

MOLTEN SALT FLUX COMPOSITION EFFECTS IN ALUMINUM SCRAP REMELTING

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The mechanism of the empirically proven effectiveness of the use of salt fluxes to improve metal recovery in aluminum scrap remelting is not well understood. The effect on coalescence of increased fluoride concentration in the flux was studied in the absence of high oxide concentration. The physical and chemical interaction of well-defined oxide skins with these fluoride-containing fluxes was observed and analyzed using high speed photography and scanning electron microscopy.

BACKGROUND

Molten salt fluxes are used extensively in the primary and secondary aluminum industry to improve direct recovery of aluminum in scrap remelting and skim processing. The scrap or skim is submerged under the molten flux during melting in a rotary barrel furnace or similar unit. The flux wets oxide present with the scrap or skim charge and aluminum, thus separating the materials and promoting coalescence of the aluminum droplets into a continuous molten pad under the salt. In addition to freeing the metal from oxides, the flux layer prevents further oxide formation by acting as a barrier between metal and atmosphere. The flux used is typically 95-100% sodium and/or potassium chloride, the balance consisting of calcium or aluminum fluoride or cryolite.

Important parameters which affect flux performance are oxide concentration in the salt, flux fluoride concentration and agitation of the oxide-laden flux. Sully, Hardy and Heals (1) studied the effect of oxide concentration and particle size on flux viscosity and found that oxide concentrations as low as 10% caused sufficient thickening of the flux to inhibit coalescence. Racunas (2) developed a relationship for the dependence of aluminum droplet size on velocity gradient, flux viscosity and salt-metal interfacial energy. The viscosity is strongly dependent on velocity gradient since oxide-laden flux is thixotropic. His work showed that maximum droplet size, and thus maximum coalescence occurs when the product of viscosity and velocity gradient is minimized.

Most research concerning the effects of oxide concentration on flux performance has of necessity been empirical. The rheological properties of oxide-laden flux are strongly affected by the size and shape of oxide particles in addition to oxide concentration. Therefore, it is necessary to use

oxides present in scrap or skim to quantify the effect of oxide loading on flux performance with similar feedstocks.

It is known that additions of fluorides to chloride melts affect direct recovery positively by increasing the ability of the flux to free oxides from aluminum droplets by decreasing flux-aluminum interfacial tension. Martin-Garin, Dinet and Hichter (3) studied the interfacial tension of equimolar NaCl-KCl with small additions of common fluorides. Five-ten mole percent additions of cryolite, lithium fluoride, sodium fluoride and potassium fluoride reduced interfacial tension (flux-aluminum) by 25-50%. The order of effectiveness for the fluorides was found to be: $\text{Na}_3\text{AlF}_6 < \text{LiF} < \text{NaF} < \text{KF}$.

At fluoride concentrations greater than ten mole percent, the decrease in flux-aluminum interfacial tension was roughly the same for NaF and KF, approximately twice the decrease observed for LiF and Na_3AlF_6 . The effect of decreased interfacial tension on metal direct recovery, however, has not been quantified except under conditions of high oxide concentration, which may tend to mask effects due to variations in fluoride concentration.

An additional factor in fluoride selection is the relative stability of the fluorides with magnesium, since most scrap and skim processed contains magnesium. As shown in Figure 1, the only fluorides more stable than MgF_2 are CaF_2 and LiF. Therefore, interfacial tension measurements made on salts containing cryolite, NaF or KF may be meaningless if the flux is used in processing magnesium-containing skim or scrap, since some or all of the fluoride may react with the charge to form MgF_2 or other complexes which are more thermodynamically stable.

It was decided to study the effect of fluoride addition to fluxing salts on coalescence at low oxide concentrations. The results of this empirical fluoride evaluation will be reported below. Additionally, fundamental work which yields valuable information concerning the nature of the interaction of molten fluxes and oxide films will be discussed.

COALESCENCE AND METAL RECOVERY EVALUATIONExperimental Procedure

A test program was conducted to determine the effects of increased fluoride addition to the flux utilized in aluminum scrap recovery. Typically, the

composition of salt used is 95-100 wt.% chlorides, commonly equimolar NaCl/KCl, and 0-5 wt.% fluorides. The fluoride compound is usually cryolite, Na_3AlF_6 , or calcium fluoride, CaF_2 . The fluorides selected for the study were sodium fluoride (NaF), potassium fluoride (KF), calcium fluoride and magnesium fluoride (MgF_2). Aluminum fluoride and cryolite were not included in the study because the primary interest was in magnesium-containing alloys, which are thermodynamically unstable with AlF_3 in the flux (see Figure 1). It was also decided to only study fluoride concentrations higher than those normally used to determine the benefit in direct metal recovery of fluoride additions of 5-20 wt.%. The composition of the balance of each test salt was equimolar NaCl/KCl.

