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Phase equilibria of $NdCl_3$–NaCl–KCl

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Abstract

Molten chloride is considered to be applied to a fast-breeder-reactor fuel and a solvent in the pyrochemical reprocessing of spent nuclear fuel. In this work, phase diagrams for molten chloride systems were constructed, using $NdCl_3$ as an imitative substance in place of UCl_3 or $PuCl_3$. A compound of $3NdCl_3 \cdot NaCl$, which melts incongruently at 540°C to $NdCl_3$ and liquid and a eutectic at 437°C were found in the $NdCl_3$–NaCl system. In the $NdCl_3$–KCl system, many invariant reactions were observed: the decomposition of $NdCl_3 \cdot 2KCl$ and $2NdCl_3 \cdot KCl$ at 444 and 474°C, respectively; a eutectic at 489°C; a peritectic at 506°C and a monotectic at 624°C. It is thought that there should be a peritectic compound of $6NdCl_3 \cdot KCl$ above 474°C. A compound of $2NdCl_3 \cdot NaCl \cdot KCl$ was considered to exist in the ternary system of $NdCl_3$–NaCl–KCl, to which attention should be paid in determining the composition of the fuel of the molten-salt fast breeder reactor. © 1997 Elsevier Science B.V.

1. Introduction

Recently, solid fuels cladded with metal, alloy, or graphite are usually utilized in nuclear power reactors. These reactor configurations have the advantage of having the ability to make use of conventional generating techniques using a steam turbine generator by exchanging heat through an appropriate coolant. However, there are many difficulties such as the deformation of solid fuels, the risk of loss of coolant accident, and the fabrication, transport and reprocessing of spent nuclear fuel.

A fast breeder reactor (FBR) fueled with molten chlorides can be considered as a candidate system realizing 'in situ' plutonium recycling [1,2], which is largely safe and enables the minimization of various difficulties in the fuel reprocessing using exceedingly stable molten-salt mixtures under normal pressure. A solution of trichlorides of uranium and plutonium dissolved in alkali and/or alkaline-earth chlorides may be adequate as an FBR fuel and NaCl, KCl and $MgCl_2$ have been reported as promising components of the diluents [1,2].

On the other hand, a molten chloride/cadmium system is thought to be useful for the application of pyrometallurgy to the nuclear fuel reprocessing or HLW partitioning.

The following are possible subjects to be investigated for the design of these plants:

- Study of physico-chemical properties of molten chloride mixtures.
- Research on the materials to be utilized for the container or internals.

We can find, however, very few fundamental studies on the physical and chemical properties of the molten chloride mixtures from this viewpoint.

In this work, using lanthanide as an imitative substance in place of uranium or plutonium, phase diagrams for the chloride systems containing $NdCl_3$ were constructed. Because lanthanides belong to the same group (IIIa) as actinides and their ionic radii are almost the same, not only their chemical properties but crystallographic behaviors are very similar to one another. Furthermore, thermodynamical properties of lanthanide trichlorides are also similar to actinide trichlorides. Thus, light rare-earth trichlorides are considered to be ideal to imitate UCl_3 or $PuCl_3$.

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2. Experimental

Anhydrous neodymium chloride ($NdCl_3$) of 99.9% in purity, sodium chloride (NaCl) of 99.99% and potassium chloride (KCl) of 99.8% were used to prepare the sample mixtures. The neodymium chloride, received in a sealed glass ampule, was opened in a glove box under dry nitrogen and stored in sealed glass jars. All samples were treated in this glove box under dry inert atmosphere. Chloride mixtures which have various compositions were prepared by taking weighed amounts of the components prior to melting and freezing in a Ni-foil-spread alumina crucible. The composition was determined considering the loss in weight due to vaporization of NaCl or KCl. The mixtures were ground prior to use as samples for differential thermal analysis (DTA) and X-ray diffractometry (XRD).

The instrument used for DTA was a Shimadzu DTA-30 System, which allows an experimental run in an inert atmosphere (argon in the present work) and its Pt–Pt13%Rh thermocouple was calibrated by measuring the melting points of Sn, Zn, Al and Ag, which are fixed points of temperature in ITS-90. Small platinum containers were used for holding the sample and the reference material (α-Al_2O_3 powder in this work). Phase transition temperatures of each sample were obtained with a heating curve at a rate of 15 K/min in argon flowing at 100 ml/min.

The solid phase was characterized by XRD using CuKα radiation. The sample was powdered and loaded in a glass holder, which was sealed in an aluminum container filled with dry nitrogen and XRD patterns were obtained at room temperature. The experimental error of the diffraction angle due to using this aluminum container was confirmed to be controlled within $\pm 0.1°$ using SRM 675 (mica powder: $KAl_2Si_3O_{10}(OH)_2$, provided from NIST) as an external standard.

3. Characteristics of components

3.1. Sodium and potassium chlorides

The melting points of NaCl and KCl were 800 and 770°C, respectively. After these measurements, a considerable loss in weight of each sample was observed: a few percent of the alkali chloride sample vaporized during heating and cooling between their melting points and room temperature. Both NaCl and KCl have a comparatively high vapor pressure, for instance about 10^{-4} atm at 1000 K. A considerable loss in weight of the chloride mixtures containing $NdCl_3$ occurred while preparing the mixture samples and the compositions of the mixtures were estimated taking the loss into account.

