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HYDRATION EFFECTS IN REACTIONS BETWEEN ALUMINUM AND POTASSIUM FLUORIDES

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ABSTRACT

The reactions occurring in equimolar mixtures of aluminum and potassium fluorides in both hydrated and anhydrous states have been studied mainly by thermal and X-ray analyses from ambient temperature to 650°C. Although the principal reaction product was normally K_3AlF_6 with $KAlF_4$ less prominent, the product distribution was sensitive to hydration. For example, the formation of $KAlF_4$ appeared to be favored at the expense of K_3AlF_6 in reactions of AlF_3 with $KF \cdot 2H_2O$ but not with KF. Reaction sequences are considered for each fluoride combination and a comparison of the interactions of KF and $KF \cdot 2H_2O$ with grains of aluminum and aluminum oxide used to indicate the potential of the experimental procedures in the assessment of the materials as chemical flux systems for metal joining operations.

INTRODUCTION

Metal fluorides have many applications in chemical and metallurgical industries ranging from ore extraction and processing to alloy and metal joining operations where the salts are used as fluxes in brazing, welding or soldering. For brazing aluminum the eutectic mixture formed by potassium and aluminum fluorides which melts about 572°C is a particularly effective and widely applied flux. The phase diagram for the KF/AlF_3 system has been published [1] but, naturally, it does not reveal subtleties of reactions related to important chemical features, such as the constitution of the reactants, their concentrations and types of impurities, nor does it relate to non-equilibrium conditions. Also, in practice, when the fluoride system is used as a flux the intervention of reactions between metal oxides and metals with the magma changes the chemical nature of the system and increases its complexity.

Fluxing action may be related to the chemical reactivity towards metal oxides [2,3] of the active complexes formed by the reactions of the constituent components in the flux. Knowledge of the nature of the complexes formed and the thermal and kinetic factors associated with their formation is thus basic to an understanding of flux action. This contribution was focused on complex formation with emphasis on compositions and enthalpy changes in reactions between equimolar components of aluminum and potassium fluorides when used in both hydrated and anhydrous forms.

EXPERIMENTAL

Materials

$KF \cdot 2H_2O$ was $> 99\%$ 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 were analytical grade.

Equipment

Thermal analyses were conducted with a DuPont 1090B system equipped with a 910 scanning calorimeter cell and a 951 thermogravimetric analyzer. A Philips PW-1730 diffractometer was used for the X-ray work with Cu K_α radiation.

RESULTS

Figure 1 shows DSC scans in argon for two separate samples of equimolar mixtures of $AlF_3 \cdot 3H_2O$ and $KF \cdot 2H_2O$. The ΔH values [4] for both samples are included. The spread in values, greatest for the displacements at low temperatures, became almost imperceptible at the final thermal step. DSC and TG measurements for the individual components of the mixture are shown in Figs. 2 and 3.

Similar data were established for equimolar mixtures of (i) $AlF_3 \cdot 3H_2O/KF$, (ii) $AlF_3/KF \cdot 2H_2O$ and (iii) AlF_3/KF as summarised in Table 1, which also includes measurements obtained for equimolar mixtures of $KF \cdot 2H_2O$ with aluminum and α-alumina powders.

The X-ray analytical results determined on samples that had been heated from ambient to 600°C in argon for 57–58 min in the DSC analyzer cell and then quenched back to ambient, are summarized in Table 2. The unallocated lines were usually very weak.

The crystal forms of the AlF_3, $AlF_3 \cdot 3H_2O$, KF and $KF \cdot 2H_2O$ starting materials were rhombohedral, tetragonal, cubic and orthorhombic, respectively. In the mixtures, unreacted AlF_3 showed as the rhombohedral form while $AlF_3 \cdot 3H_2O$ was decomposed to give tetragonal γ-AlF_3. The replacement of KF by $KF \cdot 2H_2O$ in the mixtures appeared to favor the formation