AA5182 ingot saw chips were selected for the study because the magnesium level is high (approximately 4.5%) and metal recovery in melting saw chips without flux is very low, making comparison of the various fluxes less difficult. More importantly, however, the saw chips were selected as feedstock to minimize random variation between tests.

Finally, it was decided to conduct the fluoride evaluation using very high salt/oxide ratios in order to obtain the highest recovery possible. Therefore, 200 grams of salt were used in melting each 100 gram saw chip sample during the fluoride evaluation. Although the flux/scrap ratio in this work is at least an order of magnitude higher than standard industry practice, evaluation of fluoride effectiveness in a typically oxide-laden flux would be impossible if, as generally believed, oxide concentration (apparent flux viscosity) is the most important variable affecting metal recovery.

The test procedure was as follows:

1. A 200 gram salt charge (3-18 wt.% NaF, KF, CaF_2 , or MgF_2 , balance equimolar NaCl/KCl, all Fisher Certified or equivalent) was melted at 800°C under argon and held for 30 min. to insure dissolution of the fluoride. The furnace temperature was then set to 760°C, if necessary.
2. A representative 100 gram sample of AA5182 ingot saw chips was added in small increments. Each charge increment was forced under the surface of the molten flux immediately after addition with a graphite stirring rod.
3. Following the final addition, the furnace was shut off and the mixture allowed to freeze. The metal heel was removed and weighed.

Results and Discussion

The results of the fluoride evaluation program are shown graphically in Figure 2. It's clear from the figure that recovery was very high in all cases. It is assumed this is due to the use of the high salt/scrap ratio and the resulting dilute oxide/flux slurry. Obviously, the study reinforces the belief that oxide concentration in the molten flux and the effect of oxide concentration on viscosity affect recovery more strongly than fluoride type or concentration. However, conclusions concerning effects of fluorides on recovery are apparent from the results.

1. At 760-800°C, coalescence (direct metal recovery) increased with increasing fluoride concentration to 10 wt.% fluoride.
2. Recovery decreased above 10 wt.% CaF_2 or MgF_2 at 760°C; recovery was constant from 10-20 wt.% NaF or KF at 760°C.
3. Recovery was slightly better from 3-10 wt.% fluoride for NaF and KF than MgF_2 and CaF_2 .
4. Recovery for all fluorides tested was the same at 800°C, very close to that obtained with NaF and KF at 760°C.

As discussed previously, Martin-Garin et al. (3) found that aluminum-flux interfacial tension reduction due to fluoride presence was greatest for NaF and KF in the range of 10-25 mole percent, which corresponds roughly to 6-20 wt.%. This agrees well with coalescence results obtained in this work, in which recovery was maximized at 10-20 wt.% NaF or KF. This agreement suggests that, when oxide concentration in the flux is low, coalescence is primarily a function of the aluminum-flux interfacial tension. It should be noted that in normal industry practice the flux oxide concentration is much higher than in this study. Under these conditions, effects due to fluoride are masked by the deleterious effect of high oxide concentration. Interfacial tension measurements on equimolar NaCl-KCl with MgF_2 or CaF_2 additives were not available in the literature. Therefore, a comparison to coalescence results obtained in this work cannot be made.

