Phase Diagram of the KCl–NaCl–NaF–K₂NaVF₆ System

By Kôichirô Kôyama* and Yasuhiko Hashimoto*

As a part of the series of the studies on the electrolyte for the extraction of vanadium, the phase diagram of the KCl–NaCl–NaF–K₂NaVF₆ system, which is a partial system of the KF–NaF–VF₃–KCl–NaCl–VCl₃ reciprocal quaternary system, was investigated by thermal analysis and X-ray diffraction analysis. The liquidus surfaces of the surrounding KCl–NaCl–NaF, KCl–NaF–K₂NaVF₆, and NaCl–NaF–K₂NaVF₆ systems were determined. Two invariant points exist in the KCl–NaCl–NaF–K₂NaVF₆ composition region: one is a quaternary minimum point and the other is supposed to be a peritectoeutectic point. The minimum point is situated at 605°C and a composition of {KCl(41.75)–NaCl(41.75)–NaF(16.5)}–K₂NaVF₆(about 0.2 mol%), and the peritectoeutectic point is situated at 620°C and its composition is estimated to be {KCl(15)–NaCl(60)–NaF(25)}–K₂NaVF₆(several mol%).

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I. Introduction

The previous investigation⁽¹⁾ revealed that the molten salt having a composition of KCl (44)–NaCl (44)–NaF (7)–K₂NaVF₆ (5 mol%) gives good anode current efficiency in the anodic extraction of vanadium from the crude vanadium produced by the carbothermic reduction of V₂O₅. To find out a composition having a melting point lower than that of the above composition, the phase diagram of the KCl–NaCl–NaF–K₂NaVF₆ system is very useful. There is, however, no data available for this system. This system is a partial system of the KF–NaF–VF₃–KCl–NaCl–VCl₃ reciprocal quaternary system which is shown in Fig. 1. The present authors have already reported the phase diagrams of the KCl–KF–K₃VF₆, NaCl–NaF–Na₃VF₆, KF–NaF–K₂NaVF₆, and KCl–NaCl–K₂NaVF₆ ternary systems⁽²⁾⁽³⁾ which are also the partial systems of the KF–NaF–VF₃–KCl–NaCl–VCl₃ reciprocal quaternary system. This paper is mainly concerned with the phase diagram of the KCl–NaCl–NaF–K₂NaVF₆ system.

II. Experimental Procedure

The samples for thermal analysis were prepared from potassium chloride, sodium

Fig. 1 The KF–NaF–VF₃–KCl–NaCl–VCl₃ reciprocal quaternary system.

chloride, sodium fluoride, and dipotassium sodium hexafluorovanadate (III), K₂NaVF₆. The potassium chloride, sodium chloride, and sodium fluoride used were of a special reagent grade, and were dried for 3 h at about 600°C before use. The dipotassium sodium hexafluorovanadate (III) were synthesized in the following manner: A mixture of KCl, NaCl, NaF, and potassium hexafluorovanadate (III) (K₃VF₆) in a molar ratio of 49: 32: 9: 10 was fused in a graphite crucible at 950°C in a purified argon atmosphere, then cooled, and washed with water in order to remove the excess potassium chloride, sodium chloride, and sodium fluoride. The water-insoluble residue, that is, K₂NaVF₆, was fully washed with water, next with methyl alcohol, and then dried in a vacuum desiccator. The potassium hexafluorovanadate (III) used for the pre-

* Department of Materials Science, Himeji Institute of Technology, Himeji 671–22, Japan.

paration of K_2NaVF_6 was synthesized by the same method as described in the previous reports⁽²⁾⁽⁴⁾. The thermal analysis of the samples were carried out in the same manner as described previously⁽²⁾. The alumel-chromel thermocouple used was calibrated by the melting points of silver, aluminum, and zinc. The compounds present in the samples after thermal analysis were identified by X-ray diffraction. The X-ray diffraction was carried out by use of an X-ray diffractometer (Rigaku Denki, Model SG-7) with Ni-filtered CuK_α radiation.

