Improving coalescence in Al-Recycling by salt optimization

M. Sc. Sandra Besson[a, b], Dr. Anne Pichat[b], Dr. Elodie Xolin[b], Prof. Dr. Patrice Chartrand[c], Prof. Dr. Bernd Friedrich[a]

[a] RWTH Aachen University

IME Process Metallurgy and Metals Recycling,

Intzestrasse 3

52056 Aachen, Germany

[b] Alcan CRV, Voreppe Research Center

Parc Economique Centr'Alp

725 rue Aristide Bergès - BP 27

38341 Voreppe Cedex, France

[c] Centre for Research in Computational Thermochemistry (CRTC)

Dpt. Of Chemical Engineering

Ecole Polytechnique

C.P. 6079, Succursale "Downtown"

Montreal (Quebec), Canada H3C 3A7

Keywords: aluminium recycling, tilting rotary furnace, salt, slag, coalescence

Abstract

During melting of aluminium scraps under a salt flux cover, a stable suspension, mainly salt and oxides, is formed. This slag entraps metal droplets and thus prevents their recovery. For this reason, industrial aluminium recovery processes often involve the addition of fluorides, e.g. cryolite (Na_3AlF_6), to the chloride salt flux. This addition helps stripping the oxide layer that imprisons metal droplets and thus improves coalescence. It ultimately leads to increased recovery rates. In this study, the coalescence of aluminium droplets was investigated in presence of an equimolar NaCl-KCl salt mixture under different temperatures: 800ºC, 875ºC and for two common alloys: AA3104 (body of beverage cans) and AA8979 (foils). SEM and XRD analyses were carried out on the resulting beads and on the leaching residues in order to better understand the mechanism of coalescence. Factsage, a thermochemical calculation software, was also used to further understand the involved phenomena.

The experiments carried out at the IME instate in Aachen have shown the impact of cryolite additions in the coalescence process. The alloying element Mg was also found to play a major role in the coalescence behaviour. Finally, modifications in the composition of the oxide layer of aluminium droplets were exhibited as well as variations in the concentration of surface active elements.

1 Motivation

In this work, the process involved in the recycling of Used Beverage Cans (UBC) and aluminium foils was investigated. This process consists in melting aluminium scraps in a tilting rotary furnace. This melting takes place under a salt flux cover, most often a NaCl-KCl mixture, which prevents further oxidation of molten metal and thereby reduces the metal loss. This salt cover also helps collecting oxides and contaminants contained in the scraps, therefore enhancing the metal recovery. However, as a side effect, the collection of these oxides in the salt leads to a slag whose density and viscosity increases as more oxides are entrapped. This phenomenon impedes the salt/metal separation and as a result a non-negligible portion of metal stays entrapped in the salt in the form of a suspension [1].

Recovering the metal droplets requires them to settle down back to the metal bath. The settling velocity of a small sphere falling in a viscous fluid is given by Stoke's law [2]. It increases with the droplets radius as follows:

$$V = \frac{2}{9} \frac{r^2 (r_d - r_s) g}{h} \qquad (1)$$

Where V = settling velocity (m.s^{-1}), r = droplet radius (m), ρ_d = density of the metal (kg/m^3), ρ_s = density of the slag (kg/m^3), g = gravitational acceleration (m/s^2), η = slag viscosity (kg.m^{-1}.s^{-1})

Coagulation of metal droplets allows for a faster settling and therefore a better metal yield. Lower slag density/viscosity also fastens settling, but this study mainly focuses on the salt ability to enhance coagulation.

2 Background

Droplets coalescence is hindered by thin oxide layers that surround the droplets and composition should thereby be optimized in order to strip those oxides. Existing studies have shown that the fluorides are good agents to free the metal droplets from the oxides, but this mechanism is not well understood [3]. The authors generally agree to say that the mechanism of coalescence occurs in three steps [4]:

1. Cracks develop in the oxide
2. Salt penetrates through the oxide.
3. The oxide layer is stripped away and suspended.

Two types of coalescence experiments were carried out to evaluate a salt's ability to enhance coalescence, but no "standard" method has been developed until now and the results varied a lot depending on the studies:

1. The first method consists in observing the time needed for aluminium droplets to coagulate. Peterson [5] observed the coagulation of aluminium pellets through a transparent quartz crucible. Ye & Sahai [6] focused on the time needed for two metal droplets initially separated

by a rod to coagulate. Friesen & Utigard [7] observed the coalescence by the mean of a hot-stage microscope.

2. The second method focuses on the coalescence rate at a given time. Roy & Sahai [4], Sydykov [8] and Xiao & Reuter [9] loaded small aluminium pieces in the shape of pellets/chips/turnings in molten salt. After a given time they cooled down the crucible, leached the salt and counted/sieved and weighed the coagulated drops to evaluate the coalescence efficiency of the tested salts.

Most of those studies focus on the comparison of different fluorides for a given content of fluoride. The results diverge from one author to another and the results cannot be transposed to the industrial process because of too high salt/metal contents and low oxide content in the melt. Still, those results give information to better understand the coalescence mechanisms.

Sydykov [8] studied the impact of fluoride concentration in the salt for low fluoride contents. He suggested that the coalescence rate depends on the "active" fluoride ion concentration and not on the type of cation associated in the fluoride.

Different authors also studied some of the salt properties that could have a major impact on the coalescence:

- Density [10] [12]: a lower density of the salt allows for a better metal/salt settling.
- Viscosity [10] [11]: a decrease in the salt viscosity allows for a better mobility of the metal droplets in the flux and induces better conditions for the coalescence.
- Interfacial tensions [12] [13] [14] [15]: minimizing the interfacial tension between salt and metal $\gamma_{salt/metal}$ increases the affinity between metal and salt and eases striping the oxide layer. Similarly, increasing the interfacial tension between oxide and metal in salt $\gamma_{oxide/metal}$ allows for a better coalescence.
- Dissolution of the oxides [11] [16]: fluorides are known to dissolve oxides in large quantities, but the addition of chlorides in the salt has a deleterious effect on this property.

Until now, none of these properties was found to have a major impact on coalescence: it is believed that the coagulation of metal droplets results from a combination of those properties.

A better understanding of the reactions and mechanisms of coalescence is necessary to allow for the optimization of the salt and to improve the metal recovery in the industrial recycling processes. Therefore, some further coalescence tests were performed in laboratory scale with the objective to study the impact of cryolite content in an equimolar NaCl-KCl salt on coalescence for two different alloys.

3 Experimental procedure for the evaluation of the coalescence efficiency

The experiments were carried out in an electric resistance heated furnace (Figure 1). The salt was an industrial mixture of equimolar NaCl-KCl, with various amounts of reagent-grade cryolite (from 0

to 15 wt%). The scraps were produced from AA3104 (0.80 - 1.30 % Mg, 0.80 - 1.40 % Mn, 0.050 - 0.25 % Cu) and AA8979 (low-alloyed) foils. The foils were cut in small rectangular chips (volume 0.45 mm³) and oxidized for 4 hours at 550 °C. This step of oxidation re-enacts the oxidation occurring in the process during the thermolysis of organic compounds covering the scraps (paints, varnish).
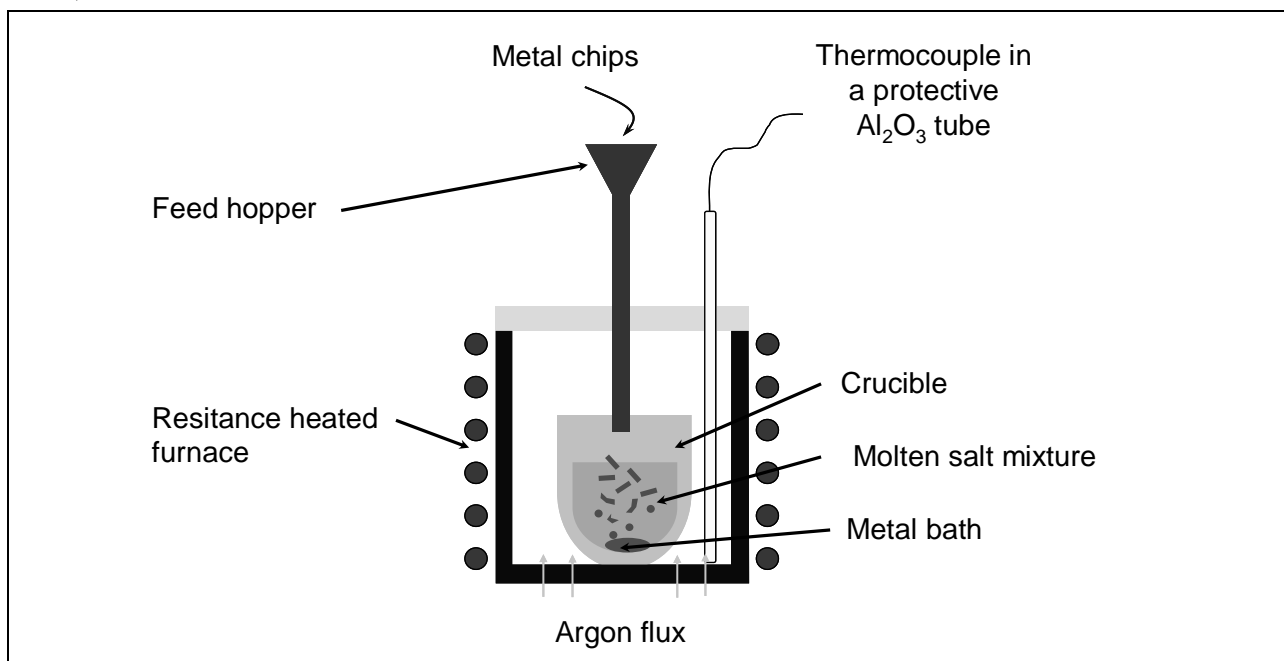

