Journal of Solid State Chemistry **161,** 80–84 (2001)
doi:10.1006/jssc.2001.9275, available online at http://www.idealibrary.com on IDEAL®

Investigation of the Ternary System AlF_3–KF–CsF

Rong Chen[1] and Qiyun Zhang

Department of Chemistry, Peking University, Beijing 100871, People's Republic of China

Received December 22, 2000; in revised form May 2, 2001; accepted June 8, 2001; published online August 22, 2001

For developing a new aluminum brazing flux, the liquidus in the ternary system AlF_3–KF–CsF was determined by DTA and visual polythermal methods. The results indicated that the region around E_4 (located in AlF_3 43 mol%, CsF 18 mol%, KF 39 mol%) and E_5 (AlF_3 45 mol%, CsF 18 mol%, KF 37 mol%), at which the melting temperatures are lower than 500°C, appears to be the best compositions for using as a modified Nocolok flux. The lower temperature region near $CsAlF_4$ may be another candidate composition. © 2001 Academic Press

Key Words: **AlF_3; KF; CsF; ternary phase diagram; Nocolok brazing.**

1. INTRODUCTION

The most significant application of the system AlF_3–KF (1–3) in industry is the eutectic which was used as an insoluble, noncorrosive flux called the Nocolok method for brazing aluminum and a few aluminum alloys. The temperature of this eutectic melting at 560°C seems to be too high for brazing most other aluminum alloys which have lower collapsed or over burn temperatures. For lowering the eutectic temperature in the system AlF_3–KF, many efforts have been made to add a third fluoride component into the binary system, but most failed because many simple fluorides with ionic structure such as alkaline-earth and rare-earth fluorides hardly dissolve in the eutectic melts even at high temperature. Alkaline fluorides RbF and CsF are the two simple compounds which could effectively influence the melting temperature of the eutectic in the system AlF_3–KF. Suzuki (4) patented the finding that some compositions in the AlF_3–KF–CsF system can be effectively used for modifying Nocolok fluxes. But no report has been published for the relative phase diagram so far. For this purpose, a detailed study has been done in this paper.

[1]To whom correspondence should be addressed. Fax: + 86(10)6275-1496. E-mail: Chenr@rose.nsfc.gov.cn.

2. EXPERIMENTAL

2.1. Preparation of Fluorides and Samples

The anhydrous K_2CO_3, $Al(OH)_3$, CsF, and 40% HF used are all AR grades. $Al(OH)_3$ and CsF were dried at 120°C for 1 h, and K_2CO_3 was dried until constant weight. The relative humidity of the environment was $<30\%$. According to the compositions of every specimen, certain weights of $Al(OH)_3$ and CsF were weighed into polypropylene containers. The samples were dissolved in excessive HF and then a K_2CO_3 solution with a known content was dropped in. The prepared blends were gradually heated to 100°C until dry and then annealed for 48 h at a higher temperature such that no melting of any phase could occur. During the annealing process, grinding and mixing of the samples were repeatedly carried out in order to obtain homogeneous and equilibrium samples.

2.2. Differential Thermal Analysis

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 dry air (relative humidity $<30\%$) in the static state.

2.3. Visual Polythermal Analysis

A sample was put in a 0.3-ml platinum crucible, which was welded on the tip of a Pt–PtRh thermocouple. The thermal potential was measured by a SANSE DMM 2650 digital voltmeter. The thermocouple used in the experiment was calibrated by standard substances. The melting of samples was observed under a magnifier. The error in measured temperature was ± 1°C.

3. RESULTS AND DISCUSSION

The side systems AlF_3–KF (3), AlF_3–CsF (5), and KF–CsF (6) have been thoroughly reported. It is indicated

0022-4596/01 $35.00
Copyright © 2001 by Academic Press
All rights of reproduction in any form reserved.

