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Phase relations in the system AlF_3-RbF

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Abstract

Phase diagram of the system AlF_3-RbF was investigated by the methods of DTA, DSC and XRD with quenching technique. Three compounds were identified: Rb_3AlF_6; $RbAlF_4$ and $RbF{\cdot}3AlF_3$. Rb_3AlF_6 melts congruently at 878°C and $\alpha \rightleftharpoons \beta$ transforms reversibly at 340°C. Eutectic E_1 between Rb_3AlF_6 and RbF is located in 10.0 mol% AlF_3 at 729°C. $RbF{\cdot}3AlF_3$ melts incongruently at 745°C, reacting with Rb_3AlF_6, second eutectic E_2 was observed in 48.4 mol% AlF_3 at 486°C. The third compound $RbAlF_4$ was formed in the solid eutectic when it cooled below 473°C. A very small thermal effect corresponding to $\alpha \rightleftharpoons \beta$ transformation at 335°C was observed on the DTA curve of this compound. All phase structures in the system were confirmed by X-ray powder diffraction analysis. © 1997 Elsevier Science B.V.

Keywords: Aluminum fluoride; Phase diagram; Rubidium fluoride; System

1. Introduction

In the phase relations between AlF_3 and alkali fluorides, three systems: AlF_3-LiF [1]; AlF_3-NaF [2] and AlF_3-KF [3] have been well investigated. As for the other two systems, AlF_3-RbF and AlF_3-CsF have only been roughly reported. Puschin [4] established that the partial phase diagram of AlF_3-RbF system in the content of AlF_3 was less than 41.5 mol%. New phase in the system was unconfirmed. Dergunov [5] determined the liquidus of the system AlF_3-RbF in the area of AlF_3<40 mol% by visual method, but he did not give the phase diagram. Further investigation of the AlF_3-RbF system would be very helpful for understanding complex aluminum fluorides and applying it in aluminum brazing technique. So the phase relations in the system AlF_3-RbF has been examined in detail.

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2. Experimental

2.1. Preparation of fluorides

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

2.2. Preparation of samples

Twenty-nine samples were prepared by reacting mixtures of anhydrous AlF_3 with certain solution of RbF and HF. Samples 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, for example, for AlF_3 less than 25 mol%

and over 75 mol% at 700°C; between 25–75 mol% at 400°C. During the annealing process, grinding and mixing of the samples were carried out repeatedly to obtain homogeneous and equilibrium samples.

2.3. Differential thermal analysis

A CR-G type high temperature DTA equipment (by Beijing Optical Instrument Inc.) was employed and calibrated by standard substances with known melting point (calibrating both the heating and cooling curves). Al_2O_3 was used as a reference substance. The heating rate was 15°C/min. The liquidus temperature was determined on cooling, and other temperatures were determined by using the extended initial temperature of the peaks on heating. The experiment was carried out in a dry air atmosphere (relative humidity <30%) in static state. The temperature error was ±3°C.

2.4. X-ray powder diffraction analysis

The intermediate compounds in the system were determined by Rigaku Dmax 2400 X-ray diffractometer (Rad. CuK_α λ=1.5409, Filter Ni). Liquid N_2 vapor current quenching technique was used for determining the structures of high-temperature phases. Si powder was added as an inter-reference for fine correcting the results of determination.

3. Results and discussion

Phase diagram of the system AlF_3-RbF, based on the results of DTA (as shown in Table 1) is given in Fig. 1. Nonvariant points are listed in Table 2.

Fig. 1 reveals that three intermediate compounds formed in the system: (1) Rb_3AlF_6 melts congruently at 878°C. This compound had two forms, α-Rb_3AlF_6 and β-Rb_3AlF_6 which transform into each other reversibly at 340. Rb_3AlF_6 reacted with RbF to form an eutectic E_1 at 729°C, and 10.0 mol% AlF_3; (2) RbF·3AlF_3 is incongruent. Peritectic reaction takes place at 745°C and decomposes into AlF_3 and a liquid phase P which contains 54.0 mol% of AlF_3; RbF·3AlF_3 reacted with Rb_3AlF_6 to form another eutectic E_2 at 486°C, and 48.4 mol% AlF_3; In the eutectic, compound (3) $RbAlF_4$ was formed in the solid phase on cooling below 473°C. $RbAlF_4$ has the α and β forms, transformation of which takes place reversibly at 335°C.

