration causes a limited coagulation for oxides concentration above 20 wt%.
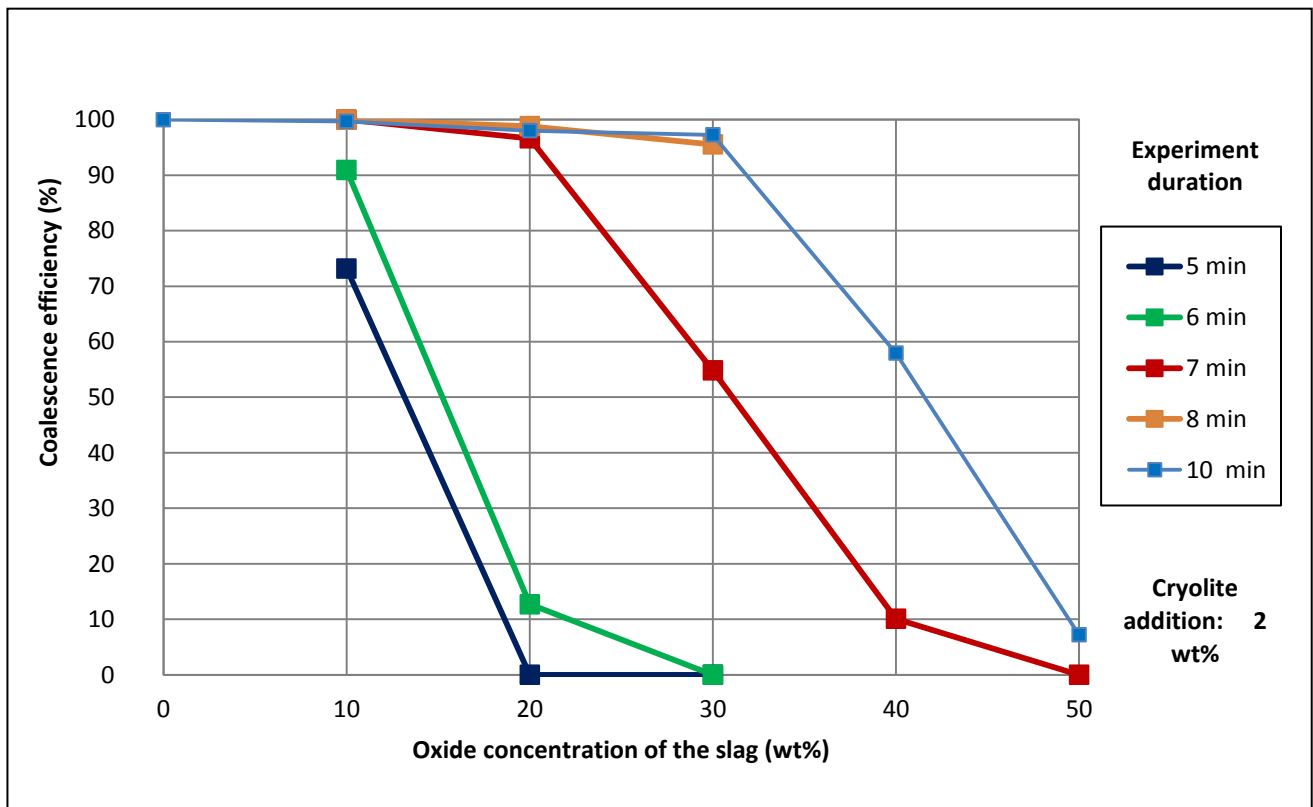
Figure 4:   Influence of the experiment duration on the coalescence

The obtained metal droplets for a duration of experiment about 7 minutes are presented Figure 5. The evolution of the final droplets is obvious. A raise of the oxide content in the salt slag leads to an increase of the number of droplets and a reduction of their diameter. In the case of 50 wt% oxide, the aluminium chips have partially started to melt and reduce their surface tension by transforming into spheres. This can be explained by the high viscosity of the slag and a lower heat transfer through the highly contaminated salt slag as this is a discontinuous system.
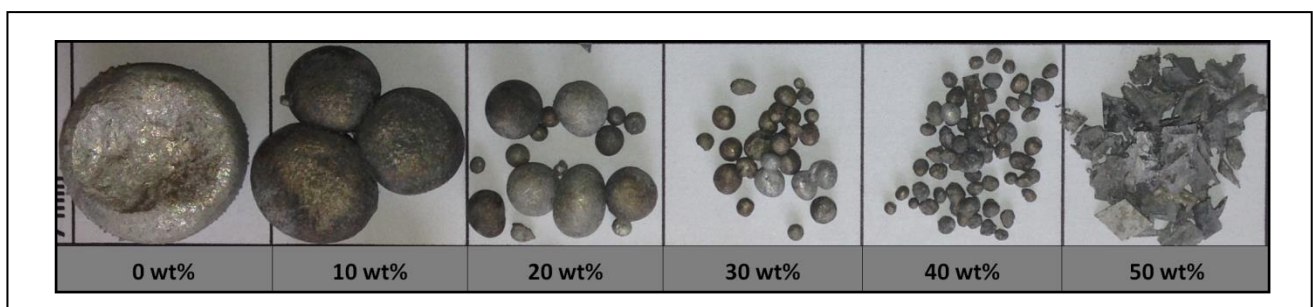

Figure 5:   Obtained droplets for an experiment duration of 7 minutes depending on the oxide content in slag (cryolite addition = 2 wt%)

Slag composition effect on coalescence

In a second time, the coalescence efficiency was rated by using the optimized experiment duration (7 minutes) and varying the oxide and cryolite contents of the salt slag. The obtained results can be found on Figure 6.

