Thermochimica Acta, 107 (1986) 321–329
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

# STRUCTURAL PROPERTIES AND CHEMICAL FLUX REACTIVITIES OF AQUEOUS SUSPENSIONS OF MIXTURES OF POTASSIUM TETRAFLUOROBORATE AND POTASSIUM FLUORIDE

ROBERT ANDERSON ROSS, SHAWN DORANN HEIER and REJEAN LEMAY

*ALCAN International Limited, Research and Development Centre, Box 8400, Kingston, Ontario K7L 4Z4 (Canada)*

(Received 14 April 1986)

## ABSTRACT

The nature of the products formed from aqueous suspensions of $KF/KBF_4$ mixtures was determined by optical microscopy, scanning calorimetry, thermogravimetry and X-ray diffraction. Emphasis was placed on identifying any changes which occurred as a result of ageing the suspensions at ambient temperature for various lengths of time, up to 21 h. Differences in the $\Delta H$ values obtained for the potassium tetrafluoroborate orthorhombic/cubic transition commencing at 282°C and for the decomposition/distillation reactions at 530–590°C, have been related to the surface activity of the metals used for the sample containers in the thermal analyses. The practical implications associated with ageing have been assessed through tests of the properties of the suspensions when these were used as chemical fluxes for brazing aluminum.

## INTRODUCTION

Inorganic halides have an important application as strong fluxes for metal-joining operations, including welding, soldering and brazing [1]. Fluoride systems are particularly applicable to the fluxing of surfaces whose oxide films are normally highly stable and unreactive towards most reagents. For example, to braze aluminum alloys successfully it is usually necessary to employ aggressive fluxing agents, such as compounds formed from mixtures of potassium and aluminum fluorides [2]. However, many details regarding the reaction chemistry of fluxes have not been uncovered and, consequently, the available literature on this subject is not extensive.

Unless the flux promotes the joining of metals in a consistent and secure fashion, it is clearly not useful for applications related to fabrication processes. Thus, with formulations designed for brazing operations, the bell-wether test of the flux must be its ability to form effective fillet joints. Many questions regarding the relationships between this joining property and flux chemistry remain to be answered.

0040-6031/86/$03.50

The current study considers those thermal properties of potassium tetrafluoroborate that may relate to its performance as a principal component in chemical fluxes, and then focuses on the effect of ageing mixed aqueous suspensions of KF and $KBF_4$ on the ability to braze aluminum. It was hoped to identify any changes in the nature of the suspensions through measurements of thermal and crystallographic properties, and then to assess possible relationships between these changes and flux activities in the brazing process.

## EXPERIMENTAL

Anhydrous potassium fluoride (Baker) was $\geqslant 99\%$ pure and potassium tetrafluoroborate (Fluka) was $> 97\%$ pure. Sample authenticities were confirmed by X-ray diffraction. In mixture preparation, the individual components were dried under vacuum for 12 h and weighed amounts were then mixed and crushed to a fine powder in an agate mortar. The product was further dried under vacuum in glass vials for 12 h. Other reagents were of the highest purity obtainable.

Thermal analyses were carried out with a Cahn Instruments TGA System 113X and a Du Pont 1090B unit equipped with a 910 scanning calorimeter cell. A Philips PW-1730 diffractometer was used for X-ray work with Cu $K\alpha$ radiation.

## RESULTS

The DSC scans for $KBF_4$ and for 1/5 and 5/1 molar ratio $KF/KBF_4$ dry mixtures, are shown in Fig. 1. Samples were held in sealed aluminum containers surrounded with argon at a flow of 60 ml $min^{-1}$ (NTP). The $\Delta H$ values [3] for the various heat changes are included in Fig. 1. The scan for $KBF_4$ held in a capped platinum container is shown in Fig. 2.

Thermogravimetric measurements were done in argon, using both aluminum and platinum containers. A sharp weight loss was always recorded at about 532°C when aluminum pans were used. With platinum, a slow and steady loss of weight was observed, usually commencing at about 524°C, but no abrupt changes were recorded. No shift in pattern of any weight loss curve was observed for tetrafluoroborate samples at 280–285°C, in either container.

