Fluoride Salt Dissociation in NaCl–KCl Salt Flux and its Effect on the Coalescence of Aluminium

Abyl Sydykov, Bernd Friedrich

Effects of fluoride additive concentration, temperature, aluminium alloy type on the coalescence of aluminium in salt flux melt were studied for the standard European salt flux for aluminium remelting, based on 70 wt-% NaCl and 30 wt-% KCl. The promoting power of fluoride increased as $CaF_2 < Na_3AlF_6 < NaF < LiF$. CaF_2 addition resulted in a maximum of coalescence rate at 1 to 2 % CaF_2. Increase of temperature accelerated the coalescence. "Free" fluoride ion is discussed as an active component of the salt flux. The thermodynamics of the oxide film stripping was reviewed.

Keywords:

Fluoride – Aluminium – Coalescence – Flux – Salt

Dissoziation der Fluoridsalze im Schmelzsalz auf Basis von NaCl und KCl und deren Einfluss auf die Koaleszenz des Aluminiums

Die Einflüsse der Konzentration, Temperatur, Art der Aluminiumlegierung auf die Koaleszenz des Aluminiums im Standardschmelzsalz (70 Masse-% NaCl und 30 Masse-% KCl) wurden untersucht. Die Fähigkeit des Fluoridsalzes, die Koaleszenz zu befördern, steigt in der Reihe $CaF_2 < Na_3AlF_6 < NaF < LiF$ von links nach rechts an. Zugabe von CaF_2 ergab ein Maximum der Koaleszenzgeschwindigkeit bei 1 bis 2 % CaF_2. Bei höheren Temperaturen stieg die Koaleszenzgeschwindigkeit an. „Freie" Fluoridionen wurden als die aktive Komponente des Schmelzsalzes betrachtet. Der Artikel gibt eine kritische Übersicht auf die Thermodynamik der Oxidschichtablösung.

Schlüsselwörter:

Fluoridsalz – Aluminium– Schmelzsalz – Schmelzen – Koaleszenz

La dissociation des sels de fluoride dans le sel de fusion, sur la base de NaCl et KCl, ainsi que leur influence sur la coalescence de l'aluminium

Disociación de las sales fluoradas en el sal de fundido en base de NaCl y KCl y su efecto sobre la coalescencia del aluminio

1 Stripping of oxide film of aluminium in salt flux

1.1 Mechanism

In early studies it was suggested that the oxide film of aluminium dissolves in salt flux with fluoride addition. The solubility of aluminium oxide is very low [1-3]. The oxide film can be stripped also with salt flux saturated with aluminium oxide [3, 4].

According to various authors the oxide film is stripped mechanically [3, 6]. In the first stage cracks are formed in the oxide film and then salt penetrates to the metal surface and reacts with it forming volatile aluminium halogenides. Formed gas bubbles break the oxide film. Different thermal expansion of aluminium and oxide is also supposed to contribute a crack forming [7].

Kurdyumov [1] connected crack forming with conversion of γ-Al_2O_3 to α-Al_2O_3. In the air the conversion temperature lays between 1100 °C and 1200 °C [8]. CaF_2, MgF_2 and AlF_3 can reduce the conversion temperature by 100 to 400 °C. But LiF, NaF and Na_3AlF_6 had no effect on conversion temperature [8]. Effects of KCl and NaCl were not studied.

In the air the crack formation on aluminium begins about 550 °C, though at 640 °C no cracks were observed after 30 min. The crack formation is accompanied by increase of oxide film thickness, re-crystallisation of aluminium, and conversion of oxide film from amorphous to γ-Al_2O_3.

Ye & Sahai [5] doubted the formation of aluminium halogenides. But a microscopic study showed formation of gas bubbles even at 400 °C [7].

The next phenomenon is the oscillation of droplets of one liquid in another liquid in presence of surface active component. The higher the concentration of the surface active component the bigger is amplitude of oscillations which can lead to higher crack formation rate.

1.2 Thermodynamics of oxide film stripping in salt flux

Sully et al. [4] studied the oxide film stripping under salt flux with 30 % of γ-Al_2O_3. Oxide film was stripped in spite of saturation of salt with oxide. According to Sully the oxide film is stripped spontaneously if:

$$\sigma_{Al-Salt} + \sigma_{Oxide-Salt} < \sigma_{Oxide-Al} \qquad (1)$$

σ – interfacial tensions between aluminium and salt, oxide and salt, oxide and aluminium

Later Roy und Sahai [5] found that free energy ΔG of oxide film stripping (Equation 2) is always positive, i.e. it is not spontaneous:

$$\Delta G = \sigma_{Al-Salt} + \sigma_{Oxide-Salt} - \sigma_{Oxide-Al} \qquad (2)$$

Utigard [2] derived the Equation 3 neglecting oxide surface after stripping and assuming literature data of aluminium surface tension as a surface tension between aluminium and aluminium oxide since aluminium oxide on the surface cannot be avoided:

$$\Delta G = \sigma_{Al-Salt} - \sigma_{Al} + \sigma_{Salt} \cos\theta_{Oxide-Salt} \qquad (3)$$

$\theta_{Oxide-Salt}$ – wetting angle between oxide and salt

Utigard obtained negative ΔG, i.e. oxide film stripping is spontaneous.