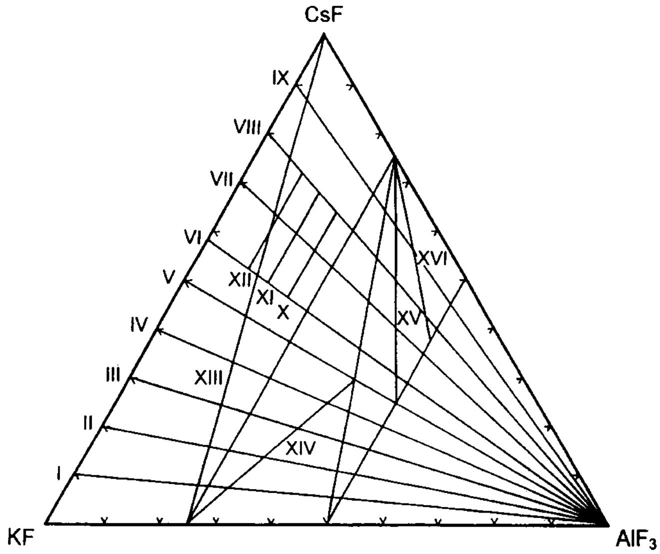

FIG. 1. Distribution of 19 sections (profiles) on the composition triangle.

TABLE 1
Terminal Composition of Profiles in the System AlF_3–KF–CsF

	Terminal 1 (mol%)			Terminal 2 (mol%)		
Profile	AlF_3	CsF	KF	AlF_3	CsF	KF
I		10	90	100		
II		20	80	100		
III		30	70	100		
IV		40	60	100		
V		50	50	100		
VI		58	42	100		
VII		70	30	100		
VIII		80	20	100		
IX		90	10	100		
X	20	64	16	20	46	34
XI	15	68	17	15	49	36
XII	10	72	18	10	52	38
XIII		100		25		75
XIV	40	30	30	25		75
XV	50	25	25	25	75	
XVI	50	37	13	25	75	

that intermediate compounds K_3AlF_6, $KAlF_4$ and Cs_3AlF_6, $CsAlF_4$ existed in the former two systems respectively. As for the system KF–CsF, Sangster and Pelton (6) optimized it as a simple eutectic one with an eutectic point at 57 mol% CsF at 625°C. According to the stability of these compounds, the system could be divided into five subsystems: 1, KF–CsF–K_3AlF_6; 2, CsF–K_3AlF_6–Cs_3AlF_6; 3, K_3AlF_6–Cs_3AlF_6–$KAlF_4$; 4, Cs_3AlF_6–$KAlF_4$–$CsAlF_4$; and 5, $KAlF_4$–$CsAlF_4$–AlF_3. Some side systems in these subsystems such as Cs_3AlF_6–K_3AlF_6, Cs_3AlF_6–$KAlF_4$, and $CsAlF_4$–$KAlF_4$ have been investigated in our previous works (7, 8).

TABLE 2
Characteristic Points on the Liquidus of Profiles in the System AlF_3–KF–CsF

	Minimal point on liquidus							
	Composition (1) (mol%)				Composition (2, 3) (mol%)			
Profile	AlF_3	CsF	KF	Trans. point (°C)	AlF_3	CsF	KF	Trans. point (°C)
I	6.5	9	84.5	780	47	5	48	560
II	5.5	19	75.5	775	46	11	43	520
III	5.0	28.0	67.0	690	45	17	38	495
IV	4.5	38	57.5	650	44	23	33	525
V	3.5	48	48.5	630	36,43	32,29	32,28	545,550
VI	3	56	41	590	35,42	37,33	28,25	525,530
VII	7	65	28	600	44,46	39,38	17,16	520,520
VIII	8	74	18	620	40,42	48,46	12,12	490,495
IX	9	82	9	650	47	48	5	445
X	10	70	20	635				
XI	15	60	25	750				
XII	20	56	24	770				
XIII	8.3	66.8	24.9	610				
XIV	37.0	25.1	37.9	550				
XV	44.0	38.1	17.9	530				
XVI	40.0	51.1	8.9	460				
AlF_3–CsF	10.0	90.0		654	42	58		471
AlF_3–KF	7.0		93.0	856	44.5		55.5	560
CsF–KF		57.0	43.0	625				