Figures 3a and b show weight loss/temperature data for $KBF_4$ samples in aluminum and platinum pans temperature programmed to reach 620°C at a rate of 10°C $min^{-1}$. The results in Fig. 3c were obtained for samples heated in platinum pans in argon, either to 550°C in 15 min and kept at that temperature for 160 min, or to 600°C in 70 min and held there for 70 min.

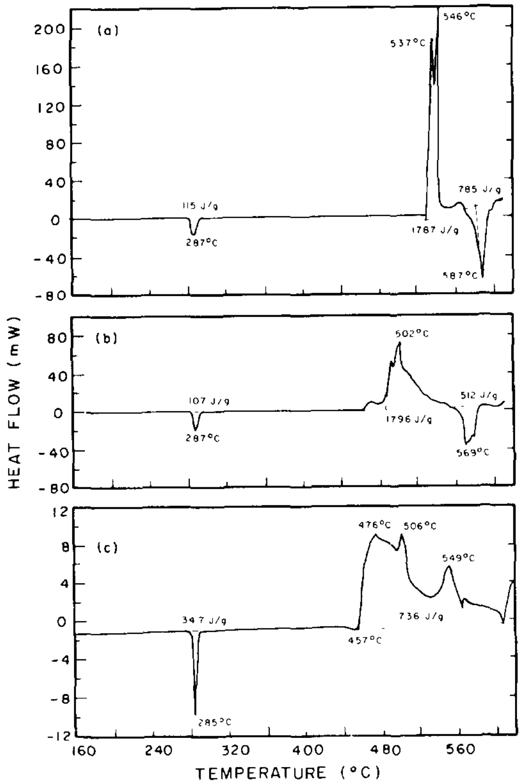

Fig. 1. DSC scans for (a) $KBF_4$, (b) 1/5 $KF/KBF_4$ and (c) 5/1 $KF/KBF_4$ molar ratio mixtures in sealed aluminum pans.

Under these conditions, the weight losses steadied at 57.7 and 60.3% at 550 and 600°C, respectively. Figure 4 shows weight loss/time curves for $KBF_4$ at 550 and 600°C, using platinum containers.

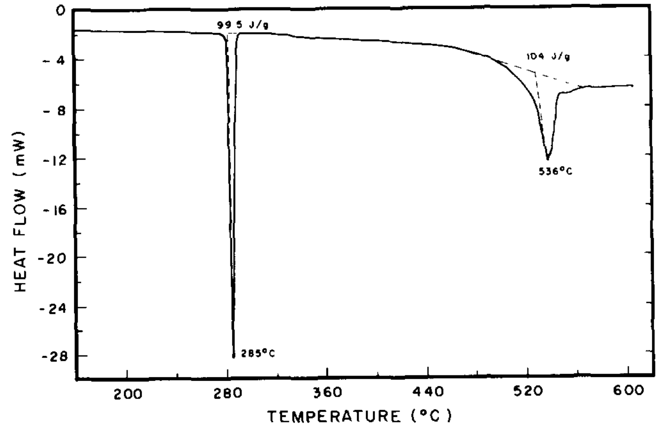

Fig. 2. DSC scan for $KBF_4$ in closed platinum pan.

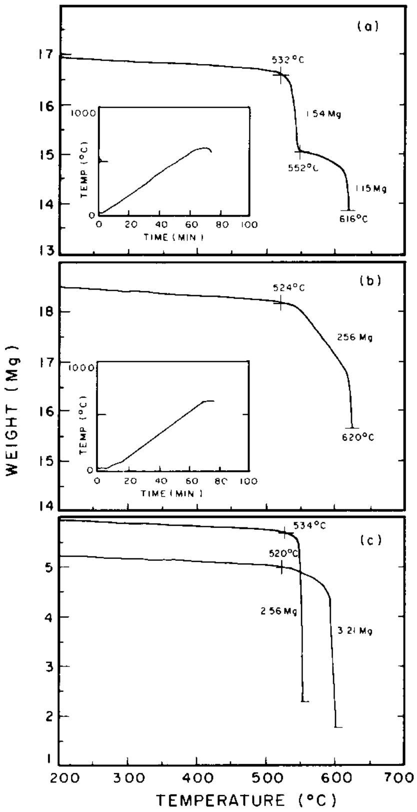

Fig. 3. Thermogravimetric data for $KBF_4$ in argon with open (a) aluminum, (b) and (c) platinum pans.