Figure 1:   Experimental set-up for the coalescence tests

The procedure consists in melting 37.5 g of dried and pre-mixed salt into a porous ceramic crucible with a ZrO_2 inner cover, under argon atmosphere. Once the required salt temperature is reached (800 or 875°C), 12.5 g of aluminium chips (approximately 700 pieces) are introduced in the crucible within 15 sec by means of a stainless steel funnel. After a given time, the crucible is carefully taken out of the furnace and quickly cooled down in a bucket of copper chippings. The crucible content is then leached by water and the solidified droplets are dried and sieved. The length of stay in the furnace has been adjusted for each alloy. This allowed us to observe a non complete coalescence for every setup and made the comparison of the coalescence efficiency for each cryolite content possible. The AA3104 alloy was tested at 800°C (1min50sec) and 875°C (50sec), and the AA8979 alloy only at 800°C (40 and 50sec). The evolution of the temperature in the molten salt after the introduction of the metal pieces is given in Figure 2.

A single molten aluminium chip that solidifies under a spherical form has a diameter inferior to 2.5 mm. Therefore the coalescence efficiency CE was calculated based on the weight percentage of particles whose diameter is bigger than 2.5 mm, i.e. the weight percentage of the particles which coalesced at least one time (Eq. 1).

$$CE = \frac{weight > 2.5\,mm}{total\,weight\,of\,recovered\,balls} * 100 \qquad (1)$$
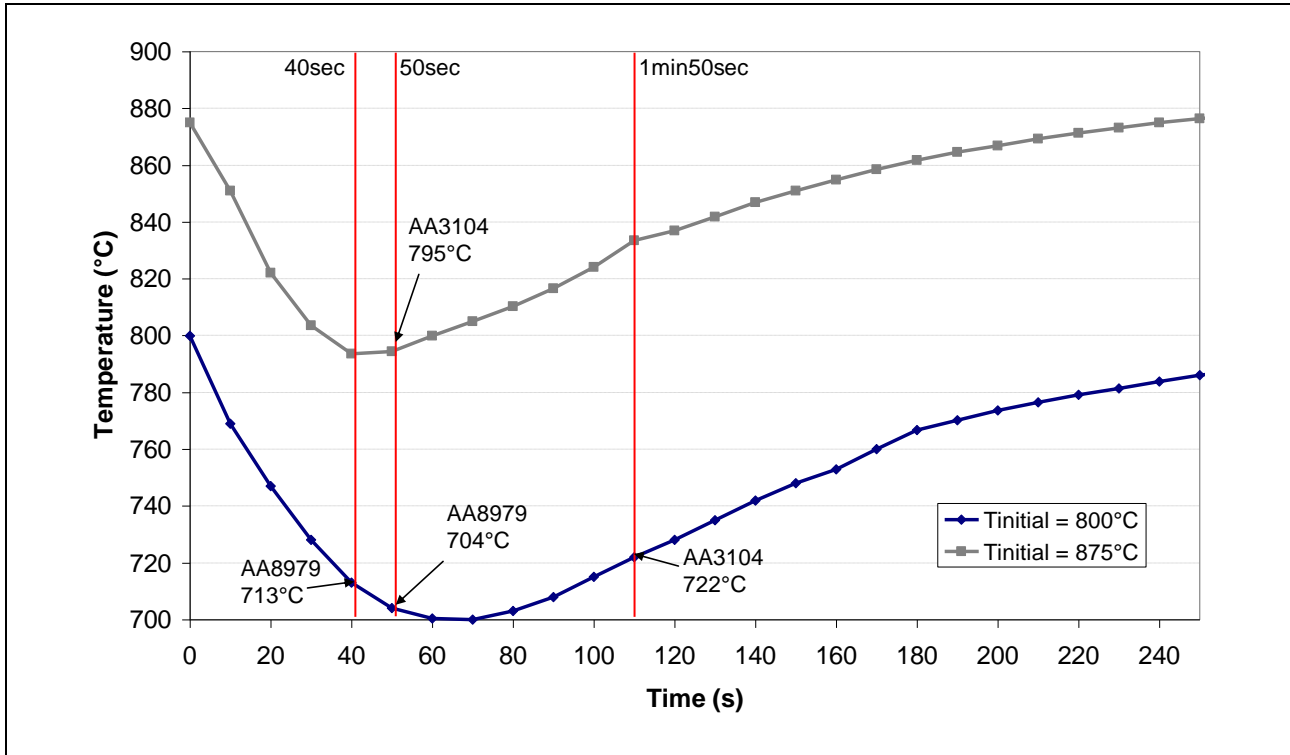
Figure 2:   Evolution of the temperature in the molten salt after the introduction of the chips and final temperature for the different series

4   Results and discussion

4.1   Formation of the oxide layer

The SEM observation of the oxide layer developed on the surface of Mg-containing chips (AA3104) during the oxidation step shows a discontinuous layer (Figure 3, left).
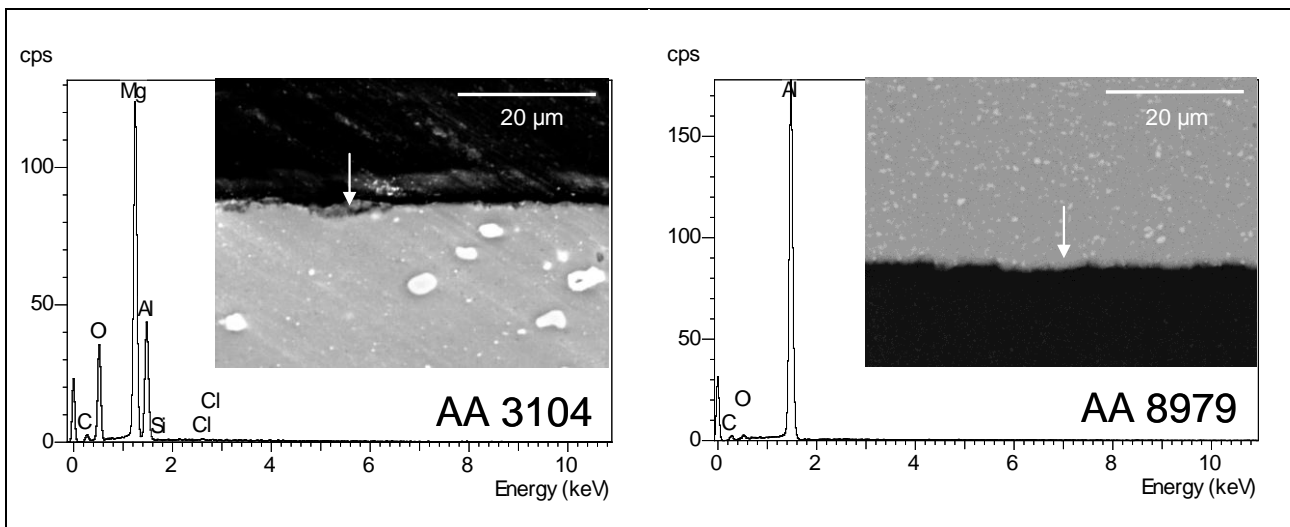

Figure 3:   SEM picture and EDX pattern of the sections of the chips after artificial oxidation

The EDX pattern shows that the developed oxide is a spinel. The weight gain of the chips due to oxidation was approximately 0.17 %. The oxide developed on the AA8979 chips was too thin to be observed with SEM for the same magnification.