The melting point of Rb_3AlF_6 was determined as 878°C, which is lower than 985°C reported by Puschin and 914°C reported by Dergunov. The liquidus curve near the melting point is comparatively smooth and is not as sharp as being reported by Puschin and Dergunov. Jenssen [3] also described the characteristic of smooth liquidus curve near K_3AlF_6 in AlF_3-KF system. The fact indicates that the thermostability of these compounds are not so high.

This paper firstly reported the existence of the compound RbF·3AlF_3, and also described the features of $RbAlF_4$ via complete phase diagram. The latter shows that $RbAlF_4$ might have been prepared from water solution, under general conditions, with great difficulty.

The existence of Rb_3AlF_6, $RbAlF_4$ and RbF·3AlF_3 as well as their structures have been confirmed by X-ray powder diffraction analysis.

XRD data on α-Rb_3AlF_6 are listed in Table 3. Analytical results indicated that α-Rb_3AlF_6 is cubic, the cell parameter $a = 7.612 \pm 0.004$ Å. The sample of β-Rb_3AlF_6 was firstly annealed at 700°C for 8 h, then quenched in vapor current of liquid N_2. The XRD data on the sample are shown in Table 4. β-Rb_3AlF_6 phase is orthorhombic with cell parameter: $a = 7.748 \pm 0.005$; $b = 5.365 \pm 0.003$ and $c = 4.388 \pm 0.002$ Å. α=β-Rb_3AlF_6 reversibly transforms at 340°C. The energy of that is 5.33 J/g which was determined by DSC method on a Du Pont 1090B thermal analyzer (shown in Fig. 2).

In this research, the lattice type of α-Rb_3AlF_6 was identified as cubic which agrees with that reported by [6], but XRD data are quite different from that in the latter. The sample in [6] was precipitated directly from solution containing AlF_3 and RbF; in this paper, however, it was prepared by reacting mixtures of AlF_3 with a solution of RbF and HF, after drying, followed by repeated grinding and mixing in the annealing process at 700°C for a period of over 48 h. So we considered that homogeneity and equilibrium of the sample in this research appeared to be more reliable.

XRD data of RbF·3AlF_3 are given in Table 5. The compound RbF·3AlF_3 is tetragonal, $a = 6.226 \pm 0.002$, $c = 8.846 \pm 0.006$ Å.

Table 1
Data in the system AlF_3-RbF

AlF_3 (mol%)	Liquidus temp. (°C)	Eutectic 1 temp. (°C)	Incongr. melt. (°C)	Eutectic 2 temp. (°C)	Solid react. temp. (°C)	Polymorphic. trans. 1 (°C)	Polymorphic. trans. 2 (°C)
0.0	781						
2.0	771						
5.3	740	730				337	
8.0	737	724				345	
10.0	736	732				340	
12.3	814	728				348	
16.4	877	722				310	
21.3	877	711				343	
25.0	878	755				340	
28.7	877					343	
33.3	840				477	342	
37.0	778						
41.0	748			483	475		336
42.2	660			496	474		332
45.5	540			484	463		
47.0	528			485	477		337
48.4	490			490	475		336
50.0	540				478		340
51.1	541			480			338
52.3	703			480	470		343
53.7	759						345
56.4			750		458		341
59.4			748				341
64.3			745				341
66.7			751				342
69.2			750				335
75.0			738				
79.9			730				
92.5							

Table 2
Nonvariant points in AlF_3-RbF system

Nonvariant point	Temperature (°C)	AlF_3 (mol%)
E_1	729	10.0
E_2	486	48.4
P	745	54.0
m.p. (Rb_3AlF_6)	878	25.0

Table 3
XRD data on α-Rb_3AlF_6: Cubic, $a = 7.612 \pm 0.004$ Å.