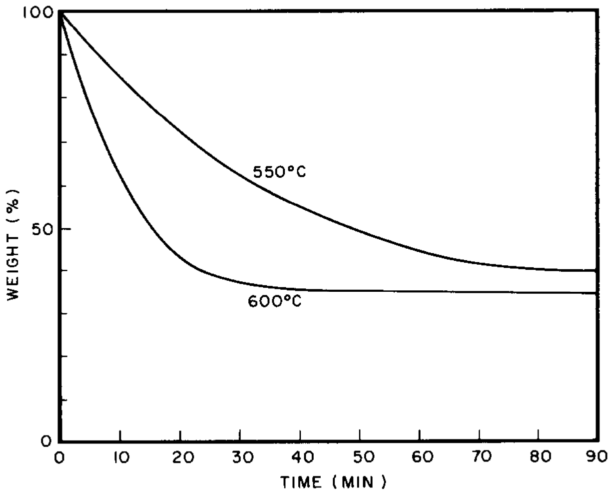

Fig. 4. Isothermal TGA curves for $KBF_4$ in argon with open platinum pans.

Potassium tetrafluoroborate samples were prepared in argon at temperatures on either side of the first DSC endotherm (250 and 310°C) in platinum containers for 12 h, quenched in liquid nitrogen and then allowed to recover to ambient temperature in the X-ray diffractometer. Both samples of $KBF_4$ had an *ortho*rhombic structure with major lines at 3.41, 3.26, 3.06 and 5.45 Å. The transition to a cubic structure at 280°C [4] was not observed since the phase was not retained on cooling to ambient temperature.

After reaction at 550 to 600°C, the aluminum containers were heavily discoloured and covered with a black film deposit. Platinum pans had a white deposit. The quantities of the residues in aluminum were too small to complete accurate X-ray identification and so the reactions were repeated, for confirmation, using granular samples of the reactants on a 5 g scale.

Aqueous suspensions of the two $KF/KBF_4$ mixtures were prepared for flux-brazing tests using L-bends of AA3003 alloy on AA 12 brazing sheet. Coupons of the sheet were degreased with acetone, dried and dip-coated in a stirred suspension for 60 s. Excess flux was shaken off and the coupons were dried in an air furnace for 5 min at 100°C. The L-bends were then placed securely on the coupons at 100°C in argon flowing at 1 l $min^{-1}$ (NTP) The furnace was programmed to reach 600°C in 12 min and then cooled to 500°C before the specimens were removed. The average flux coating weight on the coupons with this procedure was $10 \pm 1$ g $m^{-2}$ from a 15% w/v suspension. The range of thickness of the flux residue after brazing would be expected to lie between 3 and 23 $\mu$m [5].

All the suspensions demonstrated acceptable surface adhesion and spreading qualities, but only the 5/1 molar ration $KF/KBF_4$ mixture promoted fillet joint formation in the brazing experiments. In general, fillet joints were formed at about 585°C, but the uniformity of brazing was not high with this flux/alloy combination, within a given set comprising eight samples. Joints could be incomplete, irregular, discoloured and weak, even when pressure was applied across the samples during the brazing cycle.

The 5/1 $KF/KBF_4$ mixture was chosen for subsequent experiments related to suspension ageing, since this concentration ratio appeared most promising for brazing applications. Table 1 gives the essential details for the various stages of the preparation of the suspensions at 26°C.