III. Results and Discussion

1. KCl–NaCl–NaF system

Sauerwald and Dombois⁽⁵⁾ investigated the KCl–NaCl–NaF system by thermal analysis and reported that this system was of the minimum-point type and had a minimum point at a temperature of 590°C and a composition of KCl (47)–NaCl (38)–NaF (15%)[†]. The preliminary experiment for this system by the present authors showed that this composition is not the minimum point. In order to determine more precisely the position of the minimum point, the samples having the compositions shown in Fig. 2 were examined by thermal analysis. It was found that the minimum point is situated at a composition of KCl (41.75)–NaCl (41.75)–NaF (16.5%) and a temperature of 606°C . Figure 3 shows the KCl·NaCl (equimolar)–NaF section where the minimum point is situated.

2. KCl–NaF– K_2NaVF_6 system

Figure 4 shows the compositions of this ternary system examined by thermal analysis. The X-ray diffraction analyses revealed that the samples after thermal analysis were composed of KCl, NaF, and K_2NaVF_6 . Figure 5 shows the phase diagram of the KCl–NaF– K_2NaVF_6 system which was constructed on the basis of the results of the thermal analysis. This system was found to be of the ternary eutectic type. The ternary eutectic

Fig. 2 Compositions examined by thermal analysis in the KCl–NaCl–NaF system.

Fig. 3 KCl·NaCl(equimolar)–NaF section.

point (E in Fig. 5) was situated very close to the binary eutectic point (e_8) of the KCl–NaF system $\{650^\circ\text{C}, \text{KCl (72)}-\text{NaF (28)}\}$, and its temperature was 648°C and its composition was evaluated to be $\{\text{KCl (72)}-\text{NaF (28)}\}-\text{K}_2\text{NaVF}_6$ (about 0.5%).

3. KCl–NaCl– K_2NaVF_6 system

This system has been already investigated by the present authors and it is not quasi-ternary⁽³⁾.

[†] Compositions are shown in mole percentage hereafter.

Fig. 4 Compositions examined by thermal analysis in the KCl–NaF–K₂NaVF₆ system.

Fig. 5 Phase diagram of the KCl–NaF–K₂NaVF₆ system.

- e₆: 865°C, NaF(85)–K₂NaVF₆(15%)
 e₇: 729°C, KCl(92.5)–K₂NaVF₆(7.5%)
 e₈: 650°C, KCl(72)–NaF(28%)
 E: 648°C, {KCl(72)–NaF(28)}–K₂NaVF₆(about 0.5%).

4. NaCl–NaF–K₂NaVF₆ system and KCl–NaCl–NaF–K₂NaVF₆ system

Figure 6 shows the compositions of the NaCl–NaF–K₂NaVF₆ system examined by thermal analysis and X-ray diffraction analysis. The thermal analyses gave complicated vertical

Fig. 6 Compositions examined by thermal analysis and X-ray diffraction analysis in the NaCl–NaF–K₂NaVF₆ system. Open circles: thermal analysis, closed circles: thermal analysis and X-ray diffraction analysis.

sections, while the X-ray diffraction patterns showed definitely the peaks of KCl in addition to those of NaCl, NaF, and K₂NaVF₆, and moreover in the case of the samples containing 10–15% K₂NaVF₆, Na₃VF₆ was undoubtedly detected although its peaks were weak. The identification of Na₃VF₆ was made on the basis of the diffraction data reported by Korenev *et al.*⁽⁶⁾ Figure 7 shows the results of the thermal analysis for the {NaCl (80)–NaF (20)}–K₂NaVF₆ section. Figure 8 represents the X-ray diffraction pattern of the specimen of NaCl (63)–NaF (27)–K₂NaVF₆ (10%). From the fact of the formation of KCl and Na₃VF₆, it was found that the NaCl–NaF–K₂NaVF₆ system is not quasi-ternary. This conclusion can be also obtained from the fact that the binary NaCl–K₂NaVF₆ system is not quasi-binary⁽³⁾.

As was described above, of the four ternary systems constituting the KCl–NaCl–NaF–K₂NaVF₆ system, the two systems KCl–NaCl–K₂NaVF₆ and NaCl–NaF–K₂NaVF₆ are not quasi-ternary, and Na₃VF₆ was formed in the process of the solidification of these systems. Therefore, the process of the solidification of the KCl–NaCl–NaF–K₂NaVF₆ composition region must be discussed by use of the KCl–NaCl–NaF–K₂NaVF₆–Na₃VF₆ system which includes

Fig. 7 {NaCl(80)-NaF(20)}-K₂NaVF₆ section.
Open circles: first inflection points in cooling curves,
closed circles: the other inflection points.