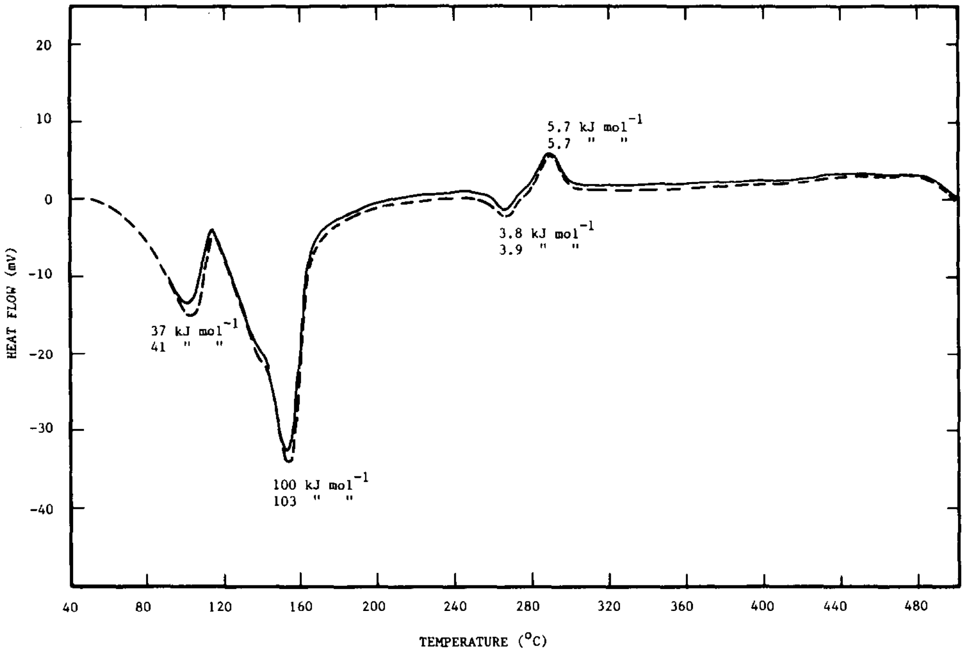

Fig. 1. DSC scan in argon for the equimolar mixture of $AlF_3 \cdot 3H_2O$ and $KF \cdot 2H_2O$.

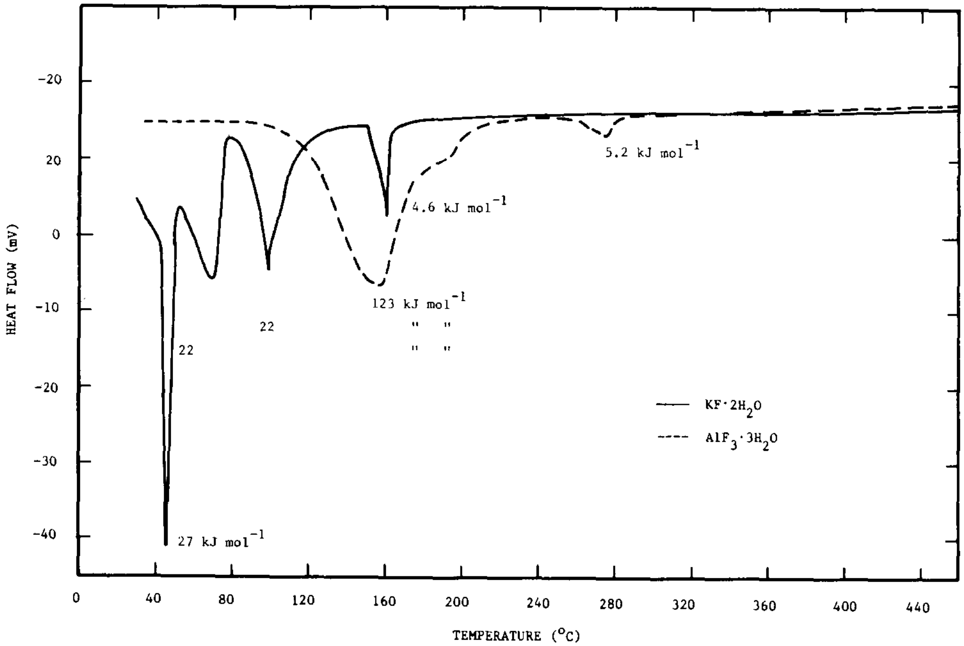

Fig. 2. DSC scans in argon for: (a) $AlF_3 \cdot 3H_2O$ and (b) $KF \cdot 2H_2O$.