$d_{obs.}$ (Å)	$d_{calc.}$ (Å)	I/I_0	h	k	l
3.378	3.411	10	2	1	0
3.110	3.108	100	2	1	1
2.539	2.540	28	3	0	0
2.194	2.198	20	2	2	2
2.030	2.038	6	3	2	1
1.794	1.796	15	3	3	0
1.556	1.555	9	4	2	2
1.177	1.175	3	5	4	1

$RbAlF_4$ is a compound formed in the solid eutectic on reacting Rb_3AlF_6 with $RbF{\cdot}3AlF_3$ at 473°C. Pure $RbAlF_4$ was prepared in the same manner as mentioned above in Rb_3AlF_6. The phase diagram indicates that $RbAlF_4$ also has two forms, α and β. DTA peak of $\alpha \rightleftharpoons \beta$ always appears on heating, and re-heating the curves of the same sample again and again. This shows that the transformation of $RbAlF_4$ is reversible. XRD data of α-$RbAlF_4$ coincided with the results reported by Brosset [7] and indexed by JCPDS [8] (α-$RbAlF_4$ is tetragonal, $a = 3.662$, $c = 6.274$ Å). In this research, the sample of β-$RbAlF_4$ was prepared by heating α-

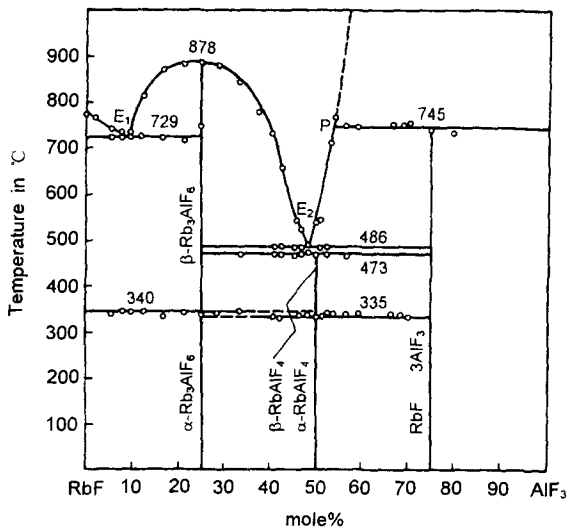

Fig. 1. The phase diagram of AlF_3-RbF system.

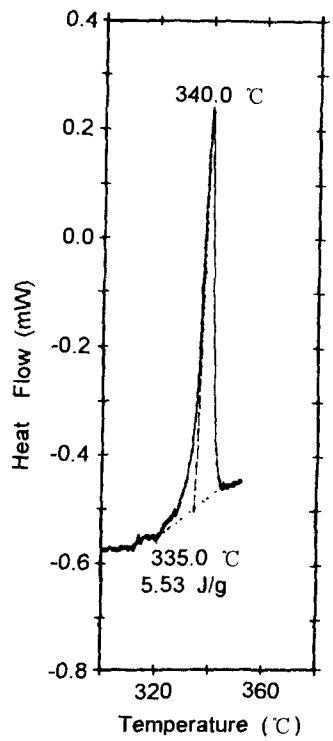

Fig. 2. DSC curve of $\alpha \rightleftharpoons \beta$ transformation of Rb_3AlF_6.

Table 4
XRD data on β-Rb_3AlF_6: Orthorhombic, $a = 7.748 \pm 0.005$, $b = 5.365 \pm 0.003$ and $c = 4.388 \pm 0.002$ Å

$d_{obs.}$ (Å)	$d_{calc.}$ (Å)	I/I_0	h	k	l
3.381	3.398	9	0	1	1
3.142	3.140	28	2	1	0
3.114	3.108	100	1	1	1
2.540	2.540	18	1	2	0
2.208	2.210	13	2	2	0
2.196	2.199	23	1	2	1
	2.194		0	0	2
2.032	2.030	5	0	1	2
1.798	1.799	11	2	1	2
1.557	1.557	9	2	2	2
1.550	1.550	3	5	0	0
1.395	1.395	4	3	3	1
1.390	1.388	4	1	1	3