TABLE 3
Nonvariant Points in the Ternary System AlF_3–KF–CsF

Type of equilibrium	Composition (mol%)			Temperature (°C)
	AlF_3	CsF	KF	
E_1	3.0	59.0	38.0	550
E_2	8.0	77.0	15.0	608
E_3	35.0	39.0	26.0	510
E_4	43.0	18.0	39.0	478
E_5	45.0	18.0	37.0	478
E_6	40.0	50.0	10.0	455
E_7	42.0	34.0	24.0	525
e_1		57.0	43.0	625
e_2	7.0		93.0	820
e_3	44.5		59.5	558
e_4	10.0	90.0		654
e_5	42.0	58.0		471
e_6	8.3	66.8	24.9	610
e_7	37.0	25.1	37.9	550
e_8	37.6	36.2	26.2	550
e_9	43.4	18.5	38.1	480
e_{10}	42.1	28.5	29.4	550
e_{11}	44.0	38.1	17.9	530
e_{12}	40.0	51.1	8.9	460
e_{13}	50.0	15.0	35.0	510
e_{14}	50.0	29.0	21.0	525
m_1	25.0	56.0	19.0	775
m_2	50.0	45.0	5.0	450

Nineteen composition–temperature sections were studied by visual polythermal methods and partially with DTA determination to construct this ternary system. The distribution of sections on the composition triangle is shown in Fig. 1. The terminal composition of profiles is listed in Table 1, while the characteristic points on the liquidus are listed in Table 2. Invariant points in the system are shown in Table 3. The correspondent phase diagram and isotherms are presented in Figs. 2 and 3.

The details of this phase diagram are as follows (in Fig. 2, the melting points of intermediate compounds and the temperatures of ternary eutectic are enclosed in parentheses).

3.1. *System KF–CsF–K_3AlF_6*

The binary side system KF–CsF was redetermined in this work. The results were in good agreement with Sangster's optimized data (6). The eutectic e_1 occurs at 57 mol% CsF with melting at 625°C. The data of eutectic e_2 for the system KF–K_3AlF_6 are taken from our recently published work (3) which reports the eutectic as being at 820°C and $X_{AlF_3} = 7.0$ mol%. Another binary system, K_3AlF_6–CsF, first researched in this work, is also a simple eutectic one. The composition of the eutectic occurs at 66.8 mol% CsF, 24.9 mol% KF, and 8.3 mol% AlF_3 with melting at 610°C (see Fig. 4). A ternary eutectic point E_1 was found in this

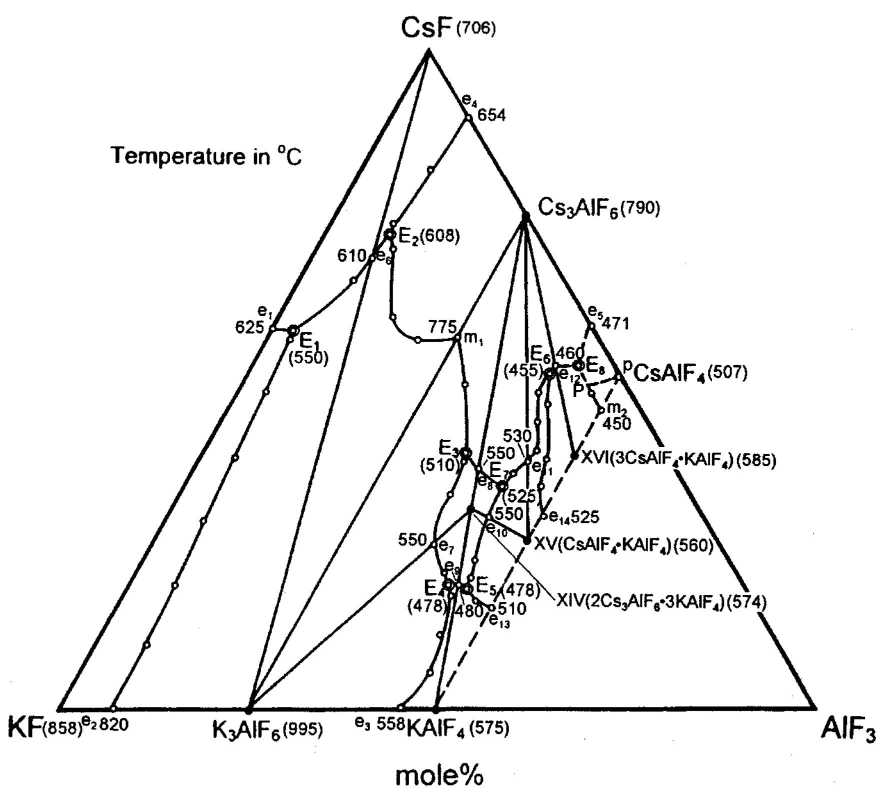

FIG. 2. Orthogonal projection of the AlF_3–KF–CsF system.

