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THE INFLUENCE OF POTASSIUM SULPHATE IMPURITY ON THERMAL REACTIONS BETWEEN ALUMINUM AND POTASSIUM FLUORIDES

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ABSTRACT

The influence of up to 10 mol% of potassium sulphate impurity on the reactions between (i) $AlF_3 \cdot 3H_2O$ and KF and (ii) AlF_3 and $KF \cdot 2H_2O$ up to 600°C has been examined mainly by differential scanning calorimetry and X-ray analysis of products. The principal chemical reactions of the fluorides were not significantly influenced by the presence of sulphate. In application of the fluorides as chemical fluxes for metal-joining operations, any negative effect of the impurity may be related simply to a physical dilution process.

INTRODUCTION

Both compounds and mixtures prepared from aluminum and potassium fluorides are widely applied as chemical fluxes in metal fabrication processes for joining aluminum and its alloys [1]. The basis of action of the fluxes can be related to the chemical reactivities of their components towards the alloy/oxide system under consideration. The oxide films may be heterogeneous in composition with a range of stoichiometries and variable surface morphology [2].

The initiation of the principal reaction thrust of a flux is normally observed when it melts. In brazing practice [1], this temperature is believed to be optimized when it lies about 50°C below that at which the filler alloy melts. Thus, evaluations of the nature and mechanism of the various stages involved in the process of joining metals with the assistance of a chemical flux would be expected to emerge from an amalgam of thermal, structural and kinetic measurements.

Results obtained recently from X-ray and thermal studies of the reactions between hydrated and anhydrous forms of KF and AlF_3 in equimolar amounts showed that the product nature and distribution was sensitive to hydration [2]. This work has now been extended to include an assessment of the possible influence of a probable impurity salt on the course of these reactions.

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EXPERIMENTAL

Materials

K_2SO_4 and $KF \cdot 2H_2O$ were $> 99\%$ pure (Fisher). KF, AlF_3 and $AlF_3 \cdot 3H_2O$ were, respectively, 99, $\geqslant 99$ and 97%, pure (Alfa Inorganics). Sample authenticities were confirmed by X-ray analysis. All other reagents used were analytical grade.

Equipment

A Philips PW-1730 diffractometer was used for the X-ray measurements, Cu$K\alpha$ radiation, and a Du Pont 1090B system, equipped with a 910 scanning calorimeter cell and a 951 thermogravimetric analyzer, was used for thermal analyses.

RESULTS AND DISCUSSION

Products formed in the reactions of K_2SO_4 with a single reaction component were identified in preliminary tests in which the mixtures were heated at 10°C min^{-1} to 600°C in argon before quenching to ambient temperature.

Grains of AlF_3, $AlF_3 \cdot 3H_2O$, KF, $KF \cdot 2H_2O$, $KAlF_4$, α-Al_2O_3 and aluminum alloy powders were mixed with about 10 wt% K_2SO_4. Mixtures showing identifiable compositional differences in products from reactants were those formed from the reactions of sulphate with (i) $AlF_3 \cdot 3H_2O$, (ii) KF, and (iii) $KAlF_4$ which gave (i) AlF_3 (rhombohedral and tetragonal), (ii) KHF_2, and (iii) K_3AlF_6 in addition to K_2SO_4. No traces of sulphides, sulphites or thiosulphates were detected in any of the products.

The principal mixtures examined in the calorimetric experiments contained equimolar amounts of (i) $AlF_3 \cdot 3H_2O$ and KF or (ii) AlF_3 and $KF \cdot 2H_2O$. To each of these combinations K_2SO_4 was added at four concentration levels chosen from six values in the range 0.05–10.0 mol%.

Figure 1 shows a DSC scan determined in argon for an $AlF_3 \cdot 3H_2O/KF$ equimolar mixture containing 0.05 mol% K_2SO_4.

All K_2SO_4 additions, 0.05, 0.50, 1.00 and 2.50 mol%, lowered the overall value of ΔH for the reaction by 6–14% from that measured for the pure $AlF_3 \cdot 3H_2O/KF$ equimolar mixture [2], but no general or specific trends in the values were apparent. In a hermetically sealed container the overall ΔH for the $AlF_3 \cdot 3H_2O/KF$ mixture containing 2.5 mol% K_2SO_4 was $+117$ J g^{-1} compared to $+725$ J g^{-1} when the reaction was carried out in argon.

