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Thermochimica Acta 354 (2000) 117–120

thermochimica acta

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Investigation of the systems $KAlF_4$–M_3AlF_6 (M=Rb, Cs)

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Received 27 August 1999; accepted 10 February 2000

Abstract

Phase relations in the systems $KAlF_4$–Rb_3AlF_6 and $KAlF_4$–Cs_3AlF_6 were investigated by DTA and XRD methods for the purpose of finding a low melting, non-corrosive aluminum flux. In each system, congruent compounds $Rb_3AlF_6{\cdot}2KAlF_4$ and $2Cs_3AlF_6{\cdot}3KAlF_4$ were observed, respectively. Eutectics located at 46 mol% Rb_3AlF_6 and 511°C, 25 mol% Rb_3AlF_6 and 512°C for the former system, and 48 mol% Cs_3AlF_6 and 550°C, 25 mol% Cs_3AlF_6 and 480°C in the latter were confirmed. The phase α-$2Cs_3AlF_6{\cdot}3KAlF_4$ was XRD indexed as having an orthorhombic cell a=10.401±0.003, b=10.078±0.006, c=8.792±0.006 Å.

Keywords: $KAlF_4$; Rb_3AlF_6; Cs_3AlF_6; Phase diagram

1. Introduction

The eutectic of $KAlF_4$–K_3AlF_6 occurring at 560°C is well known as Nocolok flux, which is widely used in the aluminum brazing technique. The temperature of the eutectic appears to be too high for brazing the most of other aluminum alloys. For the purpose of lowering the melting temperature of the flux, the ternary systems AlF_3–KF–CsF and AlF_3–KF–RbF should be taken into account. The pseudo-binary systems $KAlF_4$–Rb_3AlF_6 and $KAlF_4$–Cs_3AlF_6 are the two most important in these ternary systems. This research can be considered as a continuing study of the systems AlF_3–KF [1], AlF_3–RbF [2] and AlF_3–CsF [3], and also for the basis of patents [4,5].

2. Experimental

2.1. Preparation of fluorides

CsF (purity >99.5%, Beijing Chem. Work) was dehydrated at 400°C for 3 h; $AlF_3{\cdot}3.5H_2O$ (A.R., Tianjin Chem. Work) was heated in N_2 plus HF atmospheres at 600°C for 2 h, the product was identified as anhydrous AlF_3 by XRD. All fluorides were kept in a desiccator.

2.2. Preparation of samples

Samples were prepared by reacting mixtures of anhydrous AlF_3 with certain solutions of CsF in HF. Products were placed in Pt crucibles and heated until dry at 200°C, then annealed for 48 h at a higher temperature at which no melting of any phase would occur. During the annealing process, grinding and mixing of the samples were carried out repeatedly

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0040-6031/00/$ – see front matter
PII: S0040-6031(00)00452-4

Table 1
DTA data of the system Rb_3AlF_6–$KAlF_4$

$KAlF_4$ (mol%)	Eutectic 1 temperature (°C)	Eutectic 2 temperature (°C)	Liquidus temperature (°C)
0			878
12.5			855
25			770
39	513		690
50	513		595
52	512		573
54	511		
56	512		570
60	513		620
63	513		650
66.7			652
70			640
75		512	
78		511	605
80		513	594
85		512	
90		513	530
95			533
100			575

in order to obtain homogeneous and equilibrium samples.

2.3. Method for determination

A CR-G type high-temperature DTA equipment (Beijing Optical Instrument) was employed and calibrated with standard substances with known melting point (calibrating both in heating and in cooling). Al_2O_3 was used as the reference. The heating rate was 15°C min^{-1}. The liquidus temperature was determined from on cooling, and the other temperatures were determined by extended extrapolating initial temperature of the peaks on heating. Experiments were carried out in static dry air (relative humidity <30%). The error in measuring temperature was ±3°C.

2.4. X-ray powder diffraction analysis

Intermediates were determined by Rigaku Dmax 2400 X-ray diffractometery (Radiation

Table 2
DTA data of the system Cs_3AlF_6–$KAlF_4$

$KAlF_4$ (mol%)	Polymorphic transformation (°C)	Eutectic 1 temperature (°C)	Eutectic 2 temperature (°C)	Solidus temperature (°C)	Liquidus temperature (°C)
0					790
13.5					765
27		550			725
39		548			700
50	427				590
52					540
56					585
60	433		474		574
63					565
66.7	432		476		540
69					530
70	427		476		512
75	427				485
78					485
80	418		475		485
85			478	491	504
90			490	513	523
93			481	502	540
97			465	525	560
100					575

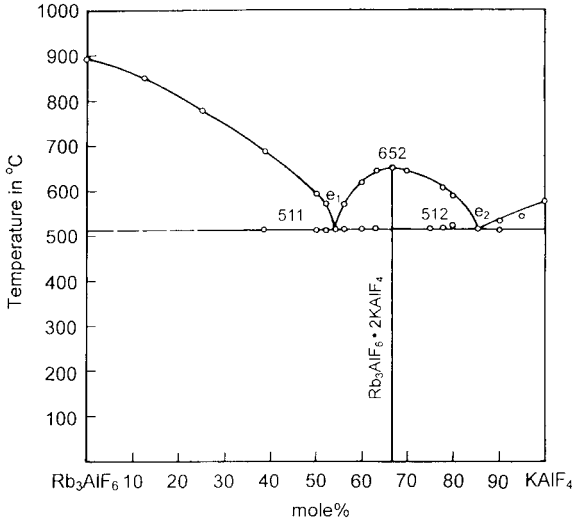

Fig. 1. Phase diagram of the pseudo-system $KAlF_4$–Rb_3AlF_6.