Fig. 8 X-ray diffraction pattern of the sample of NaCl(63)-NaF(27)-K₂NaVF₆(10%). (CuK α , Ni-filter).

the former. Figure 9 shows schematically the KCl-NaCl-NaF-K₂NaVF₆-Na₃VF₆ system; the KCl-NaCl-K₂NaVF₆ triangle and the NaCl-K₂NaVF₆-Na₃VF₆ triangle are on the same plane, and the KCl-NaCl-NaF-K₂NaVF₆ tetrahedron and the NaCl-NaF-K₂NaVF₆-Na₃VF₆ tetrahedron hold the NaCl-NaF-K₂NaVF₆ triangle in common, as can be seen from Fig. 1. The liquidus surfaces of the KCl-NaCl-NaF, KCl-NaCl-K₂NaVF₆,

KCl-NaF-K₂NaVF₆, and NaCl-NaF-Na₃VF₆ ternary systems have been described in the present paper and the previous papers⁽²⁾⁽³⁾. The NaF-K₂NaVF₆-Na₃VF₆ system should be of the ternary eutectic type because the K₂NaVF₆-Na₃VF₆⁽⁷⁾, NaF-K₂NaVF₆⁽³⁾, and NaF-Na₃VF₆⁽²⁾ systems are of the binary eutectic type. There is no invariant point in the NaCl-Na₃VF₆-K₂NaVF₆ composition region, and instead a peritectoeutectic point **p** corresponding to the invariant point of this system is situated in the KCl-NaCl-K₂NaVF₆ composition region⁽³⁾. From the results of these seven ternary systems, that is, the NaCl-NaF-Na₃VF₆, KCl-NaCl-K₂NaVF₆, KCl-NaCl-NaF, KCl-NaF-K₂NaVF₆, NaF-K₂NaVF₆-Na₃VF₆, NaCl-Na₃VF₆-K₂NaVF₆, and NaCl-NaF-K₂NaVF₆ systems, it is supposed that the ternary eutectic lines, **e**₁**M**, **PM**, **e**₂**P**, and **e**₃**P**, and peritectoeutectic line **pP** will run as drawn in Fig. 9. **P** and **M** are inside the KCl-NaCl-NaF-K₂NaVF₆ tetrahedron. **M** is a quaternary minimum point and its reaction is $L = (\text{KCl-NaCl}) \text{ solid solution} + \text{NaF} + \text{K}_2\text{NaVF}_6$. **P** is supposed to be a peritectoeutectic point and its reaction is considered to be $L + \text{Na}_3\text{VF}_6 = \text{NaCl} + \text{NaF} + \text{K}_2\text{NaVF}_6$.

Small but obvious inflections were observed at about 605°C in the thermal analysis curves of some of the samples having the compositions shown in Fig. 6. Such samples gave definite diffraction peaks of Na₃VF₆ and KCl in addition to NaCl, NaF, and K₂NaVF₆ as already mentioned above. Therefore, it is considered that these inflections in the thermal analysis curves resulted from the non-equilibrium solidification of the peritectoeutectic reaction at **P** and correspond to the minimum point **M**. The temperature of 605°C is almost the same as 606°C of the minimum point **m**₂ of the KCl-NaCl-NaF ternary system. Thus, the composition of **M** was presumed to be extremely near that of **m**₂. In order to determine more precisely the temperature and composition of **M**, the samples on the **m**₂-K₂NaVF₆ line were examined by thermal analysis. The results are shown in Fig. 10. The temperature of **M** was determined to be 605 $\pm$ 1.5°C while its composition could not be determined exactly by

Fig. 9 KCl–NaCl–NaF–K₂NaVF₆–Na₃VF₆ system.

- e₁: ternary eutectic point, 648°C, {KCl(72)–NaF(28)}–K₂NaVF₆(about 0.5%)
- e₂: ternary eutectic point, 661°C, NaCl(24.3)–NaF(70)–Na₃VF₆(5.7%)
- e₃: ternary eutectic point
- p: peritectoeutectic point, 642°C, KCl(23)–NaCl(69)–K₂NaVF₆(8%)
- P: peritectoeutectic point, 620°C, {KCl(15)–NaCl(60)–NaF(25)}–K₂NaVF₆(several %)
- m₁: ternary minimum point, 632°C, KCl(37)–NaCl(57)–K₂NaVF₆(6%)
- m₂: ternary minimum point, 606°C, KCl(41.75)–NaCl(41.75)–NaF(16.5%)
- M: quaternary minimum point, 605°C, {KCl(41.75)–NaCl(41.75)–NaF(16.5)}–K₂NaVF₆(about 0.2%).

thermal analysis, and it was estimated to be {KCl(41.75)–NaCl(41.75)–NaF(16.5)}–K₂NaVF₆(about 0.2%).