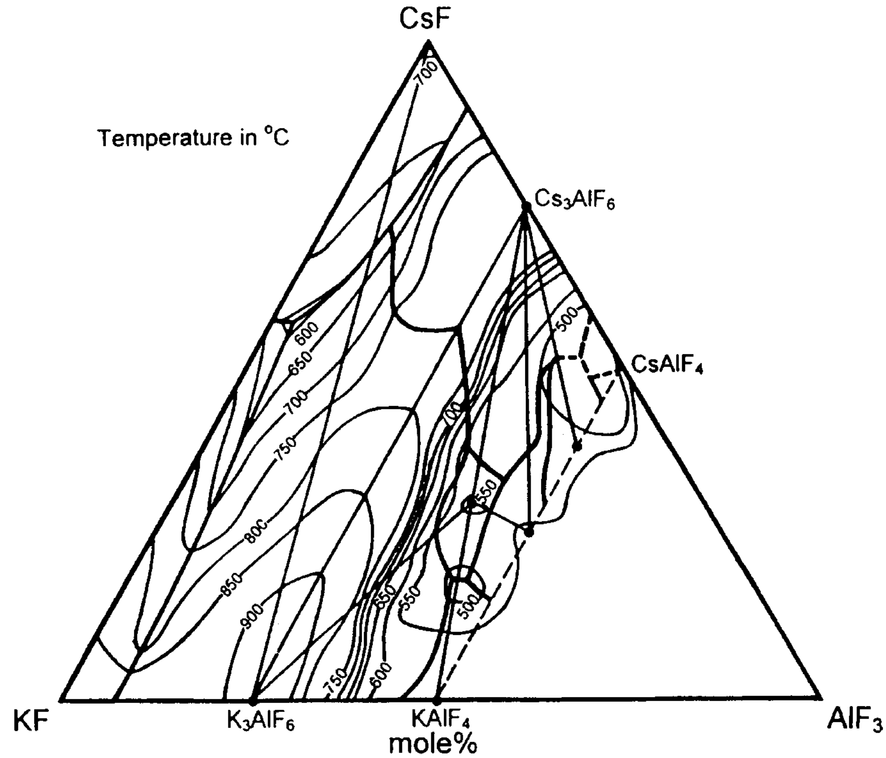

FIG. 3. Isotherms in the AlF_3–KF–CsF system.

system, the data of which are 3 mol% AlF_3, 59 mol% CsF, and 38 mol% KF, at 550°C.

3.2. *System CsF–K_3AlF_6–Cs_3AlF_6*

The side systems CsF–Cs_3AlF_6 and Cs_3AlF_6–K_3AlF_6 have been studied in our early works (5, 7). The data of eutectic e_4 (AlF_3 10 mol%, CsF 90 mol%, 654°C) and minimum point m_1 of solid solution (Cs_3AlF_6 75 mol%, K_3AlF_6 25 mol%) were taken from the above reports, while eutectic E_2 is listed in Table 3.

3.3. *System K_3AlF_6–Cs_3AlF_6–$KAlF_4$*

Because a ternary congruent melting compound $2Cs_3AlF_6 \cdot 3KAlF_4$ (presented as XIV which was borrowed from Fig. 1) was formed in the $KAlF_4$–Cs_3AlF_6 system which has been studied in our work (8), so that this system could be further divided into two subpseudosystems: Cs_3AlF_6–K_3AlF_6–XIV ($2Cs_3AlF_6 \cdot 3KAlF_4$) and K_3AlF_6–XIV–$KAlF_4$. Data of e_8 and e_9 were taken from (8), while ternary eutectics E_3 and E_4 are listed in Table 3.

