PHASE DIAGRAM CALCULATION OF QUASI-BINARY SYSTEM Na_3AlF_6-$K_3AlF_6$①

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ABSTRACT The quasi-binary system Na_3AlF_6-K_3AlF_6 was optimized based on CALPHAD technique using a computerized optimization procedure called PARROT included in Thermo-calculation. The two-sublattice model was used for the liquid phase in which K^{1+}, Na^{1+} were taken as cation, and AlF_6^{3-} as anion. The compound $2K_3AlF_6 \cdot Na_3AlF_6$ was modeled as stoichiometric phase. The phase diagram was analyzed according to the assessed result.

Key words: aluminium electrolyte Na_3AlF_6-K_3AlF_6 system phase diagram calculation

1 INTRODUCTION

The Hall-Heroult electrolytic process[1], i.e., electrolysis of cryolite-alumina, is widely used in modem aluminium industry, but the system has a high melting point and consumes a large amount of electric energy. As the energy crisis world-wide in recent years, great attention has been paid to reduce the electric energy consumption. Now it is an important subject to look for new-type low-temperature aluminium electrolyte. The quasi-binary system K_3AlF_6-Na_3AlF_6 deserve further study for its potential characteristics.

K_3AlF_6-Na_3AlF_6 system is a stable section of ternary system AlF_3-NaF-KF. As the system has a high melting point and strong erosion, it is difficult to carry on any experiment. Some of thermodynamic properties and part of the phase diagram have not been determined. It is questionable whether Na_3AlF_6 and K_3AlF_6 form the compound $2K_3AlF_6 \cdot Na_3AlF_6$, yet recent experiment results showed the existence of the compound. There is still disagreement on the type of the phase diagram. As for the compound $2K_3AlF_6 \cdot Na_3AlF_6$, there is not any thermodynamic properties being reported. This paper is to assessed the system based on the experimental data using PARROT of the Thermo-calculation, and to analyze the phase diagram, as well as to give the theoretical predict of the Gibbs energy of formation of $2K_3AlF_6 \cdot Na_3AlF_6$.

2 THEORETICAL MODEL AND CALCULATION TECHNIQUE

2.1 *Thermodynamic Model*

The thermodynamic data of pure solid and liquid Na_3AlF_6 were taken from Knacke[2], while that of pure solid and liquid K_3AlF_6 derived by our previous work[3]. They were expressed as the following form:

$$^0G - H^{SER} = A - BT + CT(1 - \ln T) - DT^2/2 - E/2T$$

All ^0G values were given relative to the enthalpy of selected reference states for the elements at 298.15 K. The compound $2K_3AlF_6 \cdot Na_3AlF_6$ have been treated as stoichiometric phase. Its Gibbs energy was expressed as

$$^0G_{2K_3AlF_6 \cdot Na_3AlF_6} = A + BT + CT\ln T$$

The liquid was described by the two-sublattice model for ionic liquids[4]. According to the model, there exist two sublattices in the ionic liquid, one for cations, and the other for anions. In this binary system, K^{1+} and Na^{1+} are cations, and AlF_6^{3-} is anion. If we postu-

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late the existence of complex ions AlF_6^{3-} and assume it enter into the appropriate sublattice like a simple anion, the liquid can be described by $(Na^{1+}, K^{1+})_P(AlF_6^{3-})_Q$, where P and Q are stoichiometric numbers. In this case they are given by $P = 3$, $Q = y_{K^{1+}} + y_{Na^{1+}} = 1$, where y denotes site fraction, i.e., the mole fraction of anion in a sublattice. The Gibbs energy of the liquid is given by

$$G_m = y_{k^{1+}} {}^0G_{K_3AlF_6} + y_{Na^{1+}} {}^0G_{Na_3AlF_6} + 3RT(y_{Na^{1+}}\ln y_{Na^{1+}} + y_{K^{1+}}\ln y_{K^{1+}}) + {}^EG_m$$

The excess Gibbs energy, ${}^EG_m$, here depends on interaction coefficient L between K^{1+} and Na^{1+} on the cation sublattice. The sub-regular model is suitable to describe the excess energy of the liquid:

$${}^EG_m = (y_{K^{1+}})(y_{Na^{1+}})[{}^0L + {}^1L(y_{K^{1+}} - y_{Na^{1+}})]$$

2.2 *Calculation Method*

A computer program called PARROT included in the Thermo-calculation was used to optimize the parameters. It can take into account various thermodynamic data simultaneously. Based on the principle of minimization of the sum of the squares, the parameters were assessed by adjusting the weight of each experiment data. The phase diagram was calculated with the program POLY-3 in the same system.