4.2 Effect of the cryolite content in the salt on the coalescence efficiency for the alloys AA 3104 (800°C and 875°C) and AA8979 (800°C)

The influence of the cryolite concentration in the salt on coalescence efficiency CE for the alloy AA3104 is shown in Figure 4 for two different initial salt temperatures. Some representative samples are shown in Figure 5.
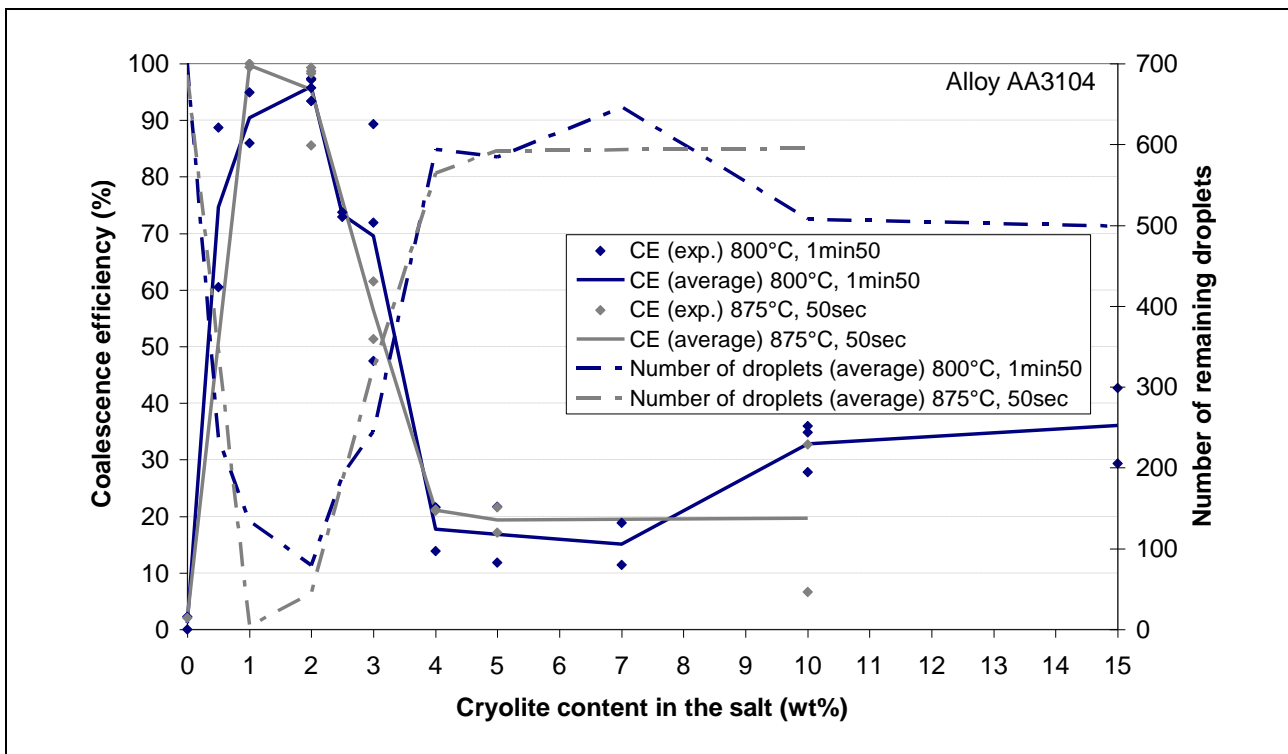

Figure 4: Coalescence efficiency of AA3104 chips as a function of cryolite content in the salt (initial salt temperature = 800°C or 875°C)

For an initial salt temperature of 800 °C (dark line), it is explicitly shown that without cryolite addition only few particles were able to coalesce: the resulting solidified droplets have a complex non-spherical form, which implies that the oxide was not weakened enough to allow the molten metal to turn into spheres (Figure 5, b).

The addition of only 0.5 wt% of cryolite in the salt induces a CE increase from near 0 to about 70 %. Furthermore, the chips were all able to turn into regular spheres (Figure 5, c). A maximum coalescence was observed with 2 wt% cryolite, where about 95 wt% of the chips coagulated at least once. The coalescence efficiency decreases then sharply and sinks to 15–20 % at 4 wt% cryolite. However, all solidified droplets remain spherical, which implies a better oxide removal than with-

out cryolite. A slight increase can be observed after 7 wt% cryolite, with a nearly constant coalescence efficiency of 30–40 % for 10–15 wt% cryolite.

Similar coalescence behaviour can be observed for an initial salt temperature of 875 °C, with an optimum cryolite addition for 1–2 wt% cryolite.

The relevance of the criterion CE was judged to be good since a similar tendency can be observed for a criterion implying the total number of resulting beads.

A similar behaviour was found by Sydykov [8] for Al chips immerged in a salt containing CaF_2: the coalescence rate increased with CaF_2-concentration and reached the highest values at 2 wt % before decreasing for higher CaF_2-concentrations.
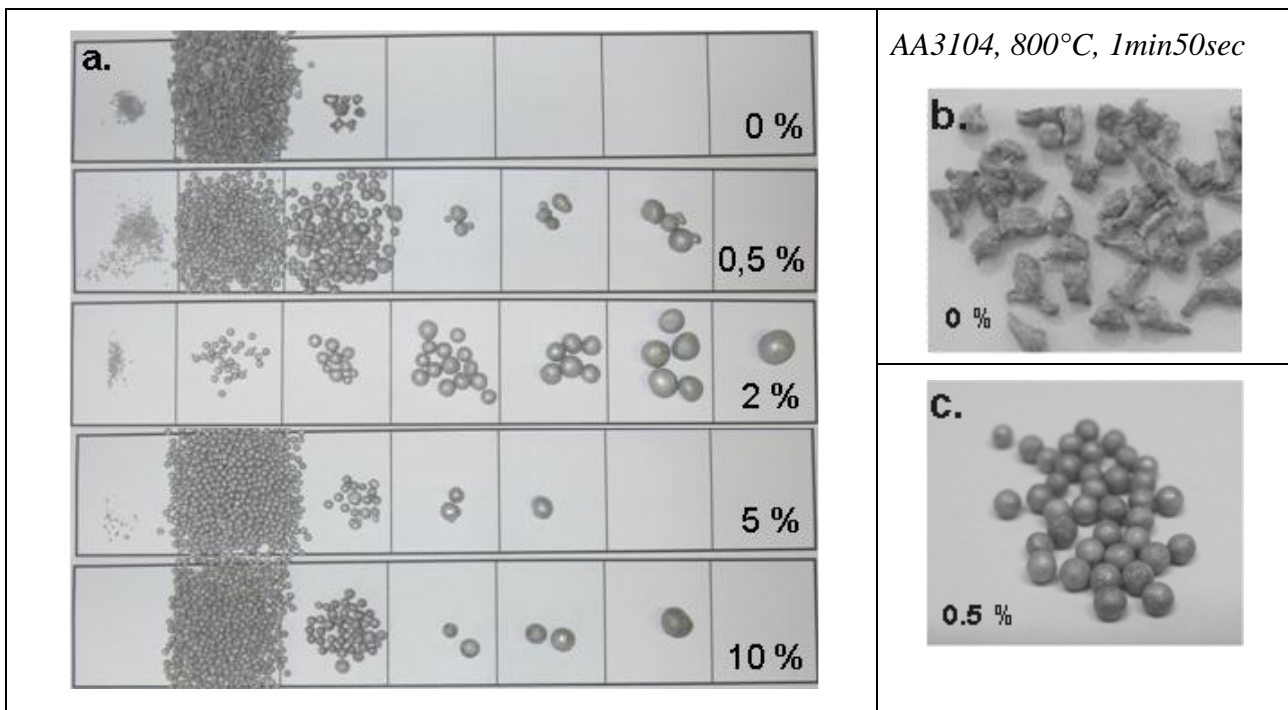

Figure 5:   Classified solidified droplets for alloy AA3104 at 800°C (a), non-coagulated particles for 0 wt% cryolite (b), non-coagulated particles for 0,5 wt% cryolite(c)

The CE for the alloy AA8979 was similarly evaluated. The CE for this alloy was generally higher than for AA3104 and the time in the furnace was adjusted accordingly (40 and 50sec) (Figure 6). Some of the particles were not able to take a spherical form because of the short time in the furnace (Figure 7); the repeatability of the experiments was also lower for the same reason.