3.4. *System Cs_3AlF_6–$KAlF_4$–$CsAlF_4$*

This is the most complicated one of the four pseudosystems. Because two congruent compounds $3CsAlF_4 \cdot KAlF_4$ (presented as XVI) and $CsAlF_4 \cdot KAlF_4$ (presented as XV) were found in the system $KAlF_4$–$CsAlF_4$ (7), the ternary system could further be divided into four subpseudosystems: Cs_3AlF_6–XIV–XV, XV–XIV–$KAlF_4$, Cs_3AlF_6–XV–XVI, and Cs_3AlF_6–XVI–$CsAlF_4$. Data of e_{13} and e_{14} were taken from (7), while E_5, E_6, and E_7 are listed in Table 3.

Because $CsAlF_4$ only formed in the solid state (5), no correspondent liqidus of $CsAlF_4$ appeared in the phase diagram of the system Cs_3AlF_6–$CsAlF_4$, and the liquidus of the system Cs_3AlF_6–XVI–$CsAlF_4$ will present a more complicated feature. A ternary peritectic point P and eutectic E_8 should be appeared on the surface of the liquidus. We have not further determined this subpseudosystem, but just expressed it in dotted lines.

3.5. *System $KAlF_4$–$CsAlF_4$–AlF_3*

Because of the dissociation of AlF_3 at higher temperatures, no exact determination has been made of this system, and we could only leave it as a blank.

From the phase diagram, the region around E_4 and E_5, at which the melting temperature is lower than 500°C, appears to be a good composition for use as a modified Nocolok flux. The lower temperature region near $CsAlF_4$ may be another candidate composition, but due to its higher content of CsF, which is more expensive, the benefit is decreased.

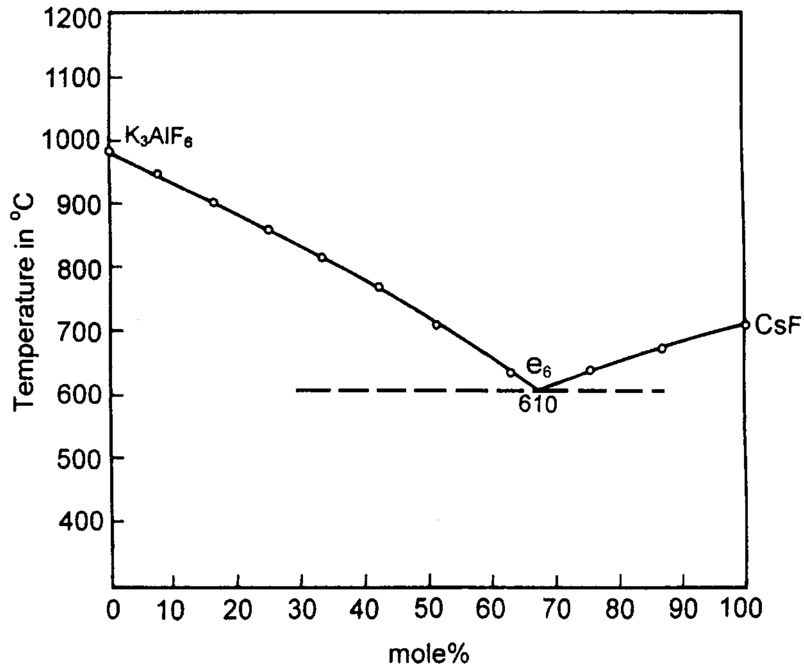

FIG. 4. Liquidus of the pseudosystem $CsF–K_3AlF_6$.

ACKNOWLEDGMENTS

The authors acknowledge support from the Beijing Science Fund.

REFERENCES

1. B. Pillips, C. M. Warshaw, and I. Mockrin, *J. Am. Ceram. Soc.* **48**(12), 631 (1966).
2. B. Jenssen, Thesis, The University of Trondheim, NTH Trondheim, 1969.
3. R. Chen, G. Wu, and Q. Zhang, *J. Am. Ceram. Soc.* **83**(12), 3196 (2000).
4. K. Suzuki, F. Miura, and F. Shimizu, Japan Kokai 61-232092, 1986.
5. R. Chen, J. Cao, and Q. Zhang, *Thermochim. Acta* **303,** 145 (1997).
6. J. Sangster and A. D. Pelton, *J. Phys. Chem. Ref. Data* **16**(3), 509 (1987).
7. R. Chen and Q. Zhang, *Thermochim. Acta* **335,** 135 (1999).
8. R. Chen and Q. Zhang, *Thermochim. Acta* **354,** 117 (2000).