Jordan & Milner [6] reported a significant reduction of oxide stripping rate at lower oxygen pressures in salt flux with relatively high fluoride concentrations. They supposed an electrochemical reaction, in which aluminium is oxidized at the anode and dissolved oxygen is reduced to O^{2-} ions at the cathode. Lukashenko & Sladkova [9] observed a faster coalescence of aluminium in salt flux under vacuum. The salt flux in their experiments was, however, without fluoride additition. These studies indicate that different reactions predominate in salt fluxes with and without fluoride addition.

According to Kurdyumov et al. [1] the reaction 2 does not describe the oxide film stripping, but the work of adhesion of the oxide film to aluminium in salt melt.

The work of adhesion according to Dupre's equation is a difference between free interfacial energies before and after oxide film stripping:

$$\Delta G = W_A = f_{Al-Salt} + f_{Oxide-Salt} - f_{Oxide-Al} \qquad (4)$$

f – free interfacial energy between aluminium and salt, oxide and salt, oxide and aluminium, W_A – the work of adhesion of oxide to aluminium in salt flux

Works of adhesion of salt fluxes to oxide and of aluminium to oxide:

$$W_a^{Oxide-Salt} = f_{Oxide} + f_{Salt} - f_{Oxide-Salt} \qquad (5)$$

$$W_a^{Oxide-Al} = f_{Al} + f_{Oxide} - f_{Oxide-Al} \qquad (6)$$

Substitution of the Equations 5 and 6 for free interfacial energies $f_{Oxide-Salt}$ and $f_{Oxide-Al}$ in Equation 4 results in:

$$W_A = f_{Al-Salt} + f_{Salt} - f_{Al} - W_a^{Oxide-Salt} + W_a^{Oxide-Al} \qquad (7)$$

According to Gibbs the relationship between free interfacial energy and surface tension is:

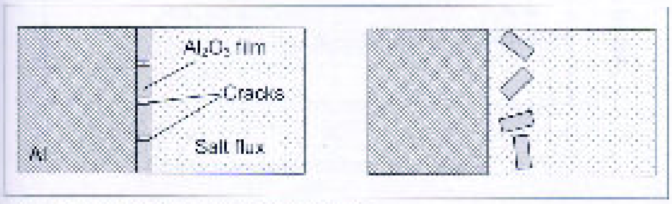

Fig. 1: Oxide film stripping in salt flux

$$f^{\omega} = \sigma + \sum_{i=1}^{2} \Gamma_i \mu_i \qquad (8)$$

f^{ω} – free surface energy, σ – surface tension, Γ_i – concentration of component i on the Gibbs surface, μ_i – chemical potential of component i

If phases consist of pure components, the components are not soluble in each other and do not absorb the gase phase, the free surface energies can be substituted by surface tensions.

Using the Young's equation for wetting (Figure 2):

$$\sigma_{Oxide-Salt} = \sigma_{Oxide-Al} + \sigma_{Al-Salt} \cdot \cos\theta \qquad (9)$$

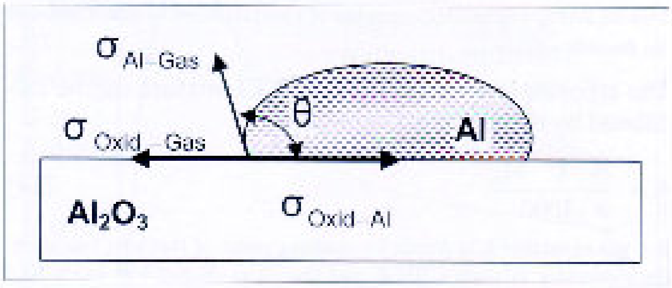

Fig. 2: To Young's equation of wetting

the following reactions can be obtained:

$$W_a^{Oxide-Salt} = \sigma_{Oxide-Salt} \cdot (1 + \cos\theta_{Oxide-Salt}) \qquad (10)$$

$$W_a^{Oxide-Al} = \sigma_{Oxide-Al} \cdot (1 + \cos\theta_{Oxide-Al}) \qquad (11)$$

From Equations 7, 10 and 11 the following can be obtained:

$$\Delta G = \sigma_{Al-Salt} - \sigma_{Salt} \cos\theta_{Oxide-Salt} + \sigma_{Al} \cos\theta_{Oxide-Al} \qquad (12)$$

σ_{Salt}, σ_{Al} – surface tensions of salt flux and aluminium, $\theta_{Oxide-Salt}$, $\theta_{Oxide-Al}$ – wetting angles of oxide by salt flux melt and aluminium

From obtained equation follows that a lower interfacial tension between aluminium and salt flux, better wetting of oxide by salt flux and worse wetting of oxide by aluminium promotes the stripping of oxide film by salt flux. The free Gibbs energy calculated by Equation 12 is however always positive, i.e. the oxide film stripping is always not spontaneous. The reason is that there is no method which lets a direct measurement of surface tension of solids, it is measured indirectly with Young's equation (Equation 9). The equation is valid for spherical droplet and does not consider the gravity, which changes the form of the droplet. Moreover the Young's equation describes the surface energies balance, not balance of forces. Furthermore the surface tension of solids is questioned.