Similarly to the experiments on AA3104, the positive effect of the addition of small quantities of cryolite in the molten salt is clear: the CE increases from 15 to 60 % for the addition of only 1 wt% cryolite. Contrary to the experiments on the Mg-containing alloy, the CE keeps on increasing until 15 wt% cryolite.

Further analyses and calculations were carried out to explain those two different behaviours for the two alloys.
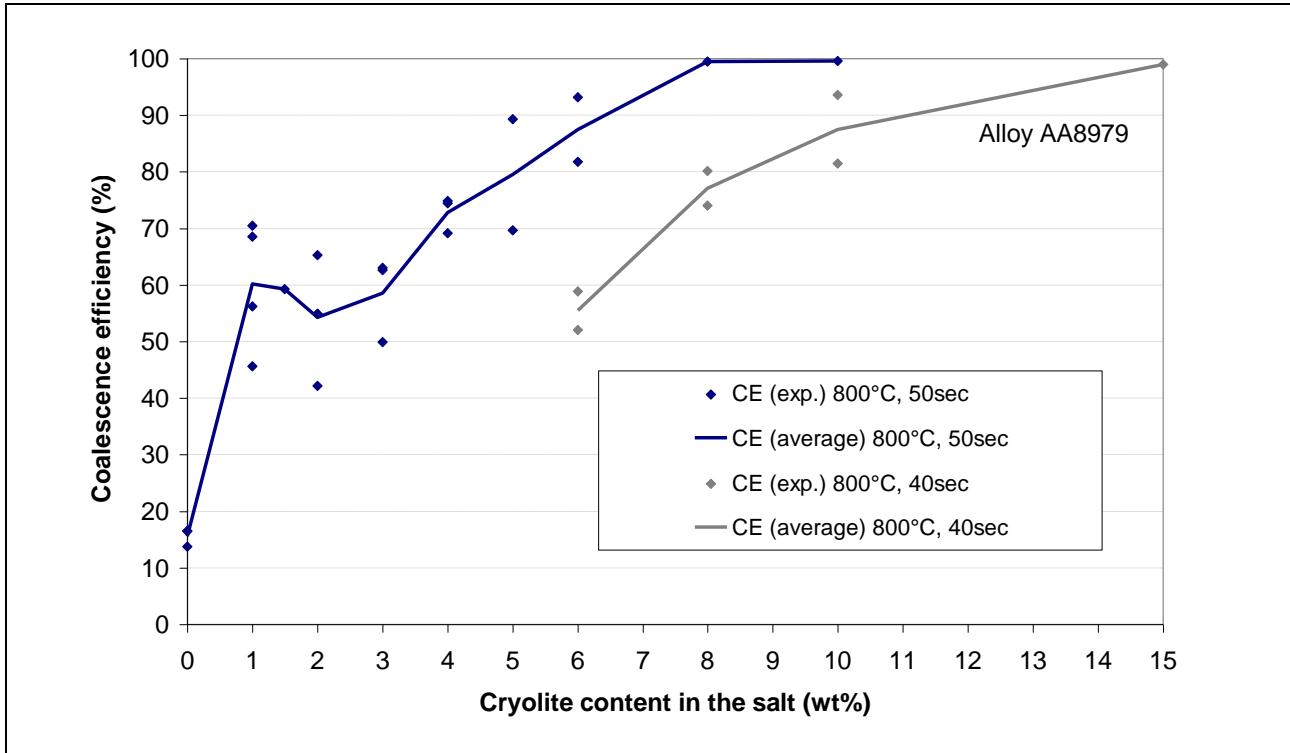
Figure 6:   Coalescence efficiency of AA 8979 chips as a function of cryolite content in the salt (initial salt temperature = 800 °C)
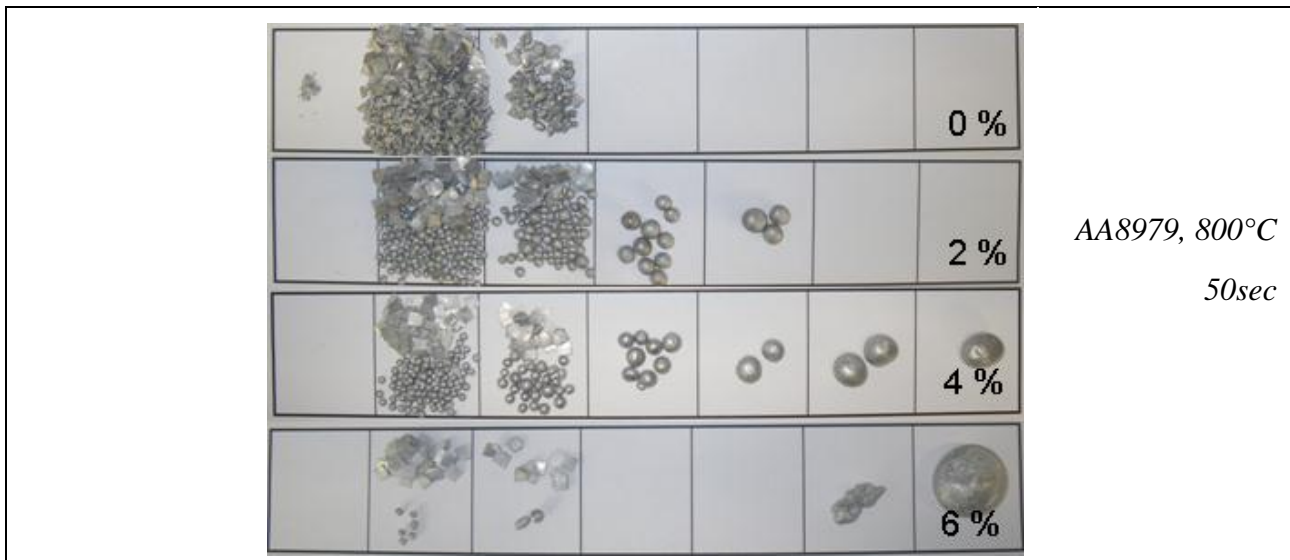

Figure 7:   Solidified droplets after leaching and sieving for alloy AA8979, Tinitial=800 °C

4.3   SEM observations of the solidified droplets

SEM and EDX analyses were carried out on the sections of the solidified droplets to observe the morphology and the chemical composition of the oxide layer (Figure 8, Figure 9). The oxide layer only partially covered the droplets, even without the addition of cryolite to the salt. This may be due