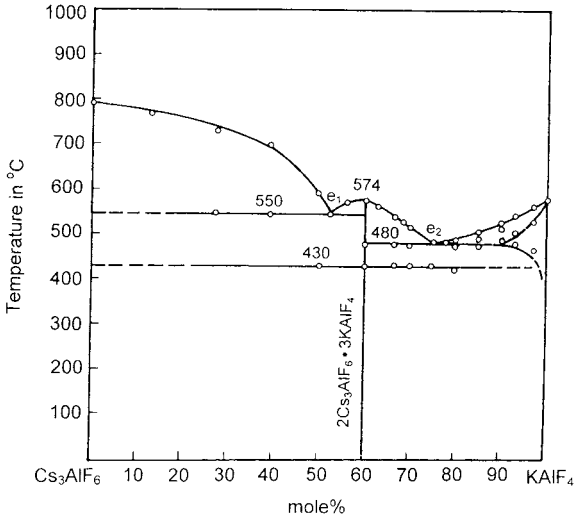

Fig. 2. Phase diagram of the pseudo-system $KAlF_4$–Cs_3AlF_6.

Cu$K\alpha$-λ=1.5409, Filter Ni). Si powder was added as a cross-reference for more precise determination of the absorbance lines in the diffraction patterns.

3. Results and discussion

Phase diagrams of $KAlF_4$–Rb_3AlF_6 and $KAlF_4$–Cs_3AlF_6 based on the results of DTA data listed in Tables 1 and 2 are given in Figs. 1 and 2.

Fig. 1 reveals the presence of an intermediate compound $Rb_3AlF_4 \cdot 2KAlF_4$ melting at 652°C and the system $KAlF_4$–Rb_3AlF_6 is divided into two eutectic systems. The e_1 and e_2 for the system were located at 46 mol% Rb_3AlF_6 at 511°C and 25 mol% Rb_3AlF_6 at 512°C, respectively.

In the pseudo-binary system $KAlF_4$–Cs_3AlF_6 which was also comprised of two sub-eutectic systems, a limited solid solution formed along with $KAlF_4$. The e_1 is at 48 mol% Cs_3AlF_6 and 550°C; e_2 at 25 mol% Cs_3AlF_6 and 480°C. The congruent melting compound $2Cs_3AlF_6 \cdot 3KAlF_4$ has a polymorphic transformation at 430°C. The XRD indexed data for α-$2Cs_3AlF_6 \cdot 3KAlF_4$ is listed in Table 3. The compound is orthorhombic, a=10.401±0.003, b=10.078±0.006, c=8.792±0.006 Å.

From these results, the binary systems $KAlF_4$–Rb_3AlF_6 and $KAlF_4$–Cs_3AlF_6 both form congruent melting compounds $Rb_3AlF_6 \cdot 2KAlF_4$ and $2Cs_3AlF_6 \cdot 3KAlF_4$. If this is compared with the system $KAlF_4$–K_3AlF_6, a simple eutectic at ca. 560°C [1] is observed. As K^+ ion is changed with the larger radius ion Rb^+, a congruent melting compound $Rb_3AlF_6 \cdot 2KAlF_4$ is formed. The larger ion Cs^+ produces more complex compound $2Cs_3AlF_6 \cdot 3KAlF_4$. Using cations with the larger radii lowers the melting point and produces more complex composition for the intermediate compounds.

In both systems the eutectic temperatures which were at 511 and 512°C for systems Rb_3AlF_6–$KAlF_4$; 550 and 480°C for Cs_3AlF_6–$KAlF_4$ were all lower than in K_3AlF_6–$KAlF_4$ (560°C). It is also important to enhance this with the eutectic e_2 in Cs_3AlF_6–$KAlF_4$. The temperature is as low as 480°C, the molten salt in this composition is expected to be a non-corrosive brazing flux for most aluminum alloys which have lower collapse or over burn temperatures.

Acknowledgements

The authors wish to acknowledge the support from Beijing Science Fund.

Table 3
Indexed data of $2Cs_3AlF_6 \cdot 3KAlF_4$[a]

d (Å) — observed	d (Å) — calculated	I/I_0	h	k	l
5.035	5.035	6	0	2	0
4.405	4.392	25	0	0	2
	4.371		0	2	1
4.081	4.092	11	2	1	1
3.748	3.751	10	1	1	2
3.619	3.616	10	2	2	0
3.195	3.195	17	1	3	0
	3.184		2	1	2
3.123	3.140	100	0	3	1
3.062	3.076	14	3	1	1
2.552	2.554	36	2	0	3
	2.519		0	4	0
2.516	2.516	16	4	1	0
2.361	2.360	7	1	4	1
2.212	2.210	32	0	3	3
2.082	2.083	6	5	0	0
2.046	2.046	7	3	2	3
	2.045		4	2	2
	1.980		1	5	0
1.978	1.978	14	1	2	4
	1.813		1	3	4
	1.809		4	4	0
1.806	1.806	24	1	5	2
	1.569		3	0	5
1.566	1.567	13	4	5	1
1.476	1.476	8	6	1	3
1.402	1.403	13	2	6	3
	1.400		4	5	3
	1.399		4	2	5
	1.337		4	3	5
1.335	1.335	6	0	6	4
1.280	1.280	5	7	4	0
	1.186		0	5	6
	1.185		7	5	1
	1.185		5	4	5
1.184	1.184	10	3	8	0
	1.183		5	7	0

[a] Orthorhombic cell $a=10.401\pm0.003$, $b=10.078\pm0.006$, $c=8.792\pm0.006$ Å.

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