Existing thermodynamic descriptions cannot explain sufficiently the oxide film stripping due to missing or not reliable data for interfacial energies, surface tensions, wetting angles and phase transformation in the system oxide–aluminium–salt.

2 Dissociation of fluoride additions in salt flux

Fluoride additons have different effects on coalescence of aluminium in salt flux. Free F^- ions produced by dissociation of fluoride are suggested to be an active component of salt flux. Dissociation reactions can be found from cryoscopic data. This data can be obtained from the corresponding ternary diagrams.

The dissolution of fluoride additive flux lowers the freezing point of salt flux. According to the Raoult's law the freezing point depression can be described by:

$$\Delta T = K \cdot \frac{P}{M_B} \cdot n \tag{13}$$

ΔT – freezing point depression (°C); K – cryoscopic constant of NaCl-KCl-mix: 35.12 kJ/mol for the equimolar mixture and 37.11 kJ/mol for the mixture 70 wt-% NaCl and 30 wt-% KCl; P – weight of dissolved fluoride additive in 1000 g of NaCl-KCl-mixture (g); M_B – mol mass of fluoride additive (g/mol); n – number of ions produced by dissociation of the fluoride additive.

The cryoscopic constant of NaCl-KCl-mixture can be calculated by the following equation:

$$K = \frac{R \cdot T^2 \cdot M_A}{\alpha \cdot 1000} \tag{14}$$

R – gas constante 8.31 J/mol; T – melting point of NaCl-KCl-mixture: the equimolar mixture – 931 K and the 70 wt.-% NaCl-30 wt.-% KCl – 994 K; M_A – molar weight of the NaCl-KCl-mixture: 66.5 g/mol for equimolar mixture and 62.5 for the mixture 70 wt-% NaCl-30 wt-% KCl; α – heat of fusion of the NaCl-KCl-mixture: 27.28 kJ/mol for the equimolar mixture and 27.64 kJ/mol for the mixture 70 wt-% NaCl-30 wt-% KCl

The Raoult's Law is applied for ideal solutions, i.e. for strongly diluted solution when the dissolution enthalpy can be neglected and there are no reactions between fluoride additive and NaCl-KCl salt flux.

The number of new ions was calculated for various fluoride additives (Equation 13) (Figure 3). This method does not allow calculation of the dissociation of fluorides which result in only one new ion, e.g. NaF.

Tab. 1: Supposed dissociation reactions of fluorides in salt flux based on NaCl–KCl

In equimolar NaCl–KCl	In 70 NaCl–30KCl
$2LiF = Li_2F^+ - F^-$	$LiF = Li^+ + F^-$
$Na_3AlF_6 = 3Na^+ + AlF^-_4 + 2F^-$	$Na_3AlF_6 = AlF^+_2 + 4F^- + 3Na$
$CaF_2 = CaF^+ + F^-$	$CaF_2 = CaF^+ + F^-$
$BaF_2 = Ba^{2+} + 2F^-$	$BaF_2 = Ba^{2+} + 2F^-$

Tab. 2: Effect of fluorides in salt flux on coalescence of aluminium

Peterson [10]	Roy & Sahai [5]	Friesen & Utigard [11]
Superior: AlF_3, Na_3AlF_6, BaF_2, KF, SrF_2	Excellent: NaF, LiF, Na_3AlF_6, KF	Excellent: Na_3AlF_6, NaF, KF
Good: LiF, CaF_2	Good: CaF_2, MgF_2	Good: AlF_3, LiF
Moderate: NaF, MgF_2, Na_2SiF_6	Moderate: AlF_3	Fair: CaF_2, MgF_2

Suggested dissociation reactions based on the calculated numbers are presented in Table 1.

Fluoride salts promote the coalescence of aluminium in various levels. Various researchers divided fluorides in the three groups shown in Table 2, but the results are contradictory.

3 Coalescence test procedures

The effects of various factors on the coalescence kinetics were studied in fused quartz crucibles (Figure 4) placed on the bottom of an electrical furnace with a slope of 20° to the horizontal plane.