to the post-treatment of the mixture salt/metal (cooling/leaching), as droplets are expected to coalesce when this oxide is stripped.
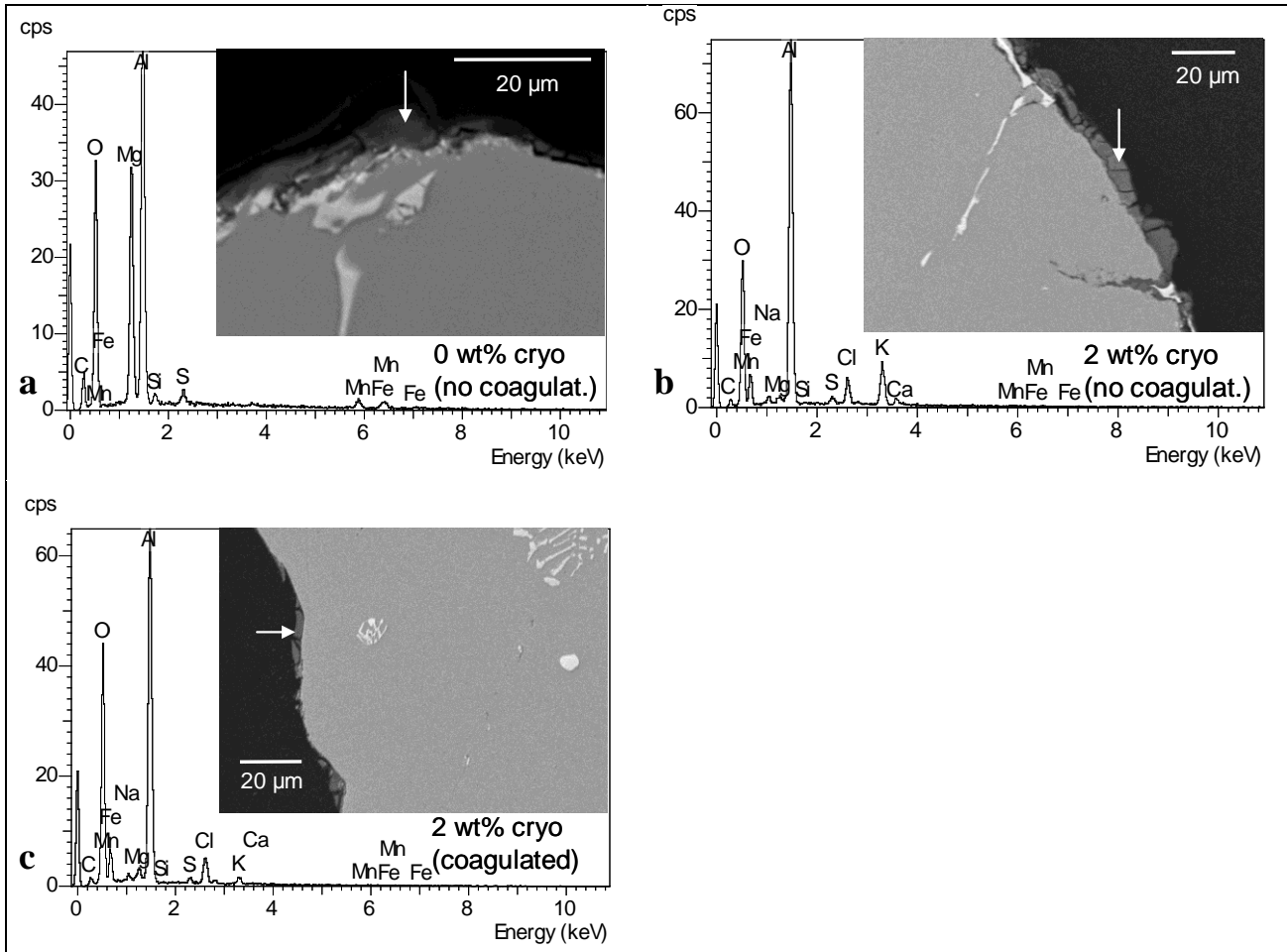

Figure 8:   SEM (BSE) observation of the section of the solidified droplets for AA3104, $T_{initial}$=800°C (a- bead <2.5 mm 0 wt% cryolite; b- bead < 2.5 mm 2 wt% cryolite, c- bead >2.5 mm 2 wt% cryolite)

As previously seen (Figure 3), the EDX pattern of the spinel developed on the AA3104 chips during the oxidation step presents a Mg-peak approximately 3 times higher than the Al-peak. After its immersion in a salt without cryolite, the oxide is still composed of a spinel, but the relative proportion of Al is higher than for the initial oxide (Figure 8, a). Furthermore, immersing the droplets in salt with cryolite leads to a Mg-free oxide (Figure 8, b, c). Those observations show that the spinel obtained during oxidation of the AA3104 chips tends to lose Mg and to turn into an aluminium oxide.

Experiments on AA8979 alloy exhibited other oxide transformations. Setups involving cryolite in the salt composition produced oxides containing alkali elements such as Na and K, whereas the setups without cryolite produced oxides exclusively composed of Al and O (Figure 9).
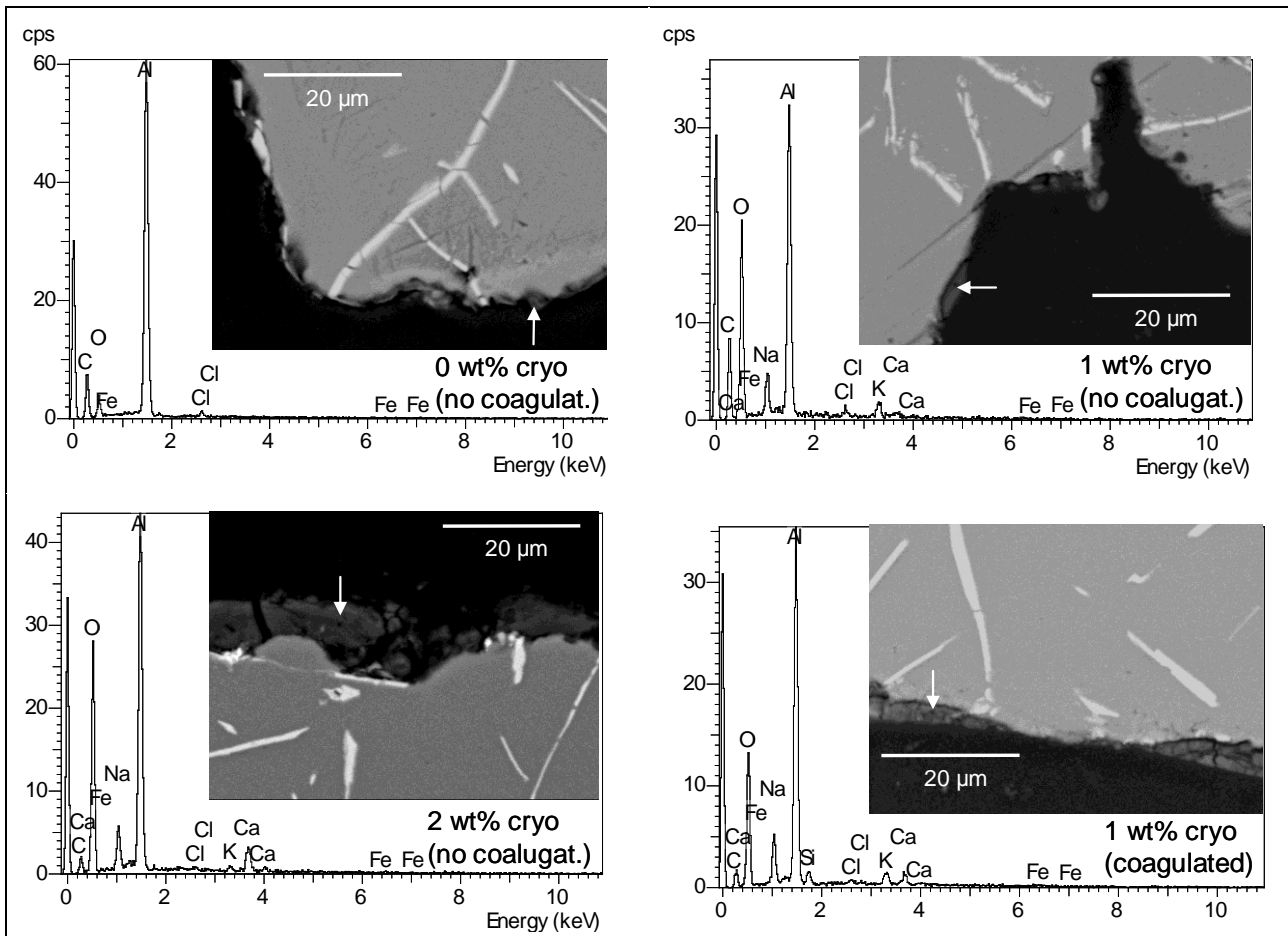
Figure 9:   SEM observation of the section of the solidified droplets for AA8979, Tinitial=800°C

Those phase transformations in the oxide lead to volume and crystallographic changes, and potentially to development of cracks in the oxide [17].

4.4   XRD analysis on the leaching residues

Small grey particles have been collected after filtering and drying the leaching effluents. The mass of those particles increases linearly with the cryolite content of the salt (Figure 10). Those so-called "leaching residues" were analysed by XRD to identify the species (Table 1).

The leaching residues at 0 wt% cryolite were mostly composed of oxides and hydroxides from Al/Mg for both alloys. This confirms the presence of spinels and Al_2O_3 in the melt, as seen by the SEM observations. For the experiments with AA3104 in presence of cryolite, a (K, Na)-Mg-F product could be observed for both temperatures 800°C and 875°C. Maason&Tagihei [1] also observed similar products while melting Mg-containing alloy in a salt with 10 wt% KF. Other fluorides (AlF_3 and MgF_2) were also detected.