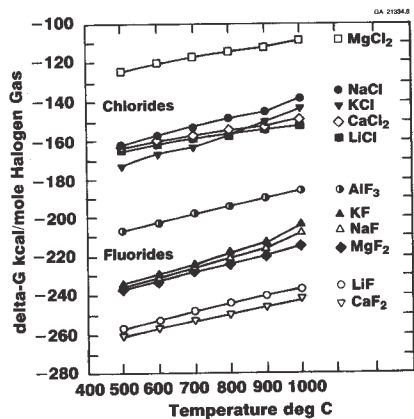
SALT-METAL-OXIDE INTERACTION

Introduction

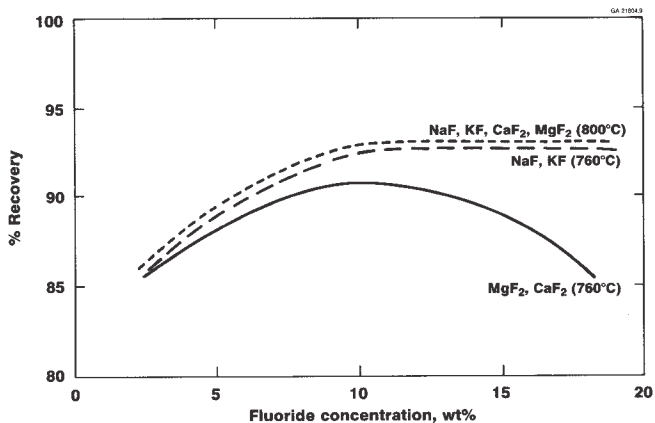
In order to obtain a better understanding of the factors governing the successful separation of oxides and metal in the presence of salt, a test method was conceived and developed which allows one to reproducibly create oxide skins on selected alloy droplets in a controlled atmosphere, in such fashion that these droplets, after a given test exposure time, could: 1) be quenched and their oxide skin measured and analyzed; or 2) be subjected to a pressure differential to measure the strength of the oxide skin; or 3) be brought in contact with molten salt to study the reduction in oxide skin strength and possibly the mechanism that causes it.

Since it is beyond the scope of this paper to describe the apparatus and test procedures extensively, only a schematic (Figure 3) and a brief explanation are provided here.

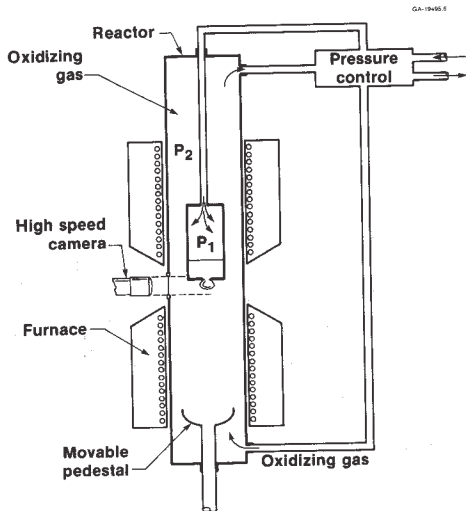
A freshly machined sample of the alloy to be studied is placed in the boron nitride nozzle, which has a 4.5 mm orifice with knife edge in its bottom and a thermocouple for furnace control in its main body. The extension tube in the top of the nozzle is connected to a very sensitive pressure control system which can maintain preset pressure differences of millimeters of water column (mm H_2O) between the nozzle and the chamber. The nozzle atmosphere consists of super-high purity argon (<5 ppm O_2) while the chamber atmosphere can be selected and changed during the experiments. During heat-up there is obviously a connection between the chamber and the nozzle through the nozzle orifice but as soon as the metal melts, a seal is formed and the preset pressure



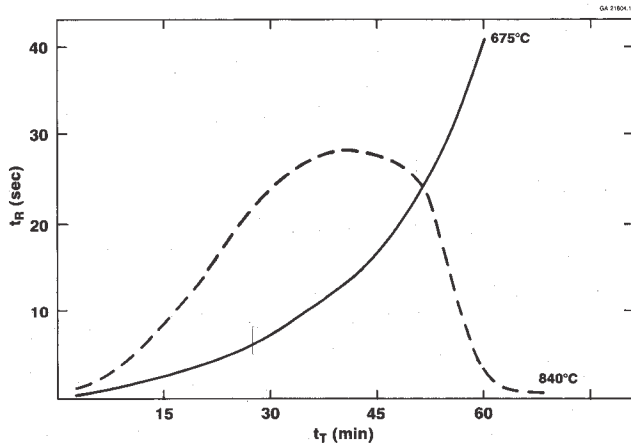
Gibbs Free Energies of Various Chlorides and Fluorides
Figure 1



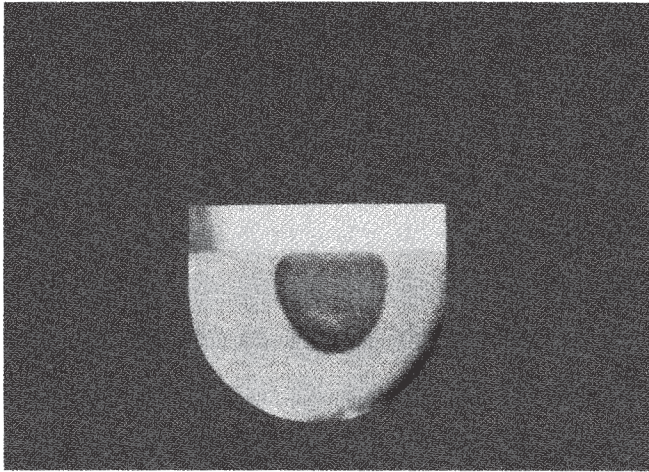
Effect of Fluoride Concentration and Temperature on Direct Recovery
Figure 2



