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Investigation of pseudo-ternary system AlF_3–KF–KCl

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Abstract

Liquidus in the pseudo-ternary system AlF_3–KF–KCl was investigated by thermal analysis. The aim of the study is to modify and improve the Nocolok flux used in aluminum brazing. The mentioned ternary system is divided into three sub-systems: K_3Cl_3–K_3F_3–K_3AlF_6, K_3Cl_3–K_3AlF_6–$KAlF_4$ and K_3Cl_3–$KAlF_4$–AlF_3. Ternary eutectics were observed in each sub-system: E_1 located at 2.5 mol% AlF_3, 44.7 mol% K_3F_3 and 52.8 mol% K_3Cl_3 at 584 °C; E_2 at 61.7 mol% AlF_3, 26.5 mol% K_3F_3 and 11.8 mol% K_3Cl_3 at 534 °C; E_3 at 63.7 mol% AlF_3, 20.7 mol% K_3F_3 and 15.6 mol% K_3Cl_3 at 541 °C. A mixture with the composition of point E_2 seems to be a good substrate for aluminum brazing flux since this lowered the melting temperature of the Nocolok flux from 558 to 534 °C.

Keywords: Fluoroaluminate; KCl; Phase diagram; Aluminum brazing; Nocolok flux

1. Introduction

In the most significant application of the system AlF_3–KF [1] in industry, the eutectic which melts at 558 °C, is used as an insoluble, non-corrosive flux for brazing aluminum and a few aluminum alloys. This is called the Nocolok method. The melting temperature of this eutectic is too high for brazing other aluminum alloys which have lower collapsed or over-burn temperatures. Hence, it is important to lower the melting temperature of this eutectic [2–4]. A number of studies of the phase relations in relevant systems have been reported in previous papers [5–8]. Here, we present a new attempt for modifying the Nocolok flux.

The system AlF_3–KF–KCl is a pseudo-ternary part in the reciprocal Al, K||F, Cl system as shown in Fig. 1. For the sake of clearity, K_3F_3 and K_3Cl_3 are used as component in all diagrams. Since K_3AlF_6 and $KAlF_4$ melts congruently [1], the system can be divided into three sub-systems: K_3F_3–K_3Cl_3–K_3AlF_6, K_3Cl_3–K_3AlF_6–$KAlF_4$ and K_3Cl_3–$KAlF_4$–AlF_3.

2. Experimental

KCl and anhydrous KF (A.R. grade, Beijing Chem. Works) were further anhydrated at 400 °C for 3 h; $AlF_3{\cdot}3.5H_2O$ (A.R. grade, Tianjin Chem. Works) was heated in N_2 plus HF atmospheres at 600 °C for 2 h, the product was identified as anhydrous AlF_3 by X-ray diffraction. All chemicals were kept in a desiccator before use.

Samples were prepared by mixing the weighed components with very small amount of NH_4HF_2. The prepared blends were put in Pt-crucibles with platinum covers, heated to 400 °C and annealed for 76 h. During the annealing process, grinding and mixing of the samples were repeatedly carried out in order to obtain homogeneous equilibrium samples.

A sample was put in a 15 ml platinum crucible which was placed in a self-evident furnace. The tem-

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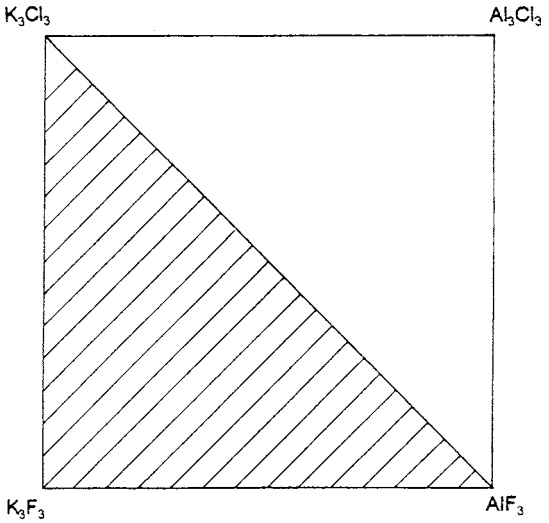

Fig. 1. The AlF_3–K_3F_3–K_3Cl_3 pseudo-ternary system in the location of Al, K||F, Cl reciprocal system.

perature of sample was recorded by a Pt–PtRh thermocouple calibrated by the melting points of standard substances. The EMF of the thermocouple was measured by a SANSE DMM 2650 digital milli-voltmeter. The error in measured temperature was ±1 °C. The melting samples were stirred during cooling to record the temperatures of the first batch crystals observed. The processes were observed under strong illuminating by a small microscope.