Sample aliquots were analyzed by differential scanning calorimetry and X-ray diffraction, after air-drying at 100°C in a thinly spread layer over glass. The DSC data are summarized in Table 2.

The suspensions were also evaluated for brazing performance by the fillet tests. The observations from these experiments are recorded in Table 3 along with the X-ray diffraction data. The product ratios bracketed in the table are only approximations and the unknown phase which appeared after ageing suspensions for 6 h was not identified.

Raising suspension temperatures to 52°C for a few preparations showed that an acceptable brazed joint was formed after about half of the ageing

TABLE 1

Designation of flux samples formed from 5/1 $KF/KBF_4$ molar ratio mixtures at 26°C
Reaction volume 200 ml; stirrer speed $500 \pm 20$ rpm; solids concentration 15% w/v

| Sample designation | Preparation time (min) | Solution pH | Optical microscopy (200×) |
|---|---|---|---|
| A | Dry mixture | – | 20–45 μm particles |
| 0 | 15 | 9.85 | Opaque spheres |
| 1 | 75 | 9.95 | Clear surface film on spheres |
| 2 | 135 | 9.40 | Increasing film thickness |
| 6 | 375 | 9.05 | Clear, homogeneous aggregates (individual particles ~ 40–50 μm) |
| 21 | 1275 | – | Translucent gel |

TABLE 2

Summary of DSC data determined on aliquots of dried suspensions
Small, medium and large comparative heat changes are signified, respectively, by s, m, and l

| Sample | Endotherm temperatures (°C) | Exotherm temperatures (°C) |
|---|---|---|
| 0 | 53 (s) 245 (l) 445 (m) | 377 (l) 475–600 (s) |
| 1 | 53 (s) 250 (l) 465 (m) | None |
| 2 | 213 (s) 373 (s) 385 (s) 588 (s) | 55 (s) 290 (s) 438 (m) |
| 6 | 53 (s) 275 (s) 300 (l) 370 (s) | 200 (s) 213 (m) 225 (l) 357 (s) 560 (l) |
| 21 | 53 (s) 250 (s) 300 (l) 447 (s) | 373 (s) 375–500 ("bumps") |

TABLE 3

X-ray diffraction analysis and results of brazing tests with AA3003 and AA 12 brazing sheet

| Sample | X-ray analysis | Brazing observations |
|---|---|---|
| A | $KF/KBF_4$ | Not applicable |
| 0 | Not determined | No braze |
| 1 | $KBF_4$ | Very slight braze |
| 2 | $KF \cdot 2H_2O/KBF_4$ (3/1) | Slight braze |
| 6 | $KBF_4$/unknown (1/2) | Noticeable braze |
| 21 | $KF/KBF_4$/unknown (5/1/1) | Good braze |

time required at 26°C (Table 3). In contrast, no improvement in brazing performance of the fluxes was achieved by introducing surface pretreatments with 4 M sodium hydroxide or nitric acid, or with methyl alcohol/carbon tetrachloride mixtures [6]. The only pretreatment which seemed useful in terms of a perceptible improvement to the brazing process was a dip in 5% v/v HF for 30 s prior to the application of flux.

## DISCUSSION

The phase-change endotherm temperature for $KBF_4$, which starts at 282 ± 0.5°C and minimizes at 286 ± 0.5°C, is independant of the material used for the sample container. A maximum at 289 ± 5°C has been observed for a heat capacity anomoly in DTA measurements with this compound [7].

The magnitude of the $\Delta H$ change accompanying the phase transition was nearly 0.6 kJ less with the platinum container than the value of 14.5 ± 0.6 kJ $mol^{-1}$ obtained in aluminum. This is in agreement with the recent measurement of 14.2 ± 0.8 kJ $mol^{-1}$ for the heat of the phase transition [7], and is close to the value of 13.8 kJ $mol^{-1}$ reported earlier for the enthalpy of transition of $KBF_4$ measured in a copper block drop calorimeter [8]. Repeat runs using closed copper containers in the present DSC cell similarly gave a lower $\Delta H$ value for this transition than that measured using aluminum and platinum pans.