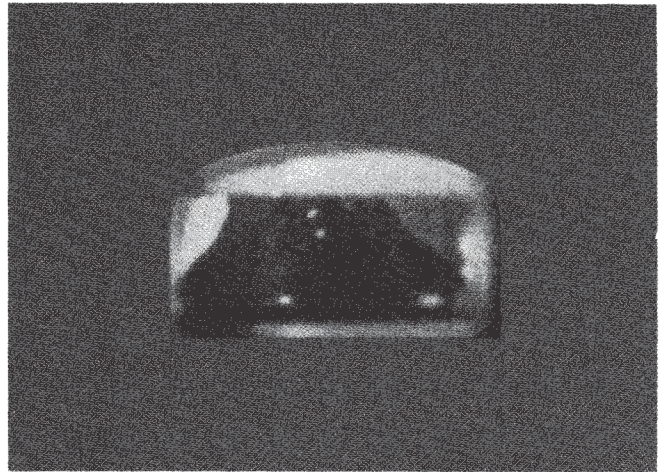
Oxidation Test Schematic
Figure 3



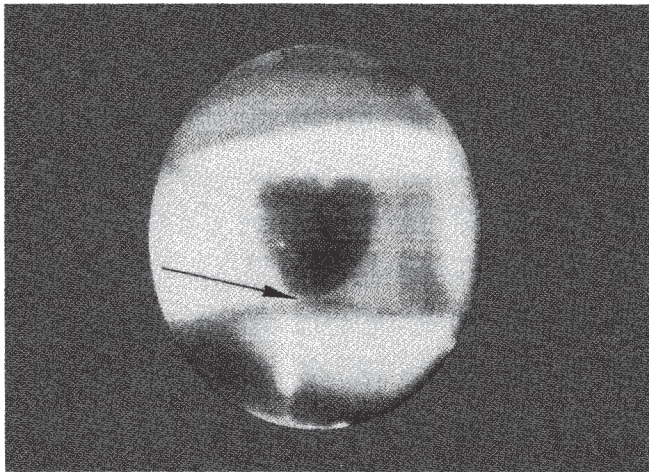
Breakdown Resistance of Oxides in Molten Salt
Figure 4



1.



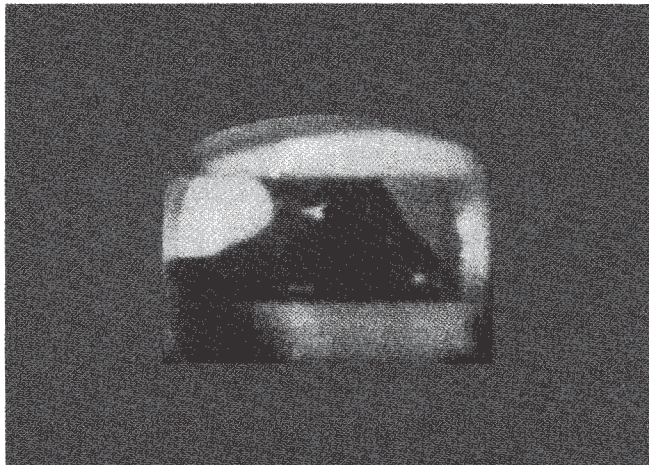
4.



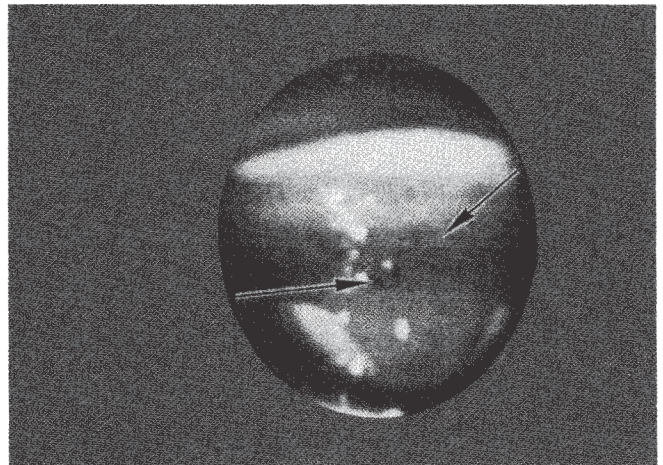
2.