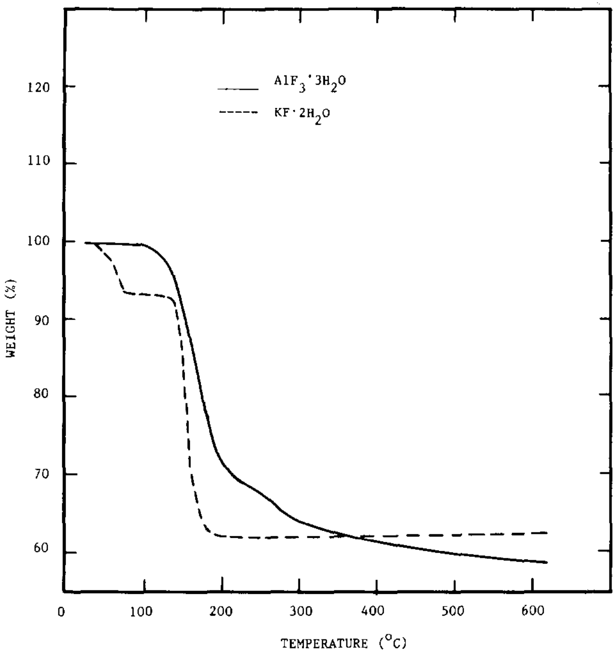

Fig. 3. TG measurements on (a) $AlF_3 \cdot 3H_2O$ and (b) $KF \cdot 2H_2O$.

of $KAlF_4$ at the expense of K_3AlF_6 as judged from the intensity ratio: $R = 3.08$ Å $(KAlF_4)/2.98$ Å(K_3AlF_6) which was measured as 0.12, 0.16, 0.93 and 1.6 in the reaction products from AlF_3/KF, $AlF_3 \cdot 3H_2O/KF$, $AlF_3 \cdot 3H_2O/KF \cdot 2H_2O$ and $AlF_3/KF \cdot 2H_2O$ mixtures, respectively.

Little or no reaction appeared to occur between Al_2O_3 and KF. In sharp contrast a violent reaction was observed when aluminum powder was mixed with $KF \cdot 2H_2O$ (CAUTION).

The reaction between AlF_3 and KF was also examined in the scanning calorimeter using hermetically sealed pans as sample containers (Fig. 4) in

TABLE 1

Thermal changes in the reactions of the equimolar mixtures of (i) the various potassium and aluminum fluorides and (ii) aluminum and α-alumina powders with $KF \cdot 2H_2O$

System	ΔH_1 (kJ mol^{-1})	Temperature range (°C)	ΔH_2 (kJ mol^{-1})	Temperature range (°C)	ΔH_3 (kJ mol^{-1})	Temperature range (°C)
$AlF_3 \cdot 3H_2O/KF$	149	160–240	–	–	–	–
$AlF_3/KF \cdot 2H_2O$	140	40–115	−7.8	180–240	–	–
AlF_3/KF	−1.8	175–240	–	–	–	–
$Al/KF \cdot 2H_2O$	21	120–190	4.3	190–240	3	365–435
$Al_2O_3/KF \cdot 2H_2O$	66	40–60	38	60–150	20	150–165

TABLE 2

X-ray analysis of the products formed from the reactions in the equimolar mixtures at 600°C in argon flowing at 60 ml min^{-1} (NTP)