Differences in both thermodynamic and kinetic results derived from thermal analyses of samples held in containers made from a range of metals are often extensive for chemical changes such as decomposition reactions [9], and imply the intervention of significant interactions between the metal/metal oxide surface of the container and the powdered sample. Although the amount of energy involved in a phase-change transition is usually 10–20 times less than that for a chemical reaction, these slight differences in $\Delta H$ values at 280–290°C may still be related to variations in interactive surface potentials among the three metals identified.

The spontaneous change initiated at 529.6°C when the tetrafluoroborate began to react in the aluminum containers gave a $\Delta H$ of $-225$ kJ $mol^{-1}$. The closely related endothermic step, which lay in a temperature region usually associated with melting of the fluoroborate, absorbed $+99$ kJ $mol^{-1}$, to complete a compounded $\Delta H$ of $-126$ kJ $mol^{-1}$ in the 525 to 600°C region. Significantly different results were obtained in platinum. Only an endotherm was observed at these temperatures, with a $\Delta H$ of $+13$ kJ $mol^{-1}$.

The residue contained by platinum after the endothermic reaction was $KBF_4$, KF (minor quantity) and possibly some traces of $B_2O_3$. Apparently, no significant chemical reaction had occurred between platinum and potassium tetrafluoroborate. In consistence with the low value of $\Delta H$, distillation would be the dominant process. The black residue formed in reactions between $KBF_4$ and aluminum at 550°C was composed of $KAlF_4$ and some $K_3AlF_6$.

The initial reaction step between the tetrafluoroborate and aluminum is likely to involve disproportionation of $KBF_4$ to yield KF(s) and $BF_3$(g). The fluoride gas would be expected to react with the aluminum oxide film on the metal to yield aluminum fluoride and boron(III) oxide. Aluminum and potassium fluorides then readily combine to form $KAlF_4$, with the boron compound volatilizing from the surface, possibly as a complex oxyfluoride [10].

As might be anticipated, mixing KF with $KBF_4$ affected both the melting temperature and $\Delta H$ values for the tetrafluoroborate. The most significant changes were shown by the 5/1 KF/$KBF_4$ system, which contrasted with the KF impurity effect demonstrated by the 1/5 KF/$KBF_4$ mixture at the higher temperatures. Previous studies of the thermal stability of $KBF_4$ in the absence and presence of 20 mol% KF have indicated that the decomposition was repressed by the presence of fluoride ion [11]. The simple eutectic composition formed at 74.5 ± 1 mol% $KBF_4$ has been reported to melt at 460 ± 2°C [12].

The DSC results (Table 2) are clearly indicative of chemical changes taking place with ageing in the 5/1 KF/$KBF_4$ suspension, consistent with the microscopy observations which demonstrated a slow transformation at 26°C from an almost discrete suspension of opaque particles, after 15 min, to a translucent gel, after 20 h. The emergence of the unidentified component in the X-ray pattern of samples aged for 6 h or more is also in agreement with these data. Further, the presence of the unidentified component coincided with a noticeable enhancement in the brazing performance of the suspensions.

Although hydrolysis of potassium tetrafluoroborate is the key reaction in an aqueous KF/$KBF_4$ suspension, giving rise to fluoroboric acid, hydroxyfluoroboric acid and potassium fluoride [13], the compound does have a low solubility of approximately 0.6 g per 100 ml in saturated aqueous solutions at 25°C [14]. No significant increase in solution ion concentrations could be expected after hydrolysis and the very small variations observed in pH (Table 1) are consistent with this deduction. The hydrolysis reaction:

$$KBF_4(c) + xH_2O(l) \rightleftharpoons H^+[BF_3OH]^-(\text{surface}) + (x - 1)KF(aq) \quad (1)$$

when largely localized over the surface of the tetrafluoroborate particles would be a likely initiation source of gelatinous films, formed by condensation and polymerization steps involving the hydroxyfluoroboric acid. The amount of the freely water-soluble potassium fluoride present in the original flux mixture would influence the extent of hydrolysis. A number of hydroxyfluoroboric acids have been identified and are known to readily exchange $F^-$ ions [15].