5.



3.



6.

1 Droplet, early oxidation
2 Ready to contact salt
3, 4, 5 Wetting of droplet

5 Start metal release
6 Salt overflow
Note oxide fragment

Salt-Oxide Contact and Skin Desintegration
Figure 5

difference will appear. This is the signal to form the droplet. Due to the strength of the preexisting oxide skin, a droplet will not form freely at test "operating" pressures. With assistance of a vibrator, with specific settings for different alloys and temperatures, well-controlled droplets can be formed with a pressure difference of 1 cm H₂O.

The movable pedestal in the lower portion of the chamber can be equipped with the appropriate tools for the type of test performed: 1) a boron nitride knife to cut off the droplets for examination; 2) a crucible for collecting the fragments of the oxide skin and the molten metal after rupture of the test droplet in the oxide skin strength determinations; or 3) a salt container with overflow reservoir for the salt-oxide contact tests.

Results and Discussion

The results of an extensive study in this "three prong" fashion on pure aluminum and binary Al-Mg alloys will be published at a later date, but the following summarized test results are of interest in the context of this paper.

The oxide skin thicknesses measured varied from ~50Å (pure Al, 30 sec. at 675°C in argon) to ~30 μm (Al-4.5 Mg, 15 hrs. at 700°C in argon + 20% O₂). Thicker skins were formed in the cases of runaway oxidation, where the diameter of the droplet could grow from ~6 mm to as much as ~10 mm, but those oxide skins were flaky, inconsistent and unmeasurable. The skins of Al-Mg alloys consisted mostly of MgAl₂O₄ spinel and MgO. Reproducibility was reasonably good.

Considering the droplet a perfect sphere and assuring that the oxide skin is relatively thin and uniform, the oxide skin strength can be determined from:

$$S_R = \frac{F}{A} = \frac{\pi R (P_N - P_C)}{2\pi R \cdot d} = \frac{R \cdot \Delta P}{2d}$$

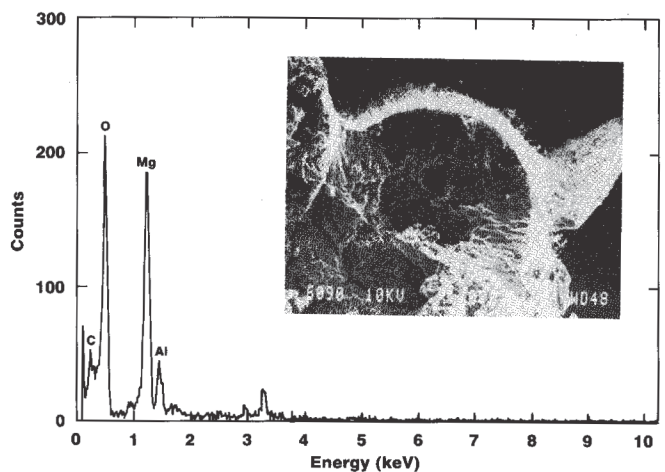
where S_R = the tensile strength of the skin, F = the force on the skin at the moment of rupture, R = droplet radius, P_N, P_C, ΔP = respectively nozzle pressure, chamber pressure and their pressure differential, d = skin thickness. The thus determined skin strength was highest just after droplet formation (test time ~ 10 sec.) at about 600 kgf/cm² and rapidly decreased with increasing skin thicknesses to ~50 kgf/cm² for skins formed in 15 hrs. at 700°C. (The decrease is to be expected because there will be a growing concentration of imperfections with the increase in skin thickness.) The measured pressure differential at the moment of skin rupture (P_R), however, increased in those tests from ~4 cm H₂O (.05 psi) to ~250 cm H₂O (3.5 psi), which is a more useful form of the data in light of the results of the salt/oxide contact tests.