After reaching the required temperature in the furnace, previously prepared 200 aluminium particles (globules or plates) were introduced into the crucible with 5 g of molten salt flux within 5 seconds by means of a quartz tube (inside diameter 8 mm). The number of charged particles

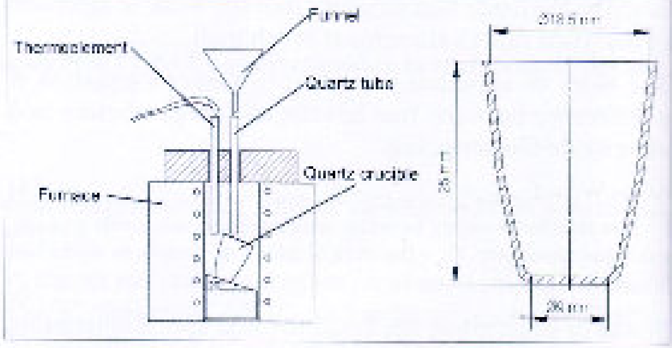

Fig. 4: Experimental set-up (left) and quartz crucible (right) for coalescence tests

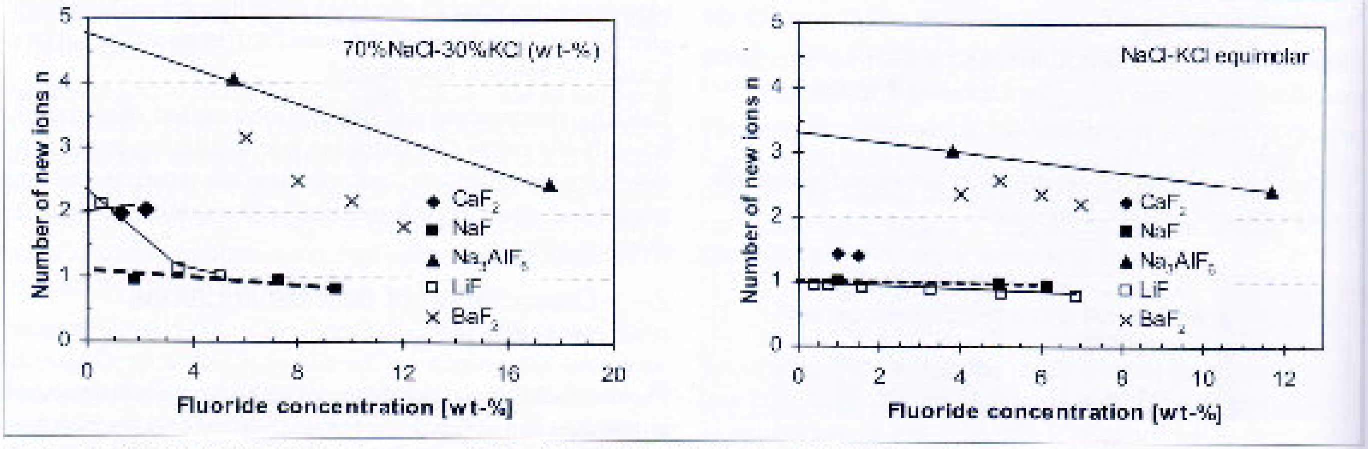

Fig. 3: Calculated number of produced new ions for the mixture 70 wt-% NaCl 30 wt-% KCl (left) and for the equimolar mixture NaCl-KCl (right)

was chosen in order to bring all of them in contact at the bottom of the crucible. After a given coalescence time, the crucible was carefully taken out from the furnace and cooled, then the crucible content was leached with water. Dried aluminium globules were graded by screening and visually. Globules of every size fraction were counted and weighed. The total specific surface area was calculated assuming ideal sphericity of the globules. The coalescence progress was evaluated by the total specific area of the globules (total surface area of all globules related to the total weight of globules):

$$A = A_{min} + (A_0 - A_{min}) \cdot e^{-k\tau} \qquad (15)$$

A_0 – initial specific area of charged particles at time $\tau = 0$; A_{min} – minimal specific surface of a single globule after the complete coalescence; k – coalescence rate coefficient

Preliminary tests with aluminium plates have disclosed a desintegration into several smaller droplets. To avoid this, aluminium globules were prepared by melting with a salt flux (equimolar NaCl-KCl mixture) without fluoride addition. About 5 min after melting of the salt flux, the crucible was taken out and cooled. No coalescence was observed because of short time and salt flux without fluoride. Comparison tests with aluminium plates and prepared globules made of not alloyed aluminium (99.8 %) did not demonstrate any significant difference between coalescence rates. In case of magnesium-containing alloy (UBC – used beverage can) prepared globules showed higher coalescence rates than initial alloy. For this reason the tests with UBC were performed for plates without pretreatment. The total coalescence test procedure is illustrated in Figure 5.

In previous tests in boron nitride crucibles, coalescence of aluminium was prevented by a formation of a solid dark shell on the aluminium droplets. Probably boron nitride or an additive in boron nitride was dissolved in the salt flux and reacted with aluminium, forming aluminium nitride or boride and resulting in incomplete coalescence. E. g. in salt flux with 3 % CaF_2 even after 75 min the coalescence was incomplete. For this reason the boron nitride crucibles were changed to quartz crucibles.