X-ray analysis of the products from the mixtures containing 0.5 and 2.5 mol% of potassium sulphate showed the presence of K_3AlF_6, $KAlF_4$ (traces) and γ-AlF_3 (tetragonal) after heating to 500°C. The sulphate was detected

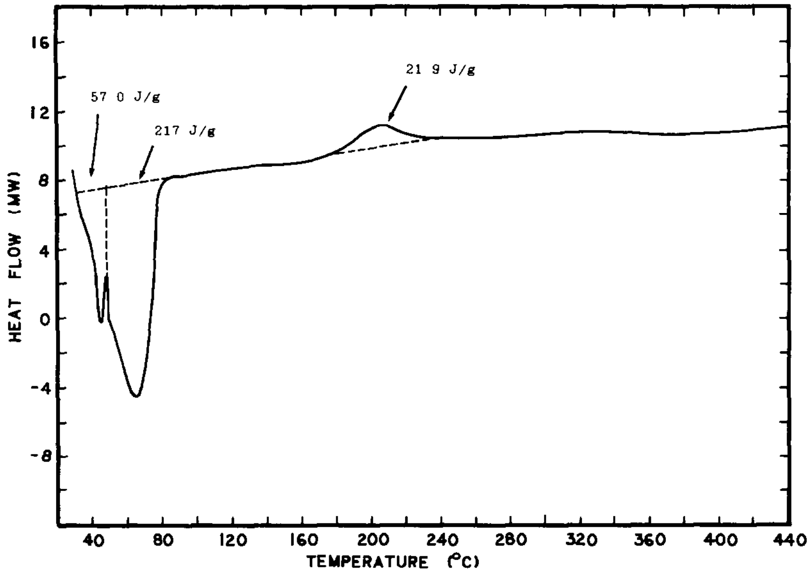

Fig. 1. DSC scan in argon for an $AlF_3 \cdot 3H_2O/KF$ equimolar mixture containing 0.05 mol% K_2SO_4.

only in the product from the 2.5 mol% addition. No sulphides, sulphites or thiosulphates were observed in either of the products.

In separate experiments, equimolar mixtures of $AlF_3 \cdot 3H_2O$ and KF with either 0.0, 0.5 or 2.5 mol% K_2SO_4 additions were heated at 10°C min^{-1} in argon flowing at 60 ml min^{-1} up to the temperatures at which the major endotherms closed. Samples were then quench-cooled to ambient temperature and analyzed by X-ray diffraction. The results are given in Table 1.

TABLE 1

X-ray diffraction data for residues quench-cooled from endotherm-closing temperatures

Reactants	Residue temperature before quenching (°C)	Products detected in residue
$AlF_3 \cdot 3H_2O/KF$	235	K_3AlF_6 (tetragonal); $K_2AlF_5 \cdot H_2O$
	283	K_3AlF_6; $K_2AlF_5 \cdot H_2O$
	500	K_3AlF_6; $KAlF_4$; γ-AlF_3 (tetragonal)
$AlF_3 \cdot 3H_2O/KF$ + 2.5 mol% K_2SO_4	235	K_3AlF_6; K_2SO_4; $K_2S_4O_6$ (?)
	285	K_3AlF_6; $K_2AlF_5 \cdot H_2O$ (?) K_2SO_4
$AlF_3 \cdot 3H_2O/KF$ + 0.5 mol% K_2SO_4	500	$KAlF_4$; K_3AlF_6
$AlF_3 \cdot 3H_2O/3KF$	500	K_3AlF_6