The leaching residues resulting from the experiments with AA8979 were mostly composed of a sodium/potassium cryolite K_2NaAlF_6.
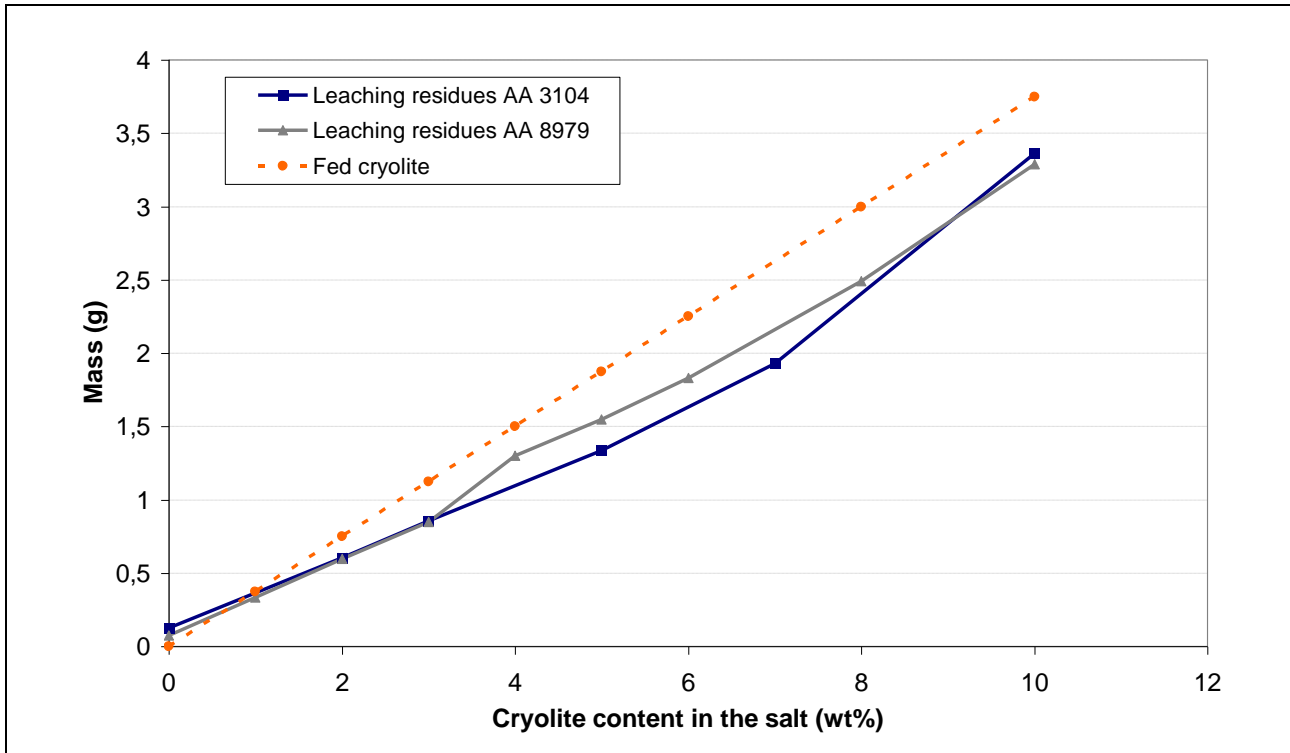
Figure 10:   Mass of collected leaching residues for both alloys at 800°C and mass of fed cryolite

Table 1:   Identified phases in the leaching residues
(✔ = phase present in the residues, ✘ = phase absent in the residues)

Alloy/Temperature	AA3104, 800°C				AA3104, 875°C	AA8979, 800°C	
Cryolite content / Species	0	2	5 and 10		5	0	2, 5, 10
			all residues	>0.42 mm			
Oxides (Mg, Al), hydroxides	✔	✘	✘	✘	✔	✔	✔
$KMgF_3$, $K_{0,15}Na_{0,85}MgF$	✘	✔	✔	✔	✔	✘	✘
$AlF_3.3H_2O$	✘	✔	✔	✔	✘	✘	✘
MgF_2	✘	✔	✘	✘	✘	✘	✘
K_2NaAlF_6	✘	✘	✘	✘	✘	✘	✔

Furthermore, a thin gray layer is visible to the naked eye around the solidified droplets at 10 wt% cryolite for AA3104, but not at 2 wt% cryolite (Figure 11). The XRD analyses on those layers (col-

lected in a sieve >0.42 mm) showed that they are mostly composed of (K, Na)-Mg-F, suggesting that cryolite has a tendency to form a new layer around the droplets.
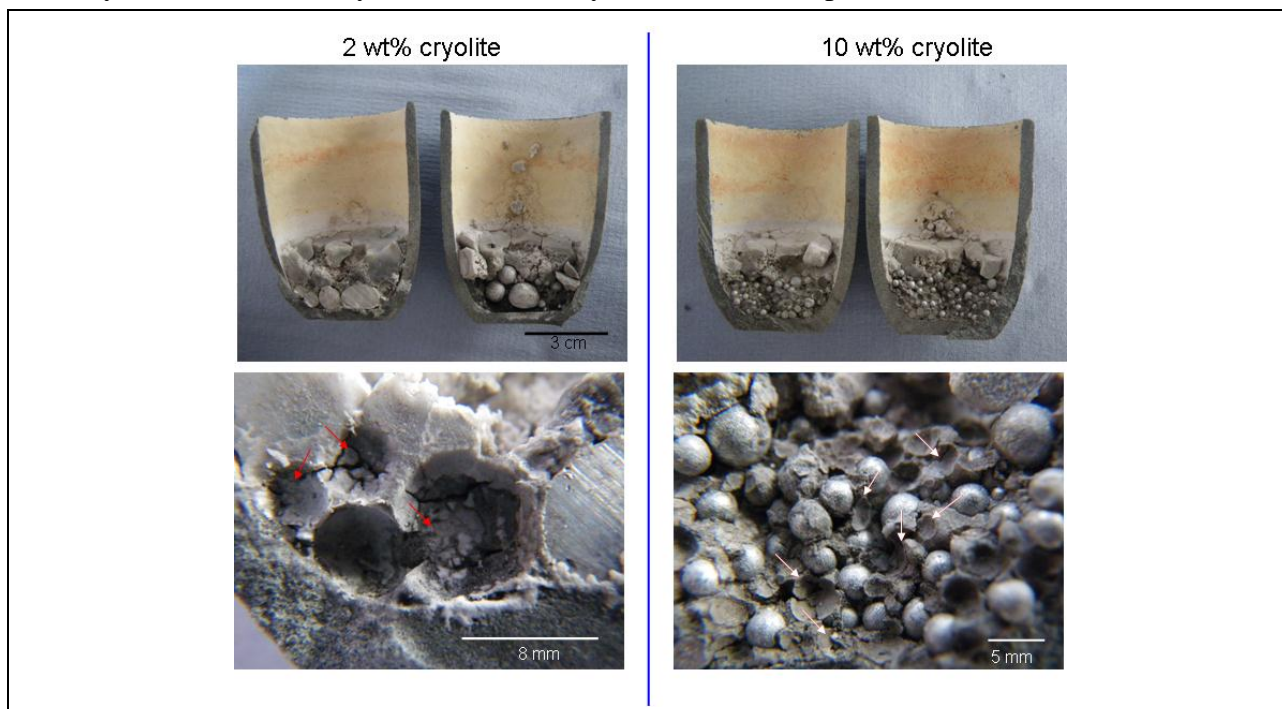

Figure 11:   Section of the crucibles for 2 and 10wt% after cooling

Since those observations have been done on cooled samples, it could not be asserted that this layer is also present at higher temperatures. Thermochemical calculations were carried in order to verify this hypothesis.

4.5   Factsage™ thermochemical calculations

Factsage™ is a thermochemical software and database package. Calculations were carried out with the combination of the Fact53 and VLAB databases (developed for aluminium industry) and with the "Equilib" Gibbs energy minimisation module. The input amounts of salt and metal from the experiments were respected, and the temperatures were chosen accordingly to Figure 2 (700°C for an initial temperature of 800°C and 800°C for an initial temperature of 875°C).