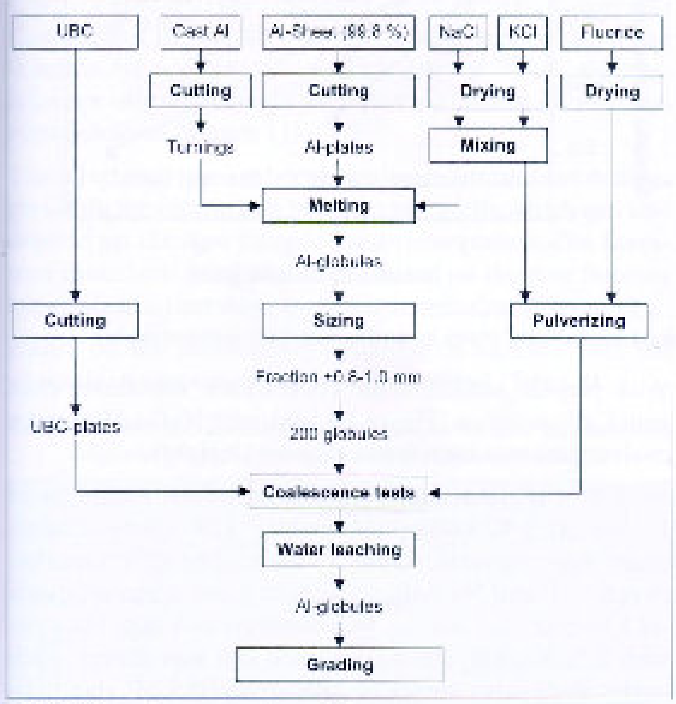

Fig. 5: The coalescence test procedure

4 Results and discussion

The coalescence rate increased with CaF_2-concentration and reached the highest values at 1 and 2 wt % (Figure 6).

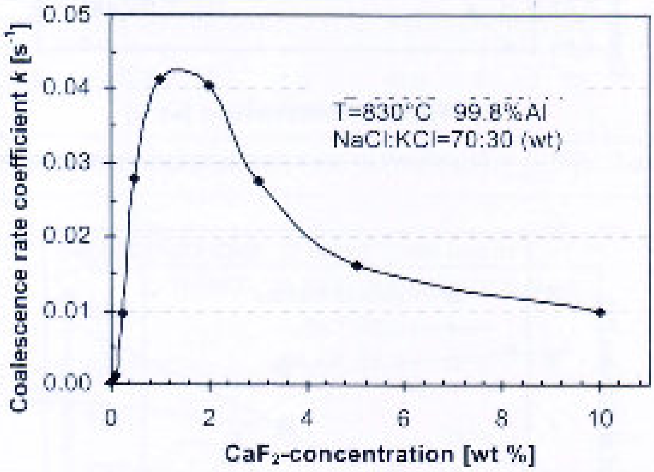

Fig. 6: Effect of CaF_2-concentration on the coalescence rate of aluminium (99.8 %) at 830 °C

At higher concentrations the coalescence rate dropped due to undissolved CaF_2 at 5 and 10 wt-%, which made the salt flux melt cloudy, especially the lower part of the melt. A decrease of the coalescence rate at 3 wt-% CaF_2 remains unexplained; it is too big to explain it by experimental error, also there was not undissolved CaF_2 [12]. Thus the recommended CaF_2-concentration in salt flux based on 70 NaCl-30 % KCl is about 1-2 wt-% for remelting not or low alloyed aluminium.

At the same concentrations the promoting power of fluoride additions weakened as LiF > NaF > Na_3AlF_6 > CaF_2 from left to right (Figure 7).

The reactions between aluminium and fluoride salts promote stripping of oxide film and consequently the coalescence. A raise of temperature intensifies the endothermic reactions between aluminium and CaF_2, Na_3AlF_6 and NaF. The bigger the reaction enthalpy is, the bigger the effect of the temperature on the coalescence rate is.

Oxidation of aluminium globules at 500 °C during 30 min on air resulted in a decrease of the coalescence rate (Figure 8, left).

Another factor affecting the coalescence rate is the alloying element. The biggest effect has magnesium, effects of other elements are small. The coalescence of globules made of cast aluminium alloy (8.5 % Si, 3.5 % Cu, 0.8 % Zn and 0.35 % Mg) was even faster than that of aluminium (99.8 %) or UBC (1.11 % Mg, 0.85 % Mn and 0.23 % Si) (Figure 8). The coalescence of UBC was studied on small plates. The size of plates was chosen in such a way that after melting down droplets with a diameter of ~1 mm were obtained. At CaF_2 and Na_3AlF_6 concentration of 0.5 % no