3 EXPERIMENTAL INFORMATION

The binary system K_3AlF_6-Na_3AlF_6 has been studied by several authors, but their results are not in agreement. Some one reported that the system belongs to the solid solution system, Na_3AlF_6 and K_3AlF_6 do not form any compound. Some researchers reported that there exists a continuous solid solution between Na_3AlF_6 and K_3AlF_6 and the liquidus has a minimum at 940 ℃ and about 50 mol.-% K_3AlF_6[5-7], or the minimum at 927 ℃ and about 26 mol.-% K_3AlF_6[8].

The others reported that Na_3AlF_6 and K_3AlF_6 can form compounds. Narry-Azobo and Sigmond[9] reported the six intermediate compounds as follows: $5K_3AlF_6 \cdot 2Na_3AlF_6$, $2K_3AlF_6 \cdot Na_3AlF_6$, $5K_3AlF_6 \cdot 3Na_3AlF_6$, $K_3AlF_6 \cdot Na_3AlF_6$, $3K_3AlF_6 \cdot 5Na_3AlF_6$ and $K_3AlF_6 \cdot 2Na_3AlF_6$. Only the compound $2K_3AlF_6 \cdot Na_3AlF_6$ could be stable at room temperature. Edoyan *et al*[10] confirmed the existence of these compounds. Bukhalova and Mal'tsev[11] reported the following compounds: $3K_3AlF_6 \cdot Na_3AlF_6$ formed in the solid phase between 715 ℃ and 796 ℃; $K_3AlF_6 \cdot Na_3AlF_6$ formed in the solid phase between 736 ℃ and 832 ℃; and $2K_3AlF_6 \cdot Na_AlF_6$ which does not decompose when cooled to room temperature. Their results showed that the compound $2K_3AlF_6 \cdot Na_3AlF_6$ divides the whole phase diagram into two simple sub-systems with eutectic points. There are solid solution on the Na_3AlF_6 and K_3AlF_6 sides of the diagram. Chin and Hollingshead[12] reported that the primary freezing point of Na_3AlF_6 decreases to 945 ℃ with the addition of K_3AlF_6, and then rises to 955 ℃ at 60 mol.-%～70 mol.-% K_3AlF_6. They also confirmed the presence of the compound $2K_2AlF_6 \cdot Na_3AlF_6$. Yoshioka and Koroda[13] determined the liquidus and their results were in agreement with those of Chin and Hollingshead[12]. Grjotheim and Holm[14] studied the system using TA, DTA, and X-ray diffraction. They determined the liquidus but they were not able to get the solidus. An intermediate compound, $2K_3AlF_6 \cdot Na_3AlF_6$, corresponding to elapsolite K_2NaAlF_6, which melt at 954 ℃, was the only compound detected. Similarly, the compound divides the diagram into two sub-system, specifically, the Na_3AlF_6-$2K_3AlF_6 \cdot Na_3AlF_6$ system and the $2K_3AlF_6 \cdot Na_3AlF_6$-$K_3AlF_6$ system. In the former system, Na_3AlF_6 and $2K_3AlF_6 \cdot Na_3AlF_6$ can form a continuous solid solution with a minimum at about 938 ℃ and 30.5 mol.-% K_3AlF_6. While in the latter system, $2K_3AlF_6 \cdot Na_3AlF_6$ and K_3AlF_6 form a binary system with a eutectic point. Morss[15] prepared the compound $2K_3AlF_6 \cdot Na_3AlF_6$ with AlF_3, NaF and KF, and confirmed that its structure is the same as

those reported for the mineral elapsolite. It is indicated that the compound are face-centered cubic with non-distorted AlF_6^{3-} octahedral.