System	Reaction products
$AlF_3 \cdot 3H_2O/KF \cdot 2H_2O$	K_3AlF_6, $KAlF_4$, γ-AlF_3(tetragonal) and lines at 3.45, 2.37, 2.25 and 2.21 Å
$AlF_3 \cdot 3H_2O/KF$	K_3AlF_6, γ-AlF_3 and line at 3.45 Å
$AlF_3/KF \cdot 2H_2O$	$KAlF_4$, K_3AlF_6, AlF_3 (rhombohedral) and lines at 3.58 (?), 2.37, 2.28 and 2.24 Å
AlF_3/KF	K_3AlF_6, AlF_3, $KAlF_4$ and lines at 3.58, 2.76, 2.38, 2.28 and 2.01 Å
$Al/KF \cdot 2H_2O$	K_3AlF_6, Al, $KF \cdot 2H_2O$ (minor) and lines at 3.58, 2.38 and 2.28 Å
Al/KF	K_3AlF_6, Al and lines at 6.95, 3.46 and 2.31 Å
$Al_2O_3/KF \cdot 2H_2O$	α-Al_2O_3, K_3AlF_6 (minor)
Al_2O_3/KF	α-Al_2O_3, KF

contrast with the previous measurements which were made using pans open to the argon atmosphere. This figure shows the endotherm given by the eutectic mixture which melts in the vicinity of 572°C.

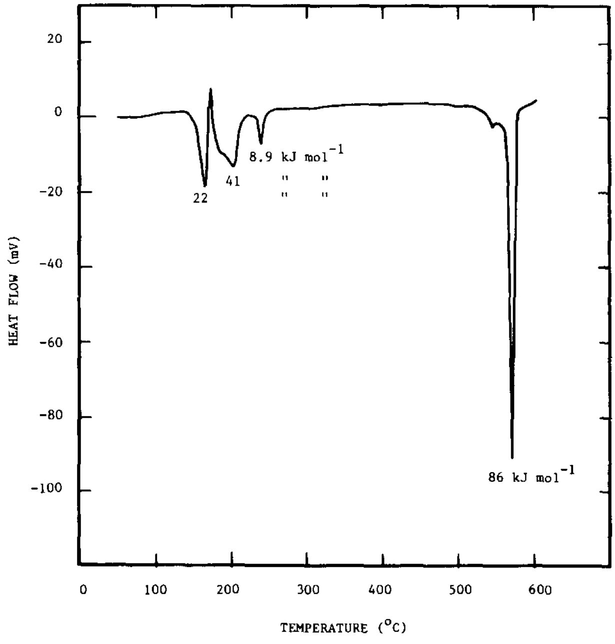

Fig. 4. DSC scan of AlF_3/KF equimolar mixture contained in a hermetically sealed pan.

DISCUSSION

The AlF_3/KF reaction starts at approximately 180°C in argon where a DSC endotherm was also observed with anhydrous KF and where TG indicated an apparent gain of 0.2% in sample mass for this fluoride. The presence of KHF_2 impurity in the potassium fluoride might have explained these initial changes since the bifluoride shows thermal transformations in this temperature region [5] but, if present, the amount was below the limit of detection by X-ray diffraction.

The principal product formed in the KF/AlF_3 reaction was K_3AlF_6:

$$3\delta KF(c) + AlF_3(c) \rightarrow \delta K_3AlF_6(c) + (1-\delta)AlF_3(c) \qquad (1)$$

AlF_3 was also detected along with a minor quantity of $KAlF_4$. Previously, for the gas phase reaction:

$$KF(g) + AlF_3(g) \rightarrow KAlF_4(g) \qquad (2)$$

an enthalpy value of about +84 kcal mol^{-1} was determined at 1020 K [6]. Thus, although an equimolar mixture does not contain sufficient KF to yield K_3AlF_6 stoichiometrically, reaction (1) was still preferred up to 600°C.

When rhombohedral AlF_3 was replaced by tetragonal $AlF_3 \cdot 3H_2O$ in the equimolar mixture, only K_3AlF_6 and γ-AlF_3 were detected in the products (Table 2). The DSC scan for the mixture showed a similar pattern to that given by the simple salt, $AlF_3 \cdot 3H_2O$, for which ΔH values of 135 and 6 kJ mol^{-1} were measured during dehydration from 80 to 240 and 240 to 300°C, respectively. In this mixture, the formation of potassium hexafluoaluminate by reaction (1) would be sequential to the dehydration of the aluminum fluoride trihydrate.