Salt-Oxide Contact Tests

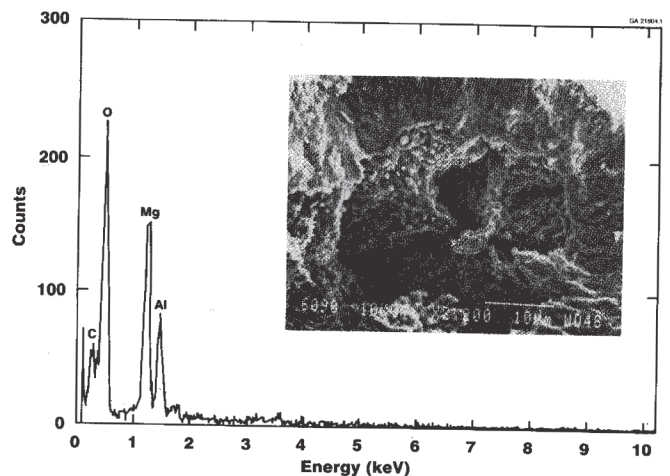
As stated previously, the purpose of the salt/oxide contact tests was to quantify the reduction in oxide skin strength due to the salt-oxide interaction by measuring the change in "rupture" pressure, P_R. The test results were unexpected and intriguing. The selected salt (equimolar NaCl/KCl + 10% KF) instantaneously wetted

the oxide skins of all test alloys and the skins disintegrated into fragments of various sizes, leaving the metal droplet "bare," which made the "rupture" pressure constant (~1 cm H₂O), equal to the surface tension of the alloy in the salt.

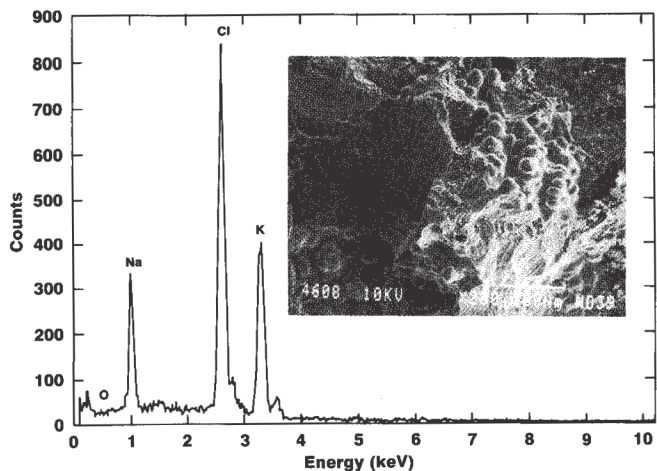
The time required to achieve metal release, at a slightly higher ΔP of 1.2 cm H₂O, varied with the test parameters. In general terms, the "release times" were directly proportional with the "rupture" pressures of oxide skins formed under identical test conditions. Figure 4 shows release time (t_R) as a function of the exposure time of the droplet to the oxidizing atmosphere at a given temperature. For test temperatures <750°C, t_R increases with test exposure time from almost instantaneous to ~40 sec. for 1 hr. exposure time (and up to 7 min. for Al-4.5 Mg for 15 hrs. at 700°C).



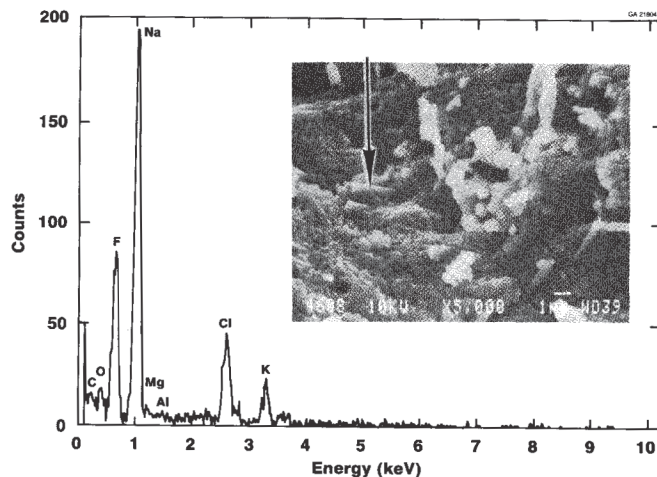
Composition of External Fibers (Al-4.5 Mg) Figure 6A