CR-G type high-temperature DTA equipment (Beijing Optical Instrument Inc.) was employed and calibrated by using standard substances with known melting points (calibrating both the heating and cooling curves). Calcined Al_2O_3 was used as a reference substance. The heating rate was 15 °C/min. Experiments were conducted in a dry air environment (relative humidity <30%).

Hydrolysis of fluorides is always a problem for constructing a phase diagram. In our early study of the phase diagram AlF_3–KF [1], a solution synthesis method was used for preparing the homogeneous and non-hydrolyzed samples. Because both Cl^- and F^- are present in the samples simultaneously in this study, we can not use the same method for preparing the samples. For dehydration of the $AlF_3{\cdot}3.5H_2O$, a protective stream of $N_2 + HF$ was used. As for preparing the blends of samples, a very small amount of NH_4HF_2 was added and milled together with components. The dissociation products of HF and NH_4F protect the blends from hydrolysis. The residues of HF and NH_4F in the samples are in the end driven out in the annealing process.

On the other hand, the moisture of the environment is also an important factor for hydrolysis. The procedures used in this study was performed in a relative humidity below 30%.

3. Results

Thirteen composition–temperature sections were studied by visual–thermal methods to construct this ternary system. The ternary eutectic points and some binary systems were also measured or confirmed by DTA determination. The distribution of sections on the composition triangle is shown in Fig. 2. The

Table 1
Experimental points on the liquidus of the system AlF_3–K_3F_3–K_3Cl_3

Numbers	Composition (mol%)			Temperature (°C)
	K_3Cl_3	K_3F_3	AlF_3	
1	5.0	78.2	16.8	800
2	12.0	74.3	13.7	794
3	20.0	69.5	10.5	751
4	35.8	58.8	5.4	660
5	45.0	51.7	3.3	627
6	49.8	47.5	2.7	618
7	55.0	41.5	3.5	603
8	59.0	34.9	6.1	648
9	62.2	26.0	11.8	686
10	59.0	19.0	22.0	709
11	50.0	21.0	29.0	693
12	45.0	22.3	32.7	676
13	35.8	25.2	39.0	642
14	20.0	27.5	52.5	574
15	15.5	27.0	57.5	554
16	9.0	27.5	63.5	540
17	5.0	28.5	66.5	548
18	14.0	24.0	62.0	538
19	5.0	23.1	71.9	563
20	9.0	22.5	68.5	555
21	12.0	21.6	66.4	548
22	20.0	18.6	61.4	550
23	27.0	13.8	59.2	558
24	32.0	9.0	59.0	566
25	35.8	4.2	60.0	573

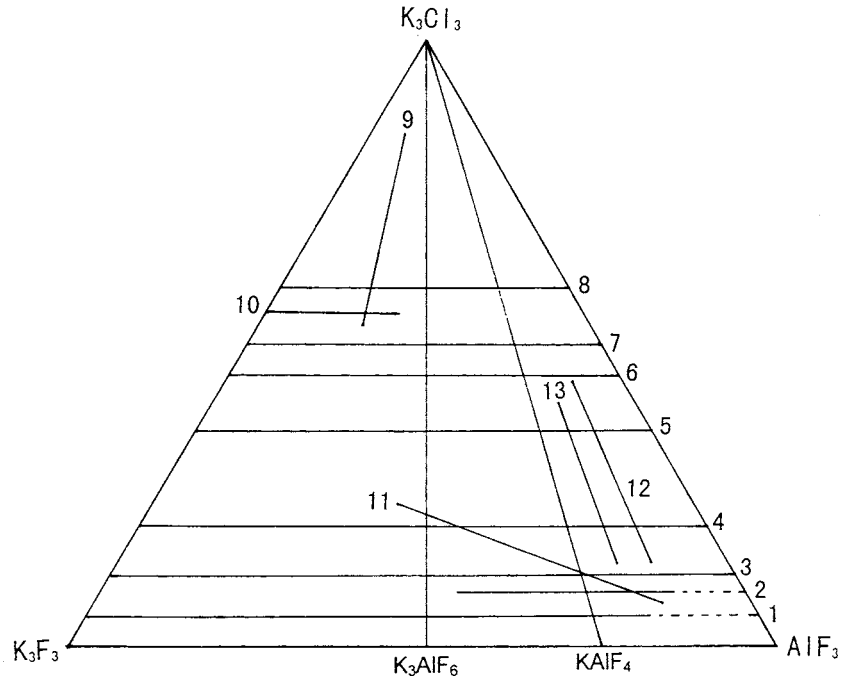

Fig. 2. The distribution of thirteen sections on the composition triangle.