For some understanding of the important properties of KF/$KBF_4$ mixtures for application as aluminum brazing fluxes, it remains to be explained why aged suspensions performed in a superior way to the more freshly prepared systems. This phenomenon is believed to be related to the availability and ease of formation of boron trifluoride from the reactants. At the brazing temperature, the fluxing action of the trifluoride on the aluminum oxide protective film may be represented:

$$Al_2O_3(c) + 2BF_3(g) \rightarrow 2AlF_3(c) + B_2O_3(l) \quad (2)$$

The aluminum oxide barrier to the free-flow of brazing alloy is removed and fillet joints are formed at the interface between the alloys. The source of boron trifluoride would be $KBF_4$ and hydrolyzed components [16]. The recognised fluxing action of $B_2O_3$ [17] might initiate subsequent reactions with other surface products or species but this possibility was not investigated.

The improvement in flux activity shown by the aged suspensions may then be a function of the gelatinous nature of the aggregate. On heating, the trifluoride will be released in a continuous and moderate way, reflecting migration from decomposition centres in the gel interior; thus, sufficient reaction contact time will occur with the aluminum oxide film. In sharp contrast, the surge of trifluoride from discrete powder samples of the tetrafluoroborate on thermal decomposition will allow most of the gas to escape into the vapour phase without contacting the alloy surfaces. This concept appeared to gain support from the positive results obtained by loosely encapsulating the L-bend specimens during separate brazing experiments, thereby securing a continuous atmosphere of the trifluoride for the test duration of approximately 30 s.

## ACKNOWLEDGMENTS

We are pleased to acknowledge the expert experimental contributions provided by our colleagues Florian East and Charles Cooney.

## REFERENCES

1 W. Rubin, Weld. J. (London), 61 (1982) 39.
2 R.A. Ross, F. East, C.B. Cooney, S. Heier, R. Lemay and A.M. Takacs, Thermochim. Acta, 101 (1986) 169.
3 S.L. Boersma, J. Am. Ceram. Soc., 38 (1955) 281.
4 M.J.R. Clark and H. Lynton, Can. J. Chem., 47 (1969) 2579; ASTM X-ray diffraction file 16-378.
5 R.A. Ross and R. Lemay, British Patent Application, 1986.
6 J.R. Kuppers, J. Electrochem. Soc., 125 (1978) 97.
7 G.S. Petrov, L.M. Volodkovich, R.A. Vecher and A.A. Vecher, Thermochim. Acta, 87 (1985) 383.
8 A.S. Dworkin and M.A. Bredig, J. Chem. Eng. Data, 15 (1970) 505.
9 R.A. Ross and A.M. Takacs, Ind. Eng. Chem., Prod. Res. Dev., 22 (1983) 280.
10 P. Baumgarten and W. Bruns, Ber. Dtsch. Chem. Ges. B, 74 (1941) 232.
11 K.H. Grothe and D. Franke, Inorg. Nucl. Chem. Lett., 7 (1971) 1173.
12 C.J. Barton, L.O. Gilpatrick, J.A. Bornmann, H.H. Stone, T.N. McVay and H. Insley, J. Inorg. Nucl. Chem., 33 (1971) 337.
13 H.S. Booth and D.R. Martin, Boron Trifluride and Its Derivatives, Wiley, New York, 1949.
14 R.C. Weast and M.J. Astle (Eds.), Handbook of Chemistry and Physics, 62nd edn., CRC Press Inc., Boca Raton, FL, 1981, p. B-133.
15 R.E. Mesmer and A.C. Rutenberg, Inorg. Chem., 12 (1973) 699.
16 R.E. Mesmer, K.M. Palen and C.F. Baes, Inorg. Chem., 12 (1973) 89.
17 C. Hirayama, J. Am. Ceram. Soc., 44 (1961) 602.