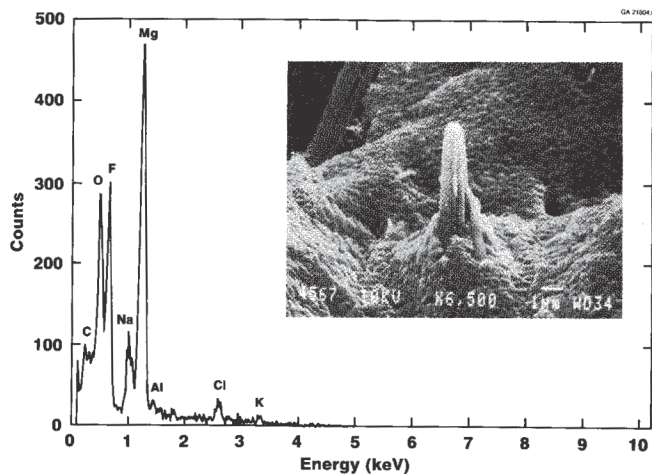
Composition of Solid Oxide Film (Al-4.5 Mg) Figure 6B



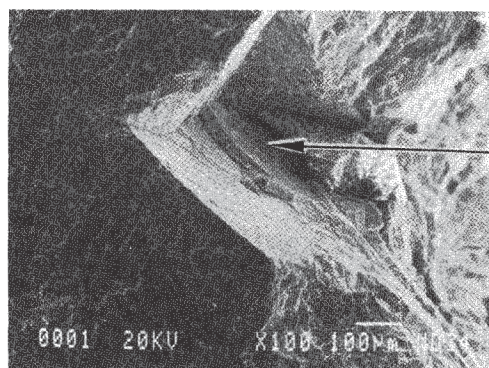
Bulk Salt Composition
Figure 7A



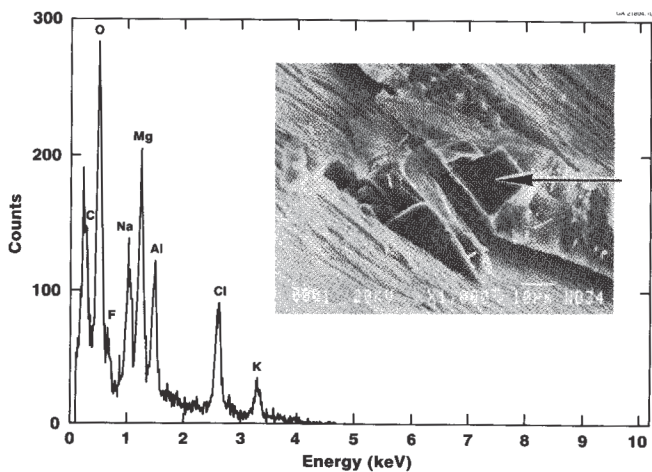
Sodium Fluoride Precipitate in Bulk Salt
Figure 7B



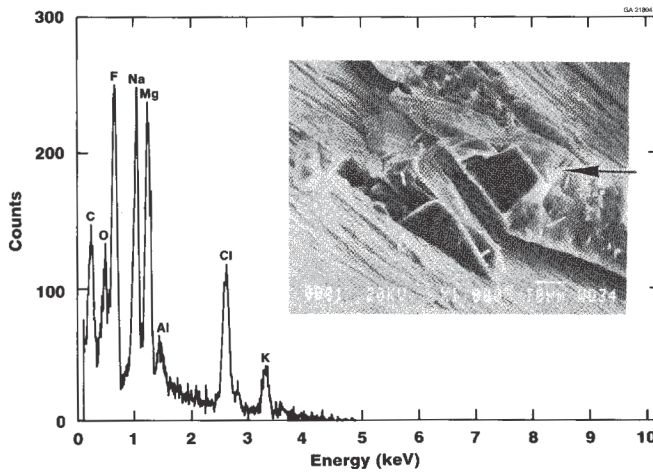
Composition of "Obelisk" in Salt - Al/Mg Oxide
Figure 8



Oxide Skin Fragment in Salt
Figure 9



Composition of Center of Oxide Fragment
Figure 10



Composition of Periphery of Oxide Fragment
Figure 11

For test temperatures $>750^{\circ}\text{C}$, t_R started to decline for tests with exposure times longer than 45 min. This corresponds with a decline in skin strength for the Al-Mg alloys under the same test conditions, caused by run-away oxidation, which destroys the structural integrity of the oxide skin. Obviously, salt can penetrate those skins more easily than tight, dense skins.

The photo series of Figure 5 show the wetting of the oxide skin of a droplet by the salt and the total disintegration of the skins, even solid, dense skins of predominantly MgAl_2O_4 spinel, such as the one depicted in Figure 6.² The EDX spectrum in Figure 6A represents the "hairy" MgO growth on the oxide-atmosphere interface and the spectrum in Figure 6B is taken from the solid, 15 μm thick, cross-section of the familiar grape-like growth of spinel on molten Al-Mg alloys. Note the different Mg-Al-O ratios.