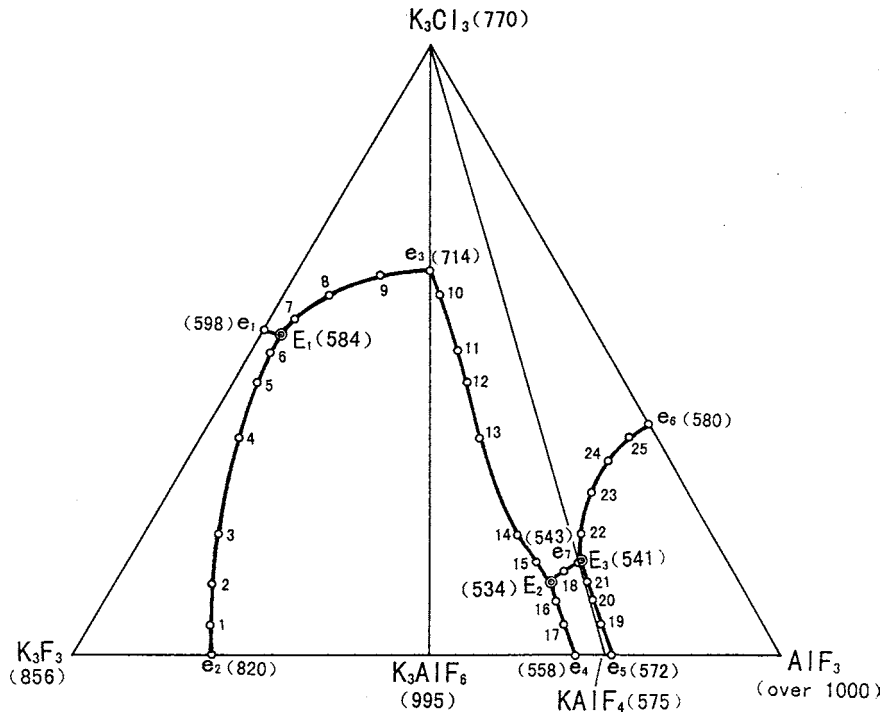

Fig. 3. Orthogonal projection of the AlF_3–K_3F_3–K_3Cl_3 system (numbers refer to samples given in Table 1).

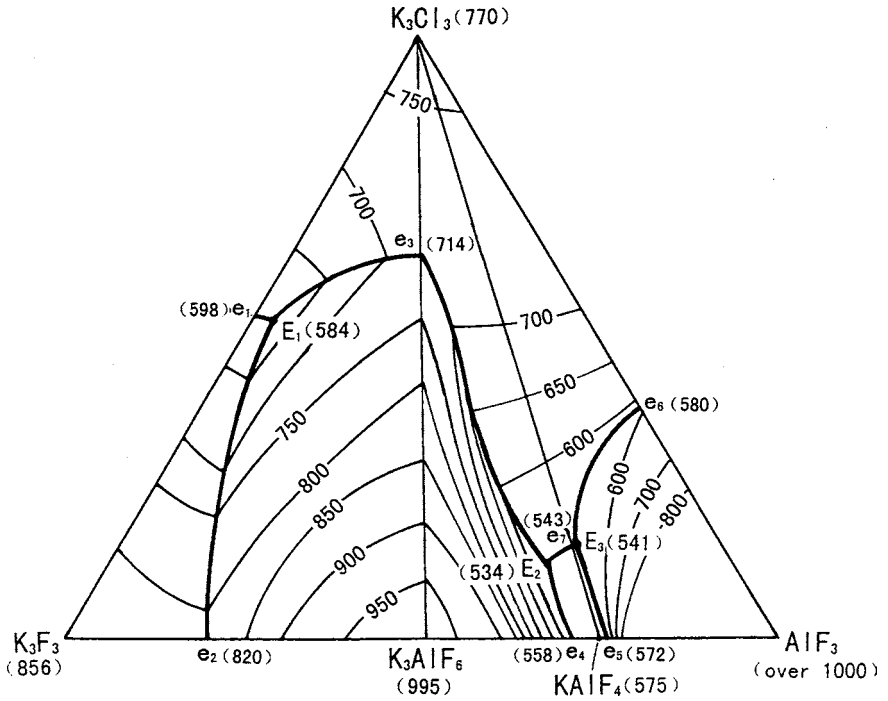

Fig. 4. Isotherms in the AlF_3–K_3F_3–K_3Cl_3 system.