$RbAlF_4$ to 400°C for 8 h and then by quenching it in liquid N_2 current. After that, the sample was determined immediately by XRD. From the results, no detectable difference in structures was found in both α-$RbAlF_4$ and β-$RbAlF_4$. The observed DTA peak of $\alpha \rightleftharpoons \beta$ of $RbAlF_4$ was quite small, but surely it was very clear. The transformation energy was found to be 0.390 J/g (as shown in Fig. 3) by DSC determination. Fourquet [9] reported the phase transition of $RbAlF_4$. He prepared the single crystals called β-$RbAlF_4$ by

Table 5
XRD data on RbF·3AlF_3: Tetragonal, $a = 6.226 \pm 0.002$, $c = 8.846 \pm 0.006$ Å

$d_{obs.}$ (Å)	$d_{calc.}$ (Å)	I/I_0	h	k	l
6.320	6.232	11	1	0	0
3.118	3.129	100	1	1	2
	3.108		2	0	0
2.947	2.957	12	0	0	3
	2.938		2	0	1
2.554	2.547	23	2	0	2
2.453	2.453	12	1	1	3
2.202	2.199	20	2	2	0
2.090	2.092	37	1	0	4
2.026			2	1	3
2.021	2.021	10	3	0	1
1.799	1.799	14	3	1	2
1.606	1.609	20	3	2	2
1.407		14			
	1.377		4	0	3
1.376	1.374	33	4	2	1
1.147	1.147	6	5	0	3
1.128	1.129	7	5	1	3

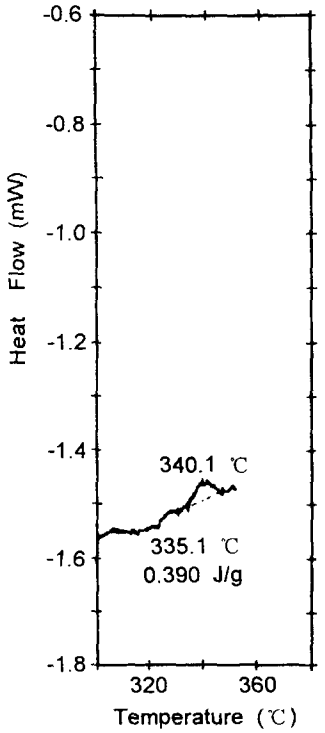

Fig. 3. DSC curve of $\alpha \rightleftharpoons \beta$ transformation of $RbAlF_4$.

hydrothermal synthesis in a medium of hydrofluoric acid. Laue photograph analysis revealed that this β-$RbAlF_4$ is also tetragonal, $a = 11.666$, $c = 12.551$ Å, which is similar to that of the laminal tetragonal tungsten bronze structure with no obvious difference from the structure of α-$RbAlF_4$. The differences between the two lie in that the Z value and cell volume of the β form are 10 times larger than those in α-$RbAlF_4$. He indicated that β-$RbAlF_4$ could transform into the stable α-$RbAlF_4$ by an irreversible, non-destructive, non-twinning and topotatic phase transition at 315°C. The $\beta \rightarrow \alpha$ topotatic phase transition was explained by a concerted $\pi/4$ rotation, around the (001)c axis of four-octahedra (AlF_6) groups. He considered that irreversible transition of $\alpha \rightleftharpoons \beta$ was based on the fact that there was no detectable DTA peak before 846 K. The transition temperature (>315) reported by Fourquet is very close to the one (335–340°C) shown in our phase diagram in this research. Many samples whose compositions were close to that of $RbAlF_4$ were determined accurately by DTA. All sample results showed that the transition peaks were small but they certainly existed. The transition peak once again appeared on re-heating DTA curves, thus indicating that the process of $\alpha \rightleftharpoons \beta$ is surely reversible. On the other hand, Fourquet also reported that he got both the crystals β-$RbAlF_4$ and α-$RbAlF_4$ simultaneously by hydrothermal synthesis. So we considered that the transition of the $\alpha \rightleftharpoons \beta$ under their preparation conditions might be also possible. Fourquet's explanation about the structural transition of $RbAlF_4$ could be accepted because the transition energy is quite small. A certain lack of clarity remained is that we can hardly identify whether the β phase between Fourquet's synthesized by hydrothermal and ours prepared by annealing are exactly the same or not. This needs further investigation.

Acknowledgements

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