The oxide fragments vary in size and the Al_2O_3 fragments from pure aluminum oxidation tests were not as easily distinguishable as the ones from the Al-Mg tests, but the blackening of the salt suggested the presence of the oxides. Several larger oxide fragments from the Al-Mg alloy tests could be traced in the salt after cooling and investigated in the SEM.

Salt Analysis

Wet chemical analysis of the salt after the tests confirmed the presence of aluminum oxide (hydrates) and possibly NaF in the pure aluminum tests, and MgO , MgAl_2O_4 , traces of MgF_2 , and possibly several other Al-Mg- δ -oxy-hydrates in the Al-Mg alloy tests.

Searching for the fragments in the SEM was difficult at first because the well-wetted particles were not exposed at the solidified salt surface or even on the surface of crushed salt particles. Using EDX scanning spectra it was possible to spot areas of increased concentration of Mg or other elements associated with the presence of the oxide fragments.

Figure 7A shows the bulk salt concentration. The fluorine and oxygen peaks are indistinguishable in the background noise.

Focusing on the rod structures in Figure 7B revealed a concentration of sodium and fluorine suggesting NaF. Although a minor presence of aluminum could be shown in the environment, no distinct oxide particles could be found in salt used in pure aluminum tests.

In salt from Al-Mg alloy tests, the "obelisks" as shown in Figure 8 were a sign of subsurface presence of a magnesium-containing oxide particle. In fact, the composition of these obelisks is a mixture of predominantly MgO , MgF_2 , and NaF, or MgNaF_3 , or may be an oxy-fluoride compound since the spectrum is rather consistent in different obelisks.

Figure 9 depicts an oxide particle, uncovered by shaving away the surface salt in an obelisk area. Figure 10 is a close-up of a fracture surface of the oxide particle and its composition, while Figure 11 represents the composition of the immediate surroundings of the particle. Note the difference in Na, F, Al and O concentrations on the two sides of the interface.

Although the actual chemical composition of the particles and the surroundings cannot be determined with this method, it is reasonable to speculate that NaF plays a role in the salt-oxide interaction. This was surprising since KF is the original compound added to the equimolar mixture of NaCl/KCl.

Thermodynamically, NaF is more stable than KF as can be seen in Figure 1. Furthermore, KCl is more stable than NaCl so the exchange reaction can take place since the net ΔG is decidedly negative in the temperature range of the tests.

Reviewing Figures 10 and 11, it is suggested that a Na-Mg-F complex is formed at the interface. Since oxide solubility in chloride salts is negligible, but significant in fluorides, it can be speculated that mechanistically the disintegration of the oxide skin is initiated by the intense wetting of the oxide by the salt, probably penetrating along grain boundaries (surface tension effect). The disintegration is completed by partial dissolution of oxides in the salt, locally enriched in fluorides (Gibbs free energy effect). This will, in time, destroy the coherency of the skin and the oxide fragments will be completely surrounded by salt and carried off in the suspension. It follows that the thicker and denser the skin originally is, the more time it will take to completely separate the oxide from the metal, which explains the behavior of t_R in Figure 4.

CONCLUSIONS

Coalescence and recovery of aluminum when melting scrap or skin under dilute molten flux are maximized at fluoride concentrations above 10 wt.% for NaF and KF at $760\text{--}800^{\circ}\text{C}$. Coalescence declines above 10 wt.% for MgF_2 and CaF_2 at 760°C , but is constant from 10–20 wt.% at 800°C . At 760°C , coalescence is higher with NaF and KF than with MgF_2 and CaF_2 .

Experimentally, it has been demonstrated that salts, especially those containing fluoride, can destroy and entirely remove strong, dense oxide skins from molten aluminum alloys, which can then freely coalesce, provided the oxide concentration is kept below approximately 10%. At higher oxide concentrations, some form of mechanical agitation is required since coalescence is increasingly impaired due to the change in viscosity.

The droplet test device proved to be a powerful tool to create reproducible oxide skins, which could be identified, measured and tested for strength. Exposure to salt reduced oxide skin strength of all test droplets to zero. The time required for complete destruction varied with skin strength and was directly proportional with the "rupture pressures" of skins exposed to identical test conditions.

There is strong evidence that the effective disintegration of oxide skins by salt is caused by a combination of surface energy reduction and increased local solubility of oxides in fluoride enriched salt.

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Recommended Reading

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