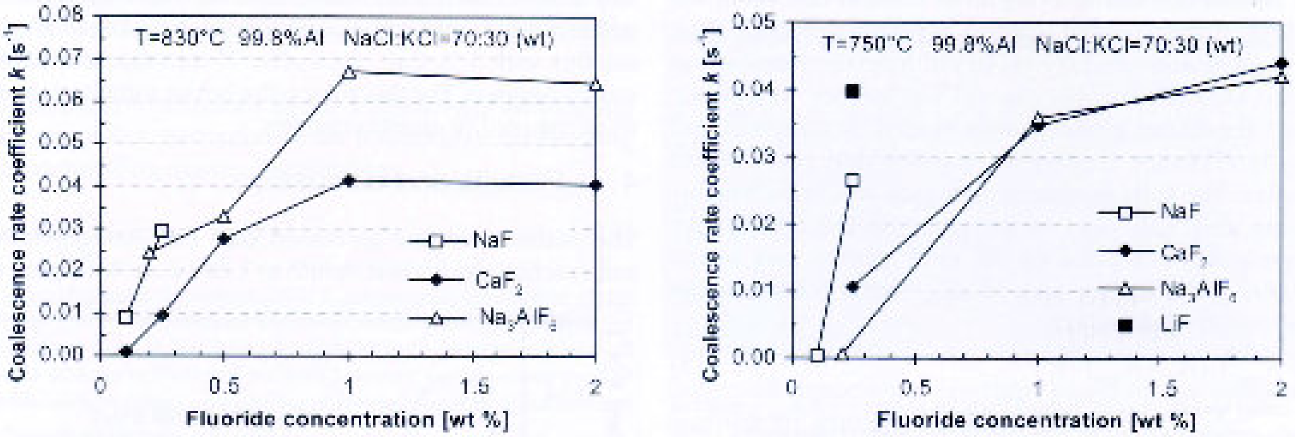

Fig. 7: Effects of fluoride salt, its concentration and temperature on the coalescence of aluminium

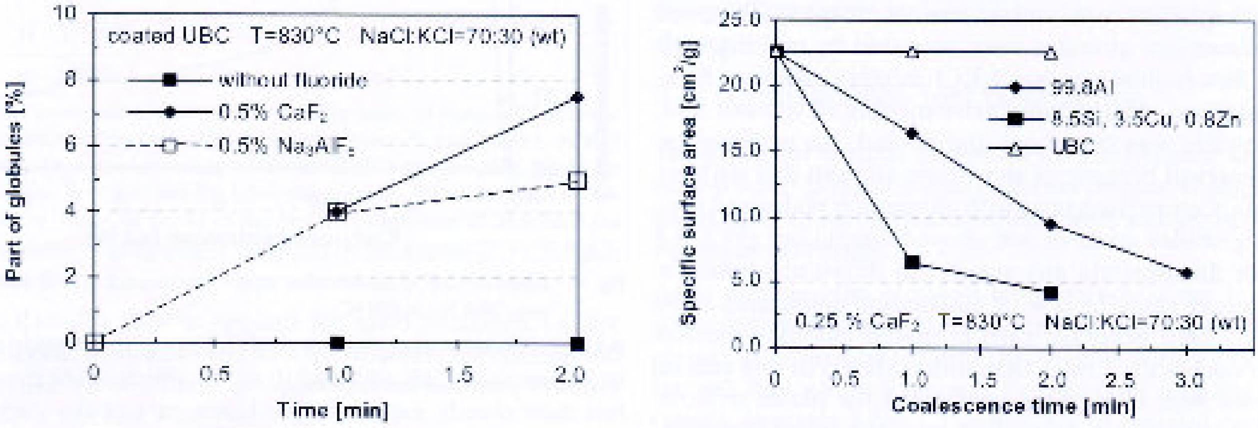

Fig. 8: Effects of alloying elements on coalescence rate (left); change of paint-coated UBC-plates to globules (right)

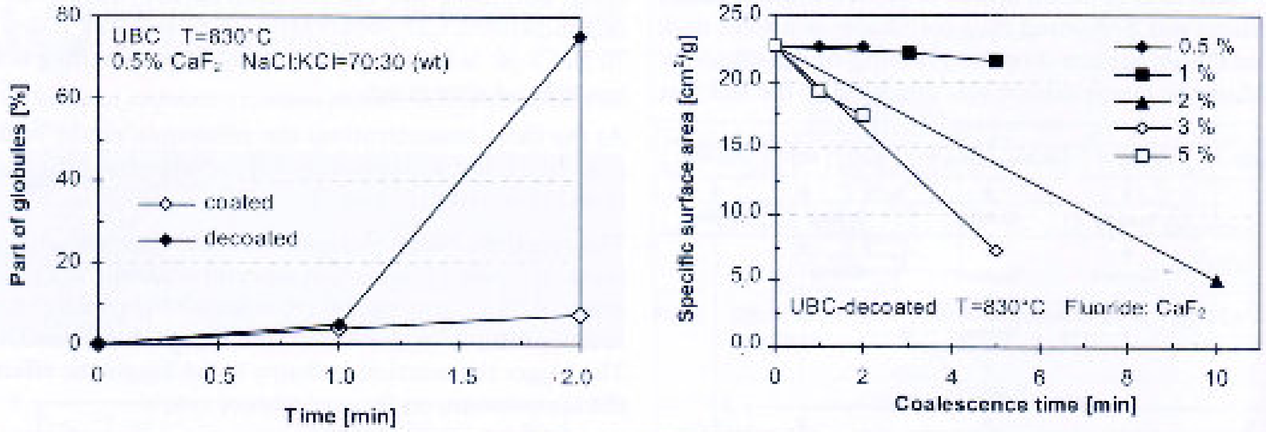

Fig. 9: Coalescence behaviour of coated and decoated UBC-plates (left) and decoated UBC-plates in salt flux with CaF$_2$-addition (right)

coalescence was observed. The tests were evaluated by change of form from plates to globules. In salt flux without fluoride addition the form of paint-coated plates was not changed at all (Figure 8, right).