As it has been seen in the previous part, the oxide concentration of the slag has a major influence on the coalescence. Whatever the cryolite percentage added to the salt, an increase of the oxide content in the salt slag causes nearly always a reduction of the coalescence efficiency. Indeed, the decrease of the viscosity and density thanks to a cryolite addition is minimal compared to the increase due to the oxide content in the salt flux.

From 0 to 30 wt% in the slag, a coalescence maximum is observed for 2 wt% of cryolite. This peak matches to the tension-active element formation in a 3104 alloy in contact with an equimolar NaCl-KCl salt depending on the cryolite concentration [6]; the coalescence is therefore enhanced by thermochemical reactions between the salt flux and the metal chips. The coalescence efficiency stays optimal until 4 wt% of cryolite for an oxide content under 10 wt%. The rotation and the tilting position of the crucible indeed help the coalescence by breaking the oxide film on the droplets surfaces and easing their meeting, and the oxide content is low enough so that the viscosity and the density of the slag are not too high.

The results for 40 and 50 wt% oxide in the slag are very similar. The coalescence efficiency shows a maximum with no addition of fluoride and the coalescence is very poor for any cryolite addition. The low coalescence efficiency values are due to the viscosity and density of the salt slags. Unlike the slags containing less than 30 wt% oxides, these slags show a coalescence minimum for 2 wt% of cryolite. This phenomenon still has not been explained. As a conclusion, the salt slag density and viscosity are predominant over the tension-active elements role for slags above 40 wt% oxide.
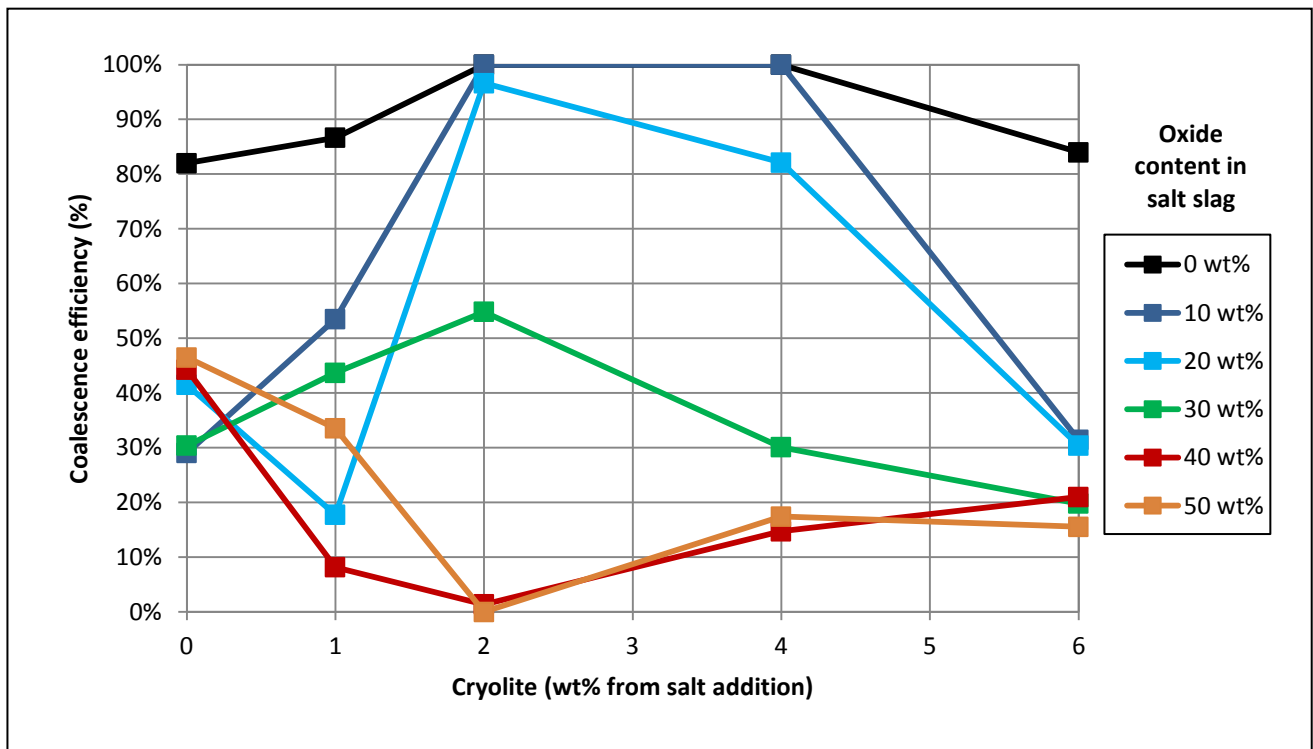
Figure 6:   Influence of the salt slag composition on coalescence (experiment duration = 7 min)

5   Conclusion

The coalescence strongly depends on the salt slag composition. Cryolite and oxide have conflicting effects on the coalescence. When the cryolite enables the formation of tension-active elements at the metal surface so that the oxide layer is removed, the oxides worsen the salt slag properties by increasing its density and viscosity and making the settling of the metal droplets and the separation of the metal from the slag difficult.

Acknowledgements

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