Those calculations show that the reaction between salt and Mg-containing metal leads to the precipitation of "perovskite" (Na, K)MgF$_3$ (Figure 12), which corresponds to the (K, Na)-Mg-F products which were previously seen in the leaching residues. The precipitation of perovskite could explain the decrease of the CE for salts including more than 2-3 wt% of cryolite at 800°C (i.e. 700°c when the crucible is taken out). This phase tends indeed to form a second layer around the droplet (see Figure 11). However, this precipitation probably cannot explain the CE decrease after 2 wt% for the experiment carried at 875°C (i.e. 800°C), since the calculations do not predict the precipitation of this phase at this temperature. Perovskite species were nevertheless also detected for those experi-

ments in the leaching residues, but they may have appeared during the cooling of the sample (as well as MgF_2, AlF_3).
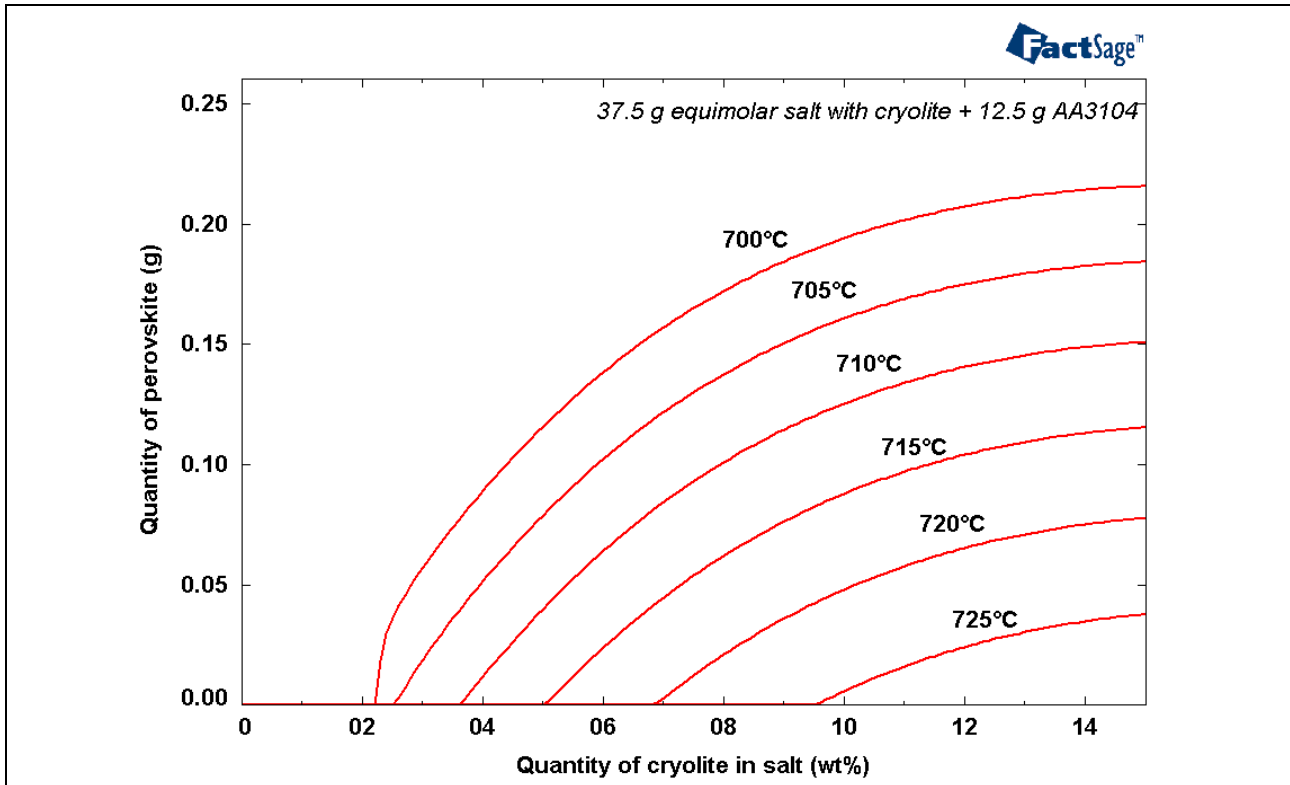

Figure 12: Factsage calculation, precipitation of perovskite for the reaction between AA3104 and salt at different temperatures

The Factsage calculations also show huge variations in the quantity of tension-active elements such as Na and K in the metal (Figure 13). Sahai [12] showed that the adsorption of these elements in the metal results in the decrease of interfacial tension between salt and metal, and thus enhances the coalescence of the droplets. The profile of the curve is the same at 700 and 800 °C: the quantity of Na and K increases with the cryolite content in the salt until 2 wt% cryolite then decreases dramatically thereafter. This behaviour fits well to the curves of CE obtained for AA3104 at 800 and 875°C.

For the alloy AA8979, no precipitation of species such as perovskite occurs at high temperature. The quantity of surface active elements increases continuously for this alloy (Figure 14). This also fits to the results of coalescence tests were the CE increases with the cryolite content in the salt.
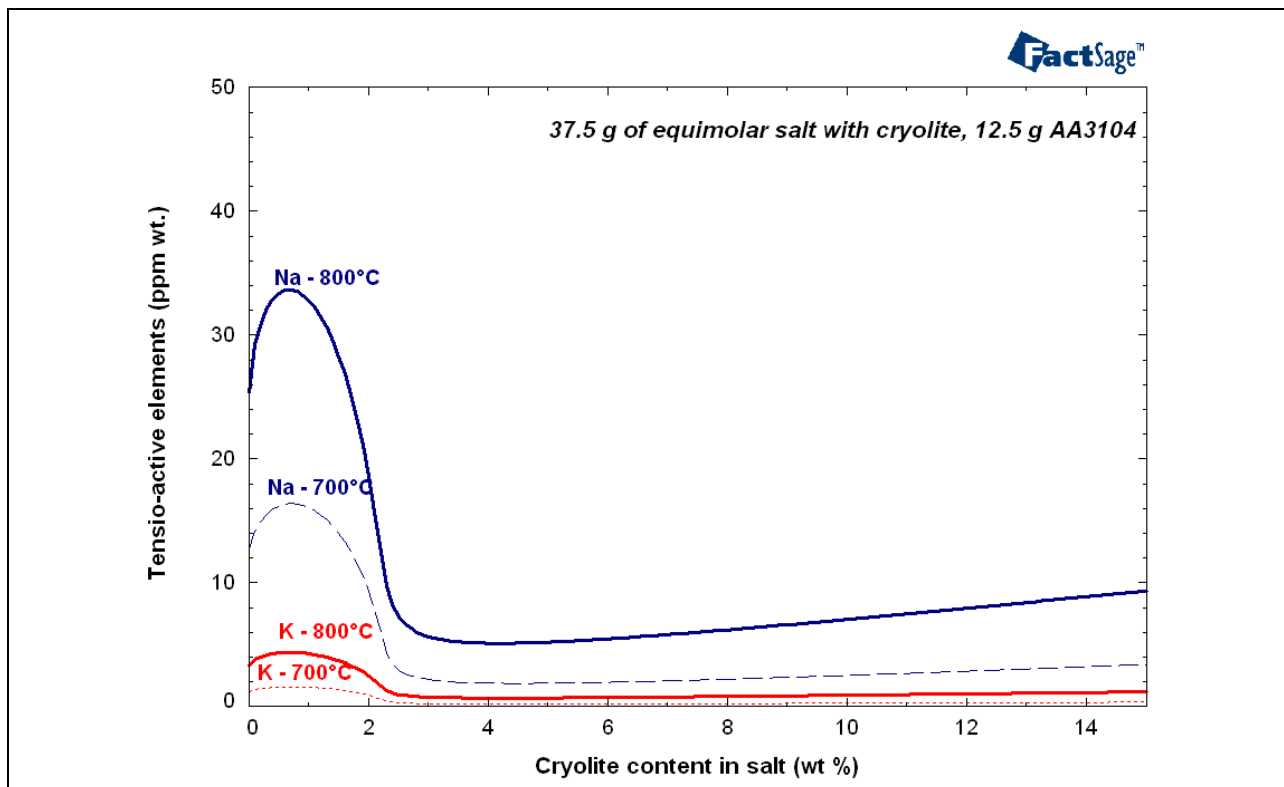
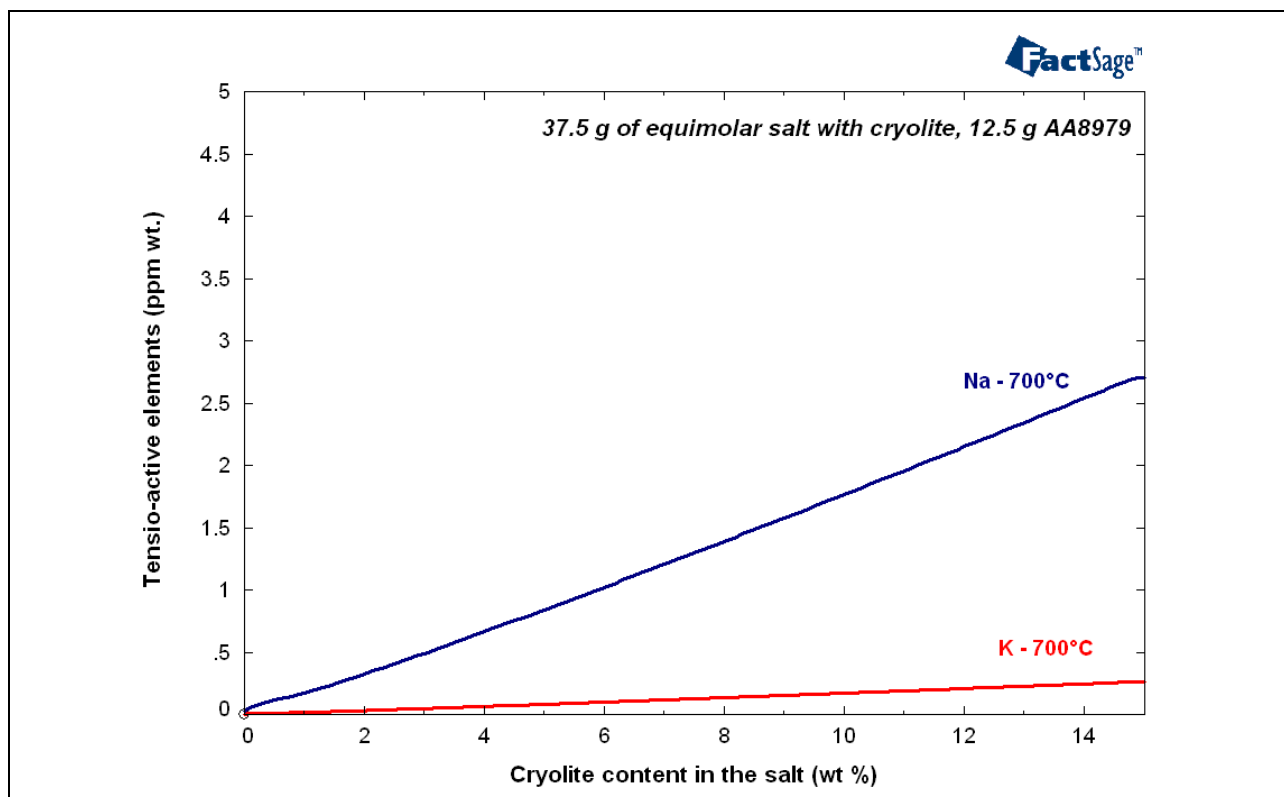Figure 13: Factsage calculation, quantity of tension-active elements in the metal for the alloy AA3104