experimental determinations of the liquidus are listed in Table 1, while invariant points in the system are shown in Table 2. The corresponding phase diagram and isotherms are presented in Figs. 3 and 4.

Table 2
Non-variant points in the ternary system AlF_3–K_3F_3–K_3Cl_3

Invariant point	Composition (mol%)			Temperature (°C)
	K_3Cl_3	K_3F_3	AlF_3	
e_1	53.2	46.8		598
e_2		81.6	18.4	820
e_3	63.0	18.5	18.5	714
e_4		29.4	70.6	558
e_5		24.3	75.7	572
e_6	38.2		61.8	580
e_7	15.3	21.3	63.4	543
E_1	52.8	44.7	2.5	584
E_2	11.8	26.5	61.7	534
E_3	15.6	20.7	63.7	541
K_3AlF_6				995
$KAlF_4$				575

e_1 to e_6: binary eutectics; E_1 to E_3: ternary eutectics in Figs. 3 and 4.

3.1. System K_3F_3–K_3Cl_3–K_3AlF_6

A study of this system has been reported by Mal'tsev and Bukhalova [9]. We have redetermined the ternary system along with the two binary sub-systems K_3F_3–K_3Cl_3 and K_3Cl_3–K_3AlF_6. The results have no large divergence from Mal'tsev's data. The data for the binary system K_3F_3–K_3AlF_6 were directly taken from our early published work [1]. All sub-systems are simple eutectic ones, whose data are listed in Table 2. The ternary eutectic point E_1 found in this K_3F_3–K_3Cl_3–K_3AlF_6 system are located in 52.8 mol% K_3Cl_3, 44.7 mol% K_3F_3 and 2.5 mol% AlF_3 at 584 °C.

3.2. System AlF_3–$KAlF_4$–K_3Cl_3

Because $KAlF_4$ is a congruent melting compound [1], the ternary system AlF_3–$KAlF_4$–K_3Cl_3 can be considered as a independent one. The binary systems AlF_3–K_3Cl_3 and $KAlF_4$–K_3Cl_3 which all are simple eutectic ones were first studied. The eutectic e_6

in the former system is located at 61.8 mol% AlF_3 at 580 °C, while the eutectic e_7 in the latter system is located at 84.7 mol% $KAlF_4$ (63.4 mol% AlF_3, 15.3 mol% K_3Cl_3, 21.3 mol% K_3F_3) at 543 °C. Data for e_5 at 572 °C were taken from our early work [1]. The ternary eutectic point E_3 melting at 541 °C is located at 63.7 mol% AlF_3, 20.7 mol% K_3F_3 and 15.6 mol% K_3Cl_3. Thus, it is found to be very close to the composition of the binary eutectic e_7.

3.3. System K_3AlF_6–$KAlF_4$–K_3Cl_3

This system seems to be the most useful one for modifying the Nocolok flux. In fact, the composition of Nocolok flux is at e_4, which denotes the binary eutectic in system K_3AlF_6–$KAlF_4$ [1]. As the content of KCl increased, the temperature of e_4 decreased along the binary eutectic line from e_4 to E_2. E_2 is the ternary eutectic point at 61.7 mol% AlF_3, 26.5 mol% K_3F_3 and 11.8 mol% K_3Cl_3 at 534 °C in this K_3AlF_6–$KAlF_4$–K_3Cl_3 system. Note that the melting temperature of E_2 is the lowest one for all the compositions of the AlF_3–K_3F_3–K_3Cl_3 system. This can be used to lower the melting temperature of Nocolok flux from 558 to 534 °C. A lowering by 24 °C is less than observed for the systems we have studied before [5–8]. However, if we consider the lower price of KCl as an additive and the improved technical properties, this system is yet meaningful for aluminum brazing.

Acknowledgements

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