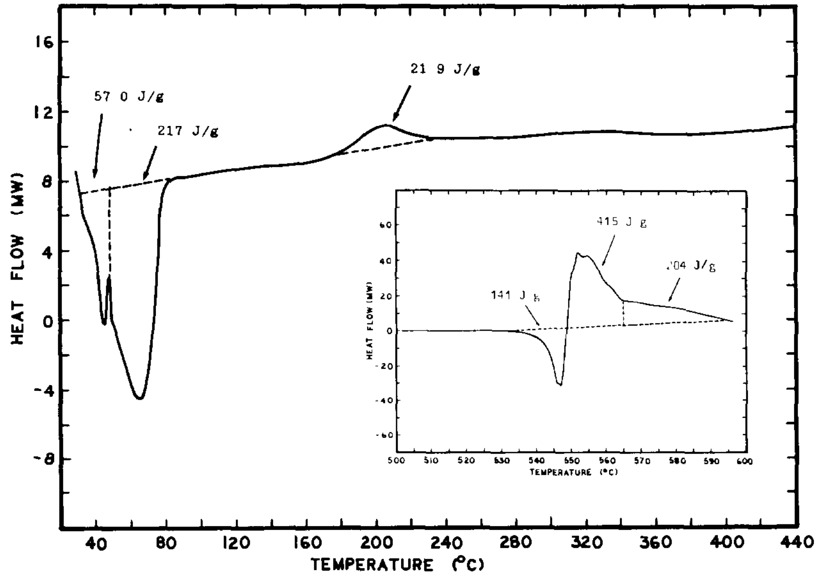

Fig. 2. DSC scan in argon for an $AlF_3/KF \cdot 2H_2O$ equimolar mixture containing 10.0 mol% K_2SO_4. Inset: DSC scan for same mixture contained in a hermetically sealed pan.

Data obtained for the residue from a 1 : 3 molar ratio mixture of $AlF_3 \cdot 3H_2O$ and KF heated to 600°C are included in the table.

For the measurements on the reactions between AlF_3 and $KF \cdot 2H_2O$, K_2SO_4 was added in molar concentrations of 0.05, 0.50, 5.00 and 10.0 mol%. In argon the heat changes observed were not so extensive with these mixtures. Figure 2 shows the DSC scan for an $AlF_3/KF \cdot 2H_2O$ equimolar mixture containing 10.0 mol% K_2SO_4. The changes in ΔH observed when samples were heated to 600°C in hermetically sealed pans are shown as an inset in Fig. 2.

X-ray measurements indicated that $KAlF_4$ was the principal component in all of the reaction products with K_3AlF_6 and AlF_3 (rhombohedral) also detected. There was again no evidence of the formation of sulphides, sulphites or thiosulphates while potassium sulphate was below the limit of detection in the residues from the 0.50 mol% additions. The mass loss of about 20% determined thermogravimetrically for these 0.05 mol% K_2SO_4 samples was similar to the calculated value.

The principal chemical reactions which occur in these fluoride mixtures on heating in the absence of impurities do not appear to have been affected significantly by the addition of potassium sulphate and the various step sequences in the reactions are likely to follow those proposed previously [2]. The K_2SO_4 additive was largely unreacted since even the formation of traces of the tetrathionate (disulphane disulphonate) in the $AlF_3 \cdot 3H_2O/KF + 2.5$ mol% K_2SO_4 reaction (Table 1) could not be proved unequivocally. A feasible sequence of formation for $K_2S_4O_6$ from K_2SO_4 would be through the oxidation of a thiosulphate intermediate [3] but no evidence supporting this possibility was apparent from the X-ray data.

No previous work has been reported regarding the possible interactions of an alkali metal sulphate with AlF_3/KF systems or with AlF_3. Some results have been recorded [4] on the thermodynamic excess functions for a series of alkali metal fluoride/sulphate liquid systems which include the potassium salts. Heats of mixing in KF/K_2SO_4 are small and mostly negative [5]. Explanations of these results have been based on charge asymmetry comparisons or the large differences in size between the small F^- and large SO_4^{2-} anions. The absence of any evidence which indicates extensive interactions between the fluoride and sulphate salts in the present experiments is consistent with these earlier observations and explanations.

The results of the few preliminary experiments which showed some distinctions between reactant and product compositions when a relatively large amount of potassium sulphate was mixed with only one reaction component can be related largely to expected thermal reactions [2]. For example, the presence of both rhombohedral and tetragonal forms of aluminum fluoride in the reaction of K_2SO_4 with $AlF_3 \cdot 3H_2O$ most probably shows the incomplete conversion of the tetragonal fluoride trihydrate to the rhombohedral anhydrous fluoride [2].

Since the deliberate addition of impurity amounts of potassium sulphate did not significantly influence the course of the thermal reactions between the various forms of aluminum and potassium fluorides, the fluxing action [6] of such a reaction product in metal-joining operations will probably only be affected deleteriously by virtue of the dilution effect created by the presence in the flux of a constituent that is chemically inactive towards the alloy/oxide interface.

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