Form the recent experiments it is seen that the compound $2K_3AlF_6 \cdot Na_3AlF_6$ can be formed between Na_3AlF_6 and K_3AlF_6 and it divides the diagram into two sub-system, and that the system $2K_3AlF_6 \cdot NaAlF_6$-K_3AlF_6 is a binary system with a eutectic point, but it is not determined that Na_3AlF_6-$2K_3AlF_6 \cdot Na_3AlF_6$ system is a solid system or a simple system with an eutectic point. The high melting point and strong erosion of binary system K_3AlF_6-Na_3AlF_6 make it difficult to determined the thermodynamic data. Only Yoshioka[13] determined the activity of K_3AlF_6 and Na_3AlF_6 on the sides of diagram by cryoscopy.

4 RESULT AND DISCUSSION

As large disparities existed in different experiment results, only some representative data points were selected in the optimization such as Phase diagram data of Bukhalova[8], Grjotheim[14] and Chin[12] and the activity coefficient data of Yoshioka[13].

The thermodynamic properties of the system including the optimized parameters are given in the Table 1. The results show that the liquid can be modeled with subregular solution, and its exess Gibbs energy is prescribed by three-parameter Redlich-Kister expression. there are three parameters in Gibbs energy of formation of the intermediate compound as well. The assessed phase diagram as well as experimental data points are shown in Fig. 1. Some important invariant points are listed in Table 2 for comparison.

It can be seen from Fig. 1 and Table 2 that our assessed phase diagram is similar to that of Bukhalova[11], i. e., an intermediate compound $2K_2AlF_6 \cdot Na_3AlF_6$ can be formed between Na_3AlF_6 and K_3AlF_6, and it separates the diagram into two simple binary systems with eutectic points. There are incontinuous solid solution near the sides of Na_3AlF_6 and K_3AlF_6. The eutectic point of the sub-system Na_3AlF_6-$2K_3AlF_6 \cdot Na_3AlF_6$ is at 1 204 K and 0. 29 mol.-% K_3AlF_6, while $2K_3AlF_6 \cdot Na_3AlF_6$-$K_3AlF_6$ system at 1 221 K and 0. 73 mol.-% K_3AlF_6 (Fig. 2). These are consistent to the eutectic points or minimum in liquidus by experiments. Bukhalova's experimental points seem too low. The difference between Grjotheim *et al*[14] and ours lies in Na_3AlF_6-$2K_3AlF_6 \cdot Na_3AlF_6$ sub-system. They reported that this system is a continuous solid solution. According to Morss's experiment[15], the structure of $2K_3AlF_6 \cdot Na_3AlF_6$ is similar to that of Na_3AlF_6 and K_3AlF_6. So it would be more rea-

Table 1 Themodynamic properties of binary system K_3AlF_6-Na_3AlF_6

Element	Reference state	Mass /g·mol^{-1}	$H_{298}-H_0$ /J·mol^{-1}	S_{298} /J·(mol·K)$^{-1}$	Element	Reference state	Mass /g·mol^{-1}	$H_{298}-H_0$ /J·mol^{-1}	S_{298} /J·(mol·K)$^{-1}$
Na	*BCC-A2*	22. 99	6 447. 54	51. 45	Al	*FFC-A1*	26. 98	4 577. 30	28. 32
K	*BCC-A2*	39. 10	7 083. 51	64. 67	F	1/2 mol $F_2(g)$	19. 00	4 412. 50	101. 34

Na_3AlF_6

${}^0G_{Na_3AlF_6} - 3H_{Na}^{SER} - 6H_F^{SER}$

$836.0 < T < 1153$

$-3\,401\,757 + 1\,473.35T + 294.888T(1 - \ln T)$

$1153 < T < 1285$

$-3\,471\,386 + 1\,901.294T + 355.64T(1 - \ln T)$

K_3AlF_6

${}^0G_{K_3AlF_6} - 3H_K^{SER} - H_{Al}^{SER} - 6H_F^{SER}$

$2K_3AlF_6 \cdot Na_3AlF_6$

${}^0G_{2K_3AlF_6 \cdot Na_3AlF_6} - 6H_K^{SER} - 3H_{Na}^{SER} - 3H_{Al}^{SER} - 12H_F^{SER}$