Figure 14: Factsage calculation, quantity of tension-active elements in the metal for the alloy AA8979

5   Conclusions

The influence of cryolite on the coalescence of metal droplets for two different aluminium alloys has been investigated in a very small scale (50 g of material). The experiments showed that the adjunction of cryolite in the chloride salt has a positive impact on the coalescence of the metal droplets, even at low concentrations. Furthermore, they showed that for further cryolite additions, the behaviour of coalescence efficiency was strongly dependant on the presence of Mg in the alloy: a maximum of CE was reached at 2 wt% cryolite for AA3104, whereas the CE for AA8979 was found to always increase with the cryolite content.

According to the analyses and calculations realized for those experiments, three phenomena have been foreseen as credible explanations for those behaviours:

1. Modifications of the oxide layer composition in presence of cryolite: transformation from spinel to aluminium oxide for AA3104 or absorption of Na, K for AA8979. This leads to modifications in the structure and/or the volume of the oxide and may ease the development of cracks in the oxide.

2. Precipitation of "perovskite" (K, Na-Mg-F species) in presence of Mg in the alloy for some temperatures and cryolite contents. This phase forms a layer around the droplets and hinders coagulation.

3. Variations of tension-active elements (Na, K) concentrations in the metal leading to interfacial tension salt/metal variations.

The evolution of the salt properties such as surface tension, density or viscosity may also have an important impact on the coalescence behaviour. However, as existing literature has shown contradictory results on those factors, this study focuses on other criteria that were deemed to be more reliable.

As future work, it is planned to carry the same experiments at a bigger scale, with more realistic setups: rotating furnace, smaller salt/metal ratio, presence of oxides in the slag, etc.

References

[1]   D.B. Maason, M.M. Tagihei, "Interfacial reactions between aluminium alloys and salt flux during melting", Materials transactions JIM, Vol. 30, N. 6, 1989, pp. 411-422.

[2]   N. Kumar, "Comprehensive physics XI", 2008, pp. 1043.

[3]   J.H.L. Van Linden, D.L. Stewart, "Molten salt flux composition effects in aluminium scrap remelting", Light Metals, 1988, pp. 391-398.

[4]   R.R. Roy and Y. Sahai, "Coalescence Behaviour of Aluminium Alloy Drops in Molten Salts", Materials Transactions, JIM, Vol. 38, No. 11, 1997, pp. 995-1003.

[5]   R.D. Peterson, "Effect of Salt Flux Additives on Aluminium Droplet Coalescence", Second International Symposium-Recycling of Metals and Engineered Materials, 1990, pp. 69-84.

[6]   J. Ye and Y. Sahai, "Interfacial Behaviour and Coalescence of Aluminium Drops in Molten Salts", Materials Transactions, JIM, Vol. 37, No. 2, 1996, pp. 175-180.

[7]   K.J. Friesen and T.A. Utigard, C. Dupuis, J.P. Martin, "Coalescence behaviour of Aluminium Droplets under a Molten Salt Flux Cover", Light Meals, 1997, pp. 857-864.

[8]   A. Sydykov, B. Friedrich, A. Arnold, "Impact of parameter changes on the aluminum recovery in a rotary kiln", Light Metals, 2002, pp. 1045-1052.

[9]   Y. Xiao, M.A. Reuter, "Recycling of distributed aluminium turning scrap", Minerals Engineering, Volume 15, Issue 11, 2002, pp. 963-970.

[10]   R.R. Roy, J. Ye, Y. Sahai, "Viscosity and density of molten salts based on equimolar NaCl-KCl", Materials transactions JIM, Vol. 38 N. 6, 1997, pp. 566-570.

[11]   J.A.S. Tenorio, M.C.Carboni, D. Crocce, R. Esinosa, "Recycling of aluminium-effect of fluoride additions on the salt viscosity and on the alumina dissolution", Journal of Light metals 1, 2001, pp. 195-198.

[12]   L. Martin-Garin, A. Dinet, J.M. Hicter, "Liquid-liquid interfacial tension measurements applied to molten Al-halide systems", Journal of materials science 14, 1979, pp. 2366-2372.

[13]   A. Silny, T.A. Utigard, "Interfacial tension between aluminium and chloride-fluoride melts", J. Chem. Eng. Data, 1996, 41, pp. 1340-134.

[14]   R.R. Roy, Y. Sahai, "Interfacial tension in molten aluminium alloys and salt systems", Light Metals, 1993, pp. 1067-1072.

[15]   R.R. Roy, Y. Sahai, "Wetting behaviour in Aluminium-Alumina-Salt systems", Materials transactions JIM, Vol. 38 N. 6, 1997, pp. 571-574.

[16]   Y. Xiao, K. Tang, "Solubility of alumina in molten chloride-fluoride melts", Proceedings of the VIII Int. Conf. on molten slags, fluxes and salts, 2009.

[17]   A. Tan, P. Nicholson, "Development of stress during Na-K-Ion Exchange of polycrystalline β, β''-Al_2O_3 and its influence on the ion exchange process", Solid State Ionics, 1988, pp. 217-228.