Removing of the paint changed the coalescence rate cardinally. In salt flux with 0.5 % CaF$_2$, almost all plates turned to globules within 2 min, but still did not coalesce (Figure 9, left). At 1 % CaF$_2$ and 830 °C even after 5 min there still was not coalescence. At 5 % undissolved CaF$_2$ appeared, but its effect could not be evaluated due to missing points at shorter times (Figure 9, right).

With Na$_3$AlF$_6$-addition the coalescence was faster than with CaF$_2$-addition (Figure 10, left), with NaF-addition the coalescence was even faster (Figure 10, right).

At 5 % CaF$_2$ the coalescence was almost complete in 10 min. At 5 % of Na$_3$AlF$_6$ or NaF UBC-plates coalescence was complete within a minute. The difference between NaF and Na$_3$AlF$_6$ appears at lower concentrations. At 1 % NaF coalescence was complete in 1 min, but even with 2 % Na$_3$AlF$_6$ the coalescence still was slower. Such coalescence rates cannot be provided with CaF$_2$ due to its limited solubility in salt flux. The maximal recommended

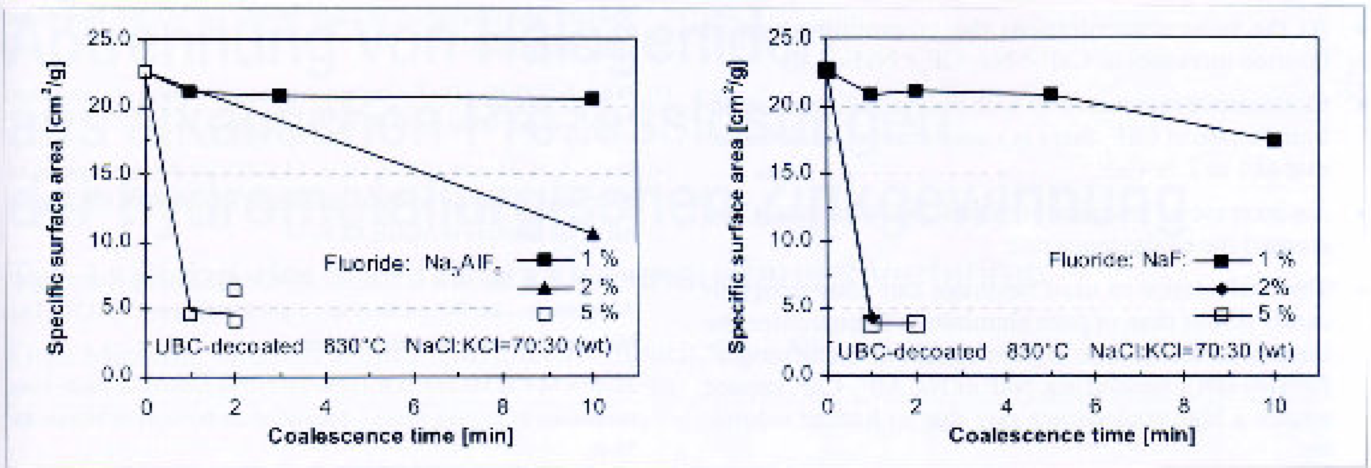

Fig. 10: Coalescence behaviour of decoated UBC-plates in salt flux with various concentrations of Na_3AlF_6 (left) and NaF (right)

