Phase Diagram of Ternary DyCl₃-KCl-NaCl System

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The phase diagrams of binary DyCl₃-KCl, DyCl₃-NaCl, and KCl-NaCl systems, and related quasi-binary systems have been determined by the DTA method. The phase diagram of ternary DyCl₃-KCl-NaCl system was determined from the results of these binary systems.

1 Introduction

Phase diagrams are the important data for mixture melts. The phase diagrams of binary DyCl₃-KCl and DyCl₃-NaCl systems were reported by Korshunov and Drobot¹⁾ and by Kutscher and Schneider²⁾, and the phase diagrams of KCl-NaCl system were reported by many authors, and recently by Scheil and Stadelmaier³⁾.

In the present experiment, to determine the phase diagram of ternary DyCl₃-KCl-NaCl system those of the same binary systems and quasi-binary systems were measured. These 3 binary diagrams were in good agreement with the results in the above references.

2 Experimental

2.1 Materials

Dysprosium chloride was prepared by heating the mixture of Dy₂O₃ and NH₄Cl according to the reaction.

This reaction was carried out at 350°C for 90 minutes *in vacuo*, and the mixing ratio of NH₄Cl to DyCl₃ was about 2.5 times the theoretical amount of NH₄Cl in the above equation. The crude DyCl₃ obtained still contained a small amount of water and NH₄Cl, and purification of this chloride was necessary. The purification was carried out by sublimation at 950~1000°C for about 8 hours *in vacuo*. The results of emission spectrochemical analysis for DyCl₃ crystal are shown in Table 1.

KCl and NaCl were of reagent grade, and were demoiured at 700°C for about 8 hours *in vacuo*.

2.2 Measurements

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Table 1 Result of emission spectrochemical analysis for DyCl₃ crystal

Element	Content/ppm
Y	60
Tb	15
Ho	15
Er	15
Ca	0.5
Mg	1

Measurements were carried out by the usual procedure of the DTA method. The melting and transition points were obtained from the cooling curves of the molten samples in an atmosphere of purified argon gas, Al₂O₃ powder being used as a reference material. The cooling rates were 11°C/min at 800°C, and 5°C/min at 400°C, and for the KCl-NaCl system the slower cooling rates were applied, *i.e.* 5°C/min at 800°C and 2°C/min at 600°C.

3 Results and Discussion

3.1 Binary Systems

Phase diagrams of binary DyCl₃-KCl, DyCl₃-NaCl, and KCl-NaCl systems are shown in Figs. 1, 2, and 3, in which the wedge marks represent the eutectic, peritectic, or congruent points.

The intermediate compounds KDy₃Cl₁₀ (KCl·3 DyCl₃) and K₃DyCl₆ (3 KCl·DyCl₃) were observed in the DyCl₃-KCl system, and in the DyCl₃-NaCl system the compounds NaDy₃Cl₁₀ (NaCl·3 DyCl₃) and Na₃DyCl₆ (3 NaCl·DyCl₃) were observed. The intermediate compound K₃DyCl₆ has a transition point at 375°C in the solid state, and the temperature is lower than that reported by Korshunov and Drobot¹⁾, but the temperatures of points represented by the wedge marks were higher by 20°C or more than theirs except points B and K.

Fig. 1 Phase diagram of DyCl_3 -KCl system

- A: Eutectic 535°C 81.0 DyCl_3 mol%
 B: Congruent 574°C 75.0 DyCl_3 mol%
 C: Eutectic 450°C 40.0 DyCl_3 mol%
 D: Congruent 805°C 25.0 DyCl_3 mol%
 K: Eutectic 675°C 15.0 DyCl_3 mol%

Fig. 2 Phase diagram of DyCl_3 -NaCl system

- F: Peritectic 440°C 69.0 DyCl_3 mol%
 G: Eutectic 402°C 45.0 DyCl_3 mol%
 H: Peritectic 540°C 35.5 DyCl_3 mol%

3.2 Ternary DyCl_3 -KCl-NaCl System

From the results of the binary systems and related 13 quasi-binary systems which were represented by the lines passing through the

Fig. 3 Phase diagram of KCl-NaCl system

- I: Minimum 667°C 49.3 NaCl mol%
 J: 543°C 75.0 NaCl mol%

apexes of DyCl_3 and KCl in DyCl_3 -KCl-NaCl triangle coordinate (Fig. 4), the phase diagram of ternary DyCl_3 -KCl-NaCl system were determined. The ternary diagram is shown in Fig. 5, and the enlarged diagram of region s-t-u-v-w in Fig. 5 is also shown in Fig. 6.

Fig. 4 Quasi-binary lines

- a: 10 NaCl mol%, b: 20, c: 30, d: 40,
 e: 50, f: 60, g: 70, h: 80, i: 90
 DyCl_3 mol%, k: 55, l: 60, m: 65

This ternary diagram has a eutectic point (397°C, DyCl_3 -KCl-NaCl: 46.5-11.0-42.5 mol%), 4 eutectic curves, 2 peritectic curves, and a

Fig. 5 Phase diagram of DyCl_3 -KCl-NaCl system

Table 2 Eutectic, peritectic, and minimum melting curves in ternary DyCl_3 -KCl-NaCl system

Curve	Point	Temp./°C	Composition DyCl_3 -KCl- NaCl/mol%
AQ eutectic	A	535	81.0-19.0-0
CQ eutectic	C	450	40.0-60.0-0
KQ eutectic	K	675	15.0-85.0-0
GQ eutectic	G	402	45.0-0-55.0
FL peritectic	Q	397	46.5-11.0-42.5
HN peritectic	F	440	69.0-0-31.0
IM minimum melting	H	540	35.7-0-64.3
	I	667	0-50.7-49.3
	L	440	70.7-1.8-27.5
	M	510	33.8-18.0-48.2
	N	620	16.1-34.0-49.9

minimum curve. The temperatures and compositions of these curves are given in Table 2.

4 Summary

In order to obtain the phase diagram of the DyCl_3 -KCl-NaCl system,

Fig. 6 Enlarged diagram of region s-t-u-v-w in Fig. 5

o: Observed points

(1) Phase diagrams of 3 binary systems and related 13 quasi-binary systems were measured, and the phase diagrams of the binary systems were presented. The temperatures of eutectic, peritectic, and minimum melting points were higher than those in the literature except points B and K in the DyCl_3 -KCl system.

(2) The phase diagram of ternary system obtained had 4 eutectic, 2 peritectic, and a minimum melting curves, and a eutectic point.

References:

- 1) B.G. Korshunov and D.V. Drobot, *Zh. Neorg. Khim.* **10**, 939 (1965).
- 2) J. Kutscher and A. Schneider, *Z. Anorg. Allg. Chem.* **408**, 135 (1975).
- 3) E. Scheil and H. Stadelmaier, *Z. Metallk.* **43**, 227 (1952).

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