With the aid of Fig. 9 and on the basis of the results of the thermal analysis for the samples in Fig. 6, the liquidus surface of the NaCl–NaF–K₂NaVF₆ system was constructed as shown in Fig. 11. A, B, C, and D are the regions of the primary crystallization of K₂NaVF₆, Na₃VF₆, NaCl, and NaF, respectively. a and b are the intersections of the NaCl–K₂NaVF₆ system and the binary eutectic lines on which the reactions $L = \text{NaCl} + \text{Na}_3\text{VF}_6$ and $L = \text{K}_2\text{NaVF}_6 + \text{Na}_3\text{VF}_6$ occur respectively⁽³⁾. c and d are the intersections of the NaCl–NaF–K₂NaVF₆ plane and the ternary eutectic lines, e₂P and e₃P, respectively. e₄ and e₅ are the binary eutectic points of the NaCl–NaF system and NaF–K₂NaVF₆ system, respectively. The bold lines, a–d, b–c, c–e₄, d–e₅, and c–d are the cross lines of the NaCl–NaF–

K₂NaVF₆ plane and the binary eutectic surfaces which are saturated with K₂NaVF₆ and Na₃VF₆, NaCl and Na₃VF₆, NaCl and NaF, K₂NaVF₆ and NaF, and Na₃VF₆ and NaF, respectively.

The temperature of P in Fig. 9 was $620 \pm 4^\circ\text{C}$ as can be seen from Fig. 7. Considering the positions of p, M, c, and d (Figs. 9 and 11), the composition of P was estimated to be {KCl(15)–NaCl(60)–NaF(25)}–K₂NaVF₆(several %).

IV. Summary

The phase diagram of the KCl–NaCl–NaF–K₂NaVF₆ system, which is a partial system of the KF–NaF–VF₃–KCl–NaCl–VCl₃ reciprocal quaternary system, was investigated by thermal analysis and X-ray diffraction analysis. The results obtained are summarized as follows:

- (1) The KCl–NaF–K₂NaVF₆ system is

Fig. 10 {KCl(41.75) – NaCl(41.75) – NaF(16.5)} – K_2NaVF_6 section.

Fig. 11 Liquidus surface of the NaCl–NaF– K_2NaVF_6 system.

a: 880°C, NaCl(69)– K_2NaVF_6 (31%)

b: 680°C, NaCl(87)– K_2NaVF_6 (13%)

e₄: 680°C, NaCl(66)–NaF(34%)

e₅: 865°C, NaF(85)– K_2NaVF_6 (15%).

A, B, C, and D are the regions of the primary crystallization of K_2NaVF_6 , Na_3VF_6 , NaCl, and NaF, respectively.

of the ternary eutectic type and its eutectic point is situated at 648°C and a composition of {KCl (72) – NaF (28)} – K_2NaVF_6 (about 0.5%).

(2) The NaCl–NaF– K_2NaVF_6 system is not quasi-ternary and includes the surface of the primary crystallization of Na_3VF_6 .

(3) The KCl–NaCl–NaF system is of the minimum-point type and its minimum point is situated at 606°C and a composition of KCl (41.75)–NaCl (41.75)–NaF (16.5%).

(4) Two invariant points exist in the KCl–NaCl–NaF– K_2NaVF_6 composition region: one is a quaternary minimum point and the other is supposed to be a peritectoeutectic point. The minimum point is at 605°C and at a composition of {KCl (41.75)–NaCl (41.75)–NaF (16.5)}– K_2NaVF_6 (about 0.2%) and its reaction is $L = (KCl-NaCl) \text{ solid solution} + NaF + K_2NaVF_6$. The peritectoeutectic point is situated at 620°C, its composition is estimated to be {KCl (15)–NaCl (60)–NaF (25)}– K_2NaVF_6 (several %), and its reaction is inferred to be $L + Na_3VF_6 = NaCl + NaF + K_2NaVF_6$.

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