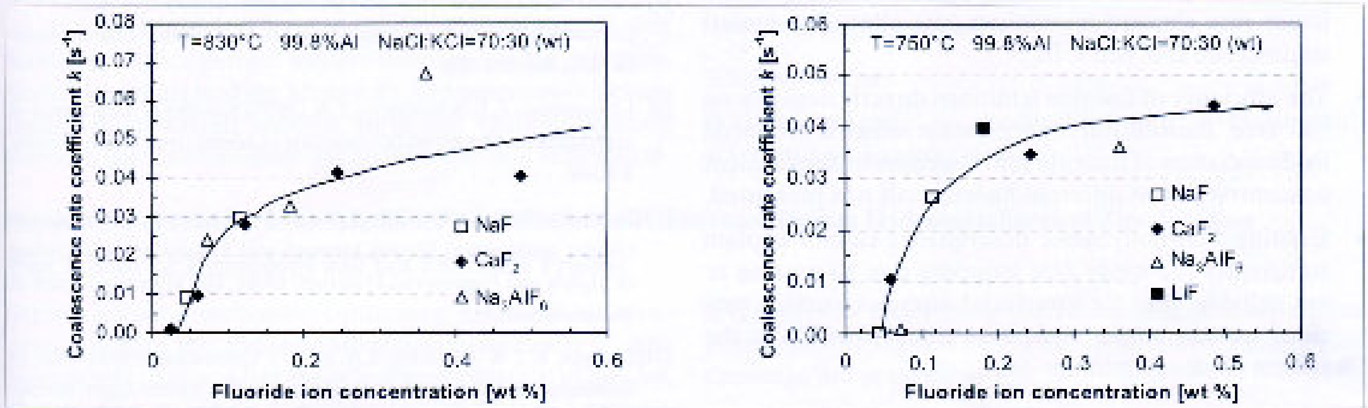

Fig. 11: Dependence of coalescence rate on free fluoride ion concentration in salt flux

NaF-concentration for remelting of little oxidized UBC-scrap is 1 % and between 2 % and 5 % in case of use of Na_3AlF_6 as a fluoride addition.

Assuming a complete dissociation of NaF, dissociation of CaF_2 according to the reaction $CaF_2 = CaF^+ + F^-$, a complete dissociation of Na_3AlF_6 at 830 °C and according to the reaction $Na_3AlF_6 \Rightarrow AlF_2^+ + 4F^- + 3Na^+$ at 750 °C the coalescence rate coefficients were plotted on free fluoride ion concentration (Figure 11).

The interfacial tension between aluminium and salt flux depends on the interaction between two melts, which can also depend on the free fluoride ion concentration. The literature interfacial tension values plotted on the free fluoride ion concentration show a certain correlation (Figure 12).

Based on the dissociation reactions of fluoride salts the equivalent concentrations were calculated (Table 3).

Tab. 3: Equivalent concentrations for various fluoride salt additions regarding the effect on the coalescence kinetics at 830 °C

Fluoride salt	Concentration of fluoride salt equivalent to 1 % of CaF_2
NaF	0.54
Na_3AlF_6	0.45
LiF	0.33
BaF_2	1.12
KF	0.74

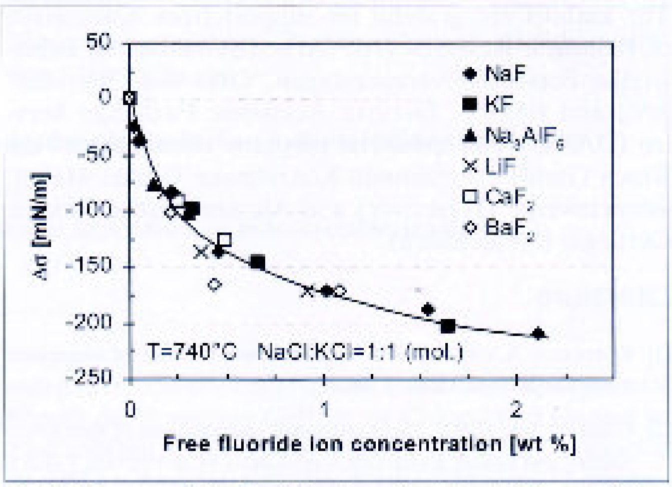

Fig. 12: Decrease of interfacial tension aluminium/salt flux with free fluoride ion concentration (interfacial tension data of Silny & Utigard)

5 Summary

In coalescence test effects of fluoride salt, its concentration, temperature and alloy type were studied in the standard European salt flux consisting of 70 wt. % NaCl and 30 wt. % KCl. Coalescence rate coefficient was introduced to evaluate coalescence test results. The results can be summarized as following:

- At the same concentrations the promoting power of fluoride increases as $CaF_2 < Na_3AlF_6 < NaF < LiF$.
- Coalescence rate increases with fluoride salt concentration. In case of CaF_2 there is a maximum of coalescence rate at 1 to 2 % CaF_2.
- An increase of temperature from 750 °C to 830 °C increased the coalescence rate.
- The coalescence of used beverage can alloy is significantly slower than of pure aluminium. To guarantee the same coalescence rate as pure aluminium, a "stronger" fluoride salt is needed, e.g. NaF or Na_3AlF_6. CaF_2 cannot ensure a high coalescence rate due to limited solubility.
- In comparison tests with three different aluminium alloys (pure aluminium, cast alloy, UBC alloy) pure aluminium resulted in the highest coalescence rate, a lower rate showed aluminium cast alloy. The lowest coalescence rate had UBC.
- The efficiency of fluoride additions directly depends on the "free" fluoride ion concentration, which is produced by dissociation of fluoride salt. Based on this equivalent concentrations of different fluoride salt was presented.
- Existing thermodynamic descriptions cannot explain sufficiently the oxide film stripping due to missing or not reliable data for interfacial energies, surface tensions, wetting angles and phase transformation in the system oxide–aluminium–salt.

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