The distribution of products in the reaction between $AlF_3 \cdot 3H_2O$ and KF can be explained by the intervention of an initial dehydration step which yields AlF_3 and paces the formation of K_3AlF_6 in relationship to the availability of the anhydrous form of aluminum fluoride (eqn. 1). This hexafluoaluminate may subsequently react with additional AlF_3 from the dehydration step to yield $KAlF_4$:

$$K_3AlF_6(c) + 2AlF_3(c) \rightarrow 3KAlF_4(c) \qquad (3)$$

Evidence supporting this possibility was obtained by analysis of products formed from reactant mixtures in various mole ratios which had been heated in argon at 600°C for 1 h. For 4:1, 2:1, 1:1 and 1:2 K_3AlF_6/AlF_3 mixtures, the $KAlF_4$ (2.52 Å)/K_3AlF_6 (2.42 Å) intensity (cps) ratios were: 50/190, 230/130, 230/trace and 300/0. These data showed a progressive disappearance of K_3AlF_6 as the mole ratio of reactants approached the stoichiometry represented in eqn. (3). The results were confirmed by FTIR analysis of the specimens using relative peak height comparisons of signals allocated [7] to $KAlF_4$ at 750 and 600 cm^{-1} and K_3AlF_6 at 580 cm^{-1}.

Both of these fluoaluminates contain AlF_6 octahedral units as in the cryolite, Na_3AlF_6, structure [8]. The formation of a $KAlF_4$ layer lattice from the potassium analog of cryolite would basically then involve the sharing of all four equatorial fluoride ions in the AlF_6 octahedral unit with neighboring octahedra.

Thermogravimetry showed that all water of hydration had been discharged by 195°C in samples of $KF \cdot 2H_2O$ (loss: found, 39%; theory, 39%). With $AlF_3 \cdot 3H_2O$ about 30% of the total sample mass was lost at a fast rate between ambient and 200°C, the next 5% was evolved more slowly between 200 and 300°C and the balancing 5% came off between 200 and 600°C at a very slow rate. The mass loss from $AlF_3 \cdot 3H_2O$ from 195 to 600°C thus lay between 0.50 and 1.00 mol H_2O, $\alpha = 2.00$–2.50. The main reaction seems likely to be:

$$KF(c) + AlF_3(3-\alpha)H_2O(c) \rightarrow KAlF_4(c) + (3-\alpha)H_2O(g) \tag{4}$$

with a minor contribution expected from (1) especially at the higher temperatures when the fully dehydrated aluminum fluoride is present. These proposals are in agreement with the X-ray evaluations of the reaction products.

ΔH for the dehydration of $KF \cdot 2H_2O$ was 73 ± 2 kJ mol^{-1} and this step is apparently the initial one in the reaction between $KF \cdot 2H_2O$ and AlF_3 from 40 to 180°C. The principal aluminofluoride formed was tetragonal $KAlF_4$ consistent with a one-to-one inter-solid reaction between KF and AlF_3 similar to that illustrated (Fig. 4) where the phase-change endotherm at 574 ± 2°C for the sample in the hermetically sealed pan corresponds to the melting temperature of $KAlF_4$ [9].

The formation of $KAlF_4$ from the intermediate $K_2AlF_5 \cdot H_2O$ has been explained by lattice defect mechanisms based on electrical conductivity measurements [10]. Contamination of the product by K_3AlF_6 was believed to occur through the solid-state reaction of KF with $KAlF_4$ prior to the melting point of the intermediate (625°C). Thus for reactions based on equimolar amounts of KF and AlF_3 if the KF is partly consumed in K_3AlF_6 formation then it would be expected that some AlF_3 would be detected in the products (Table 2).

Both thermal and X-ray measurements showed that there was practically no reaction between Al_2O_3, on the one hand, and KF or $KF \cdot 2H_2O$ on the other. A very slight trace of K_3AlF_6 was probably formed in the reaction with the dihydrate. In contrast, with aluminum metal powder, K_3AlF_6 was clearly present in the products from both the KF and $KF \cdot 2H_2O$ reactions. These observations reflect on the practical applications of the fluorides as fluxes and on existing concepts regarding the mechanism by which chemical fluxes operate in aluminum-joining operations; especially regarding the relative stabilities and reactivities of the metal and its oxide towards the fluxing agent.

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