$-12\,625\,700 + 9\,155.6T - 1\,180T\ln T$

Ionic solution

two sublattice, sites $y_{K1+} + y_{Na1+}$

constituent Na^{1+}, K^{1+}; AlF_6^{3-}

${}^0G_{Na^{1+}:AlF_6^{3-}} - 3H_{Na}^{SER} - H_{Al}^{SER} - 6H_F^{SER}$

$1285.0 < T < 2000.0$

$-3\,412\,960 + 2\,103.192T + 395.806T(1 - \ln T)$

${}^0G_{K^{1+}:AlF_6^{3-}} - 3H_K^{SER} - H_{Al}^{SER} - 6H_F^{SER}$

$1273 < T < 2000$

$-3\,410\,766 + 1\,988.18T + 392.25T(1 - \ln T)$

* All parameter values are given in SI units(J, mol, K)

Table 2 Comparison of invariant equilibria between the experiment data points and calculation values

Invariant point	Author	Temperature/K	mol.-% K_3AlK_6
$1+ss+2K_3AlF_6 \cdot Na_3AlF_6$	Buhalova *et al.*	1186	0.29
(or minimum in Na_3AlF_6—	Grjotheim *et al.*	1211	0.305
$2K_3AlF_6 \cdot Na_3AlF_6$ system)	Chin *et al.*	1218	0.40
	Yashioka *et al.*	~1215	~0.35
	Present work	1204	0.29
$1+ss+2K_3AlF_6 \cdot Na_3AlF_6$	Buhalova	1198	0.73
(or eutectic point at K_3AlF_6—	Grjotheim *et al.*	1223	0.73
$2K_3AlF_6 \cdot NaAlF_6$ system)	Yashioka *et al.*	~1222	~0.73
	Pressent work	1221	0.73
$1+2K_3AlF_6 \cdot Na_3AlF_6$	Buhalova *et al.*	1211	0.667
	Grjotheim *et al.*	1227	
	Chin *et al.*	1228	
	Yashioka *et al.*	~1222	
	Present work	1223	

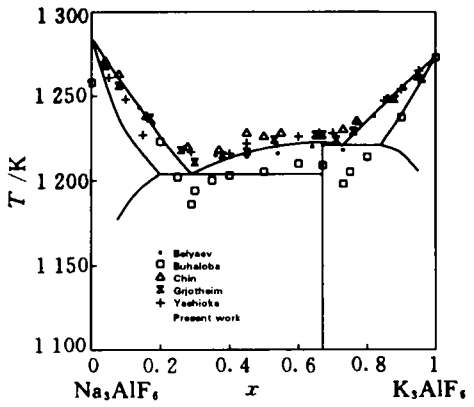

Fig. 1 Phase diagram of binary system Na_3AlF_6-K_3AlF_6

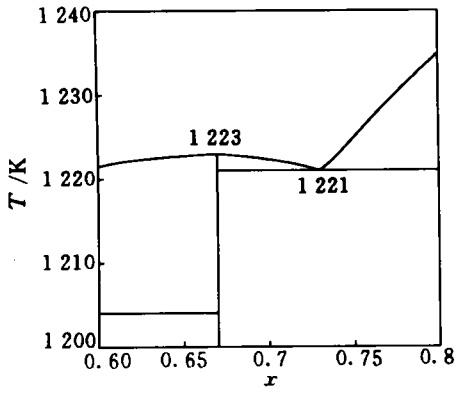

Fig. 2 Part of the phase diagram
(60 mol.-%~80 mol.-% K_3AlF_6)

sonable that the phase diagrams of the Na_3AlF_6-$2K_3AlF_6 \cdot Na_3AlF_6$ system and the $2K_3AlF_6 \cdot Na_3AlF_6$-$K_3AlF_6$ system are similar, that is, both belong to binary systems with eutectic points.

As for the $2K_3AlF_6 \cdot Na_3AlF_6$, there is not any thermodynamical value reported. Its Gibbs energy of formation can be fitted by the phase diagram data as follow:

$$^0G = -12625700 + 9156T - 1180T\ln T$$

Further experimental work is needed for understanding this system completely.

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