3.2. Neodymium chloride

Neodymium chloride is very hygroscopic and deliquescent. Moreover, it reacts with oxygen and water at a higher temperature, approximately above 300–400°C:

$$2NdCl_3 + O_2 \rightarrow 2NdOCl + 2Cl_2, \quad (1)$$

$$NdCl_3 + H_2O \rightarrow NdOCl + 2HCl. \quad (2)$$

Therefore, the atmosphere should be carefully controlled. This is also true of actinide trichlorides. To make matters worse, uranium, for instance, is ready to be oxidized to $UOCl_2$, UO_2, etc.

If NdOCl was adulterated with $NdCl_3$, a eutectic of $NdCl_3$–NdOCl would be observed. The eutectic temperature was observed to be 740°C in this work while it was reported to be 722°C [3].

The melting point of $NdCl_3$ was observed to be 755 ± 5°C, when the atmosphere was successfully controlled and the eutectic of $NdCl_3$–NdOCl was not detected. The melting point agreed with the literature value [4].

4. Phase diagrams

4.1. $NdCl_3$–NaCl system

4.1.1. Results

This system was found to have three regions which showed different aspects: peritectic and liquidus were observed in the $NdCl_3$-rich region; eutectic, peritectic and liquidus in the intermediate region and eutectic and liquidus in the NaCl-rich region. The transition temperatures are given in Table 1.

Table 1
Results of DTA on the $NdCl_3$–NaCl system

Composition (mol% NaCl)	Transition temperature (°C)		
	eutectic	peritectic	liquidus
0.0			759
3.2		540	755
9.0		537	748
17.0		546	720
27.7	438	536 [a]	678
32.4	438	520 [a]	646
38.0	435	545 [a]	604
50.0	433		515
58.1	437		482
64.8	433		
72.9	437		601
86.2	441		774
95.0	434		806
100			800

[a] The 'on-set' temperature is intrinsically uncertain.

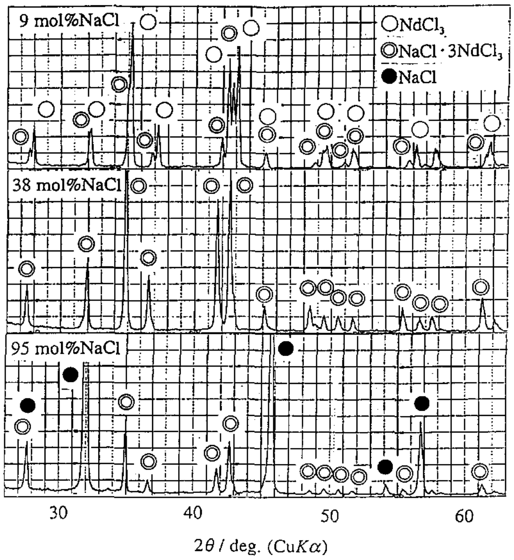

Fig. 1. Comparison of XRD patterns on the $NdCl_3$–NaCl system.

Some XRD patterns obtained in this system are shown in Fig. 1. Many peaks attributed to neither $NdCl_3$ nor NaCl were observed. Therefore, it can be assumed that a compound was formed and its composition was 25 mol% NaCl, namely $3NdCl_3 \cdot NaCl$, taking the results of DTA into consideration. The phase diagram of the $NdCl_3$–NaCl system thus obtained is shown in Fig. 2.

4.1.2. Discussion

The phase diagram for this system was once reported as a simple eutectic system [5], just like those of the UCl_3–NaCl [6] and $PuCl_3$–NaCl systems [7]. However, a peritectic compound $3NdCl_3 \cdot NaCl$ was found in the present work, which was also reported by Sharma et al. [8] and a compound having the same composition was reported in the $PrCl_3$–NaCl system [9]. The diagram obtained in this work showed very good agreement with that of Sharma et al. though the $NdCl_3$–NdOCl eutectic was still observed in their samples. Seifert et al. [10] reported a compound of '$NaNd_{1.67}Cl_6$' (i.e., 37.5 mol% NaCl) but, as seen in Table 1, an eutectic was detected between 25 and 37.5 mol% NaCl in this work.

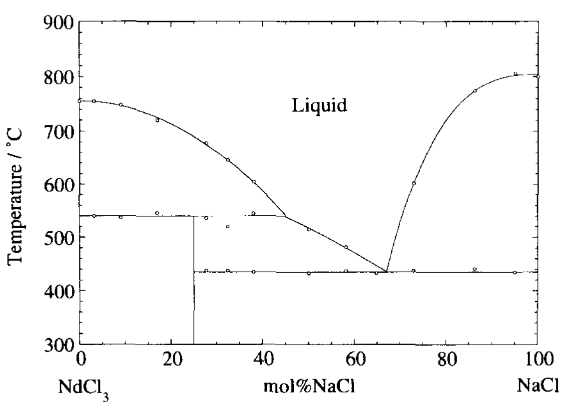

Fig. 2. The phase diagram of the $NdCl_3$–NaCl system.

The XRD pattern of the compound $3NdCl_3 \cdot NaCl$ was very similar to that of pure $NdCl_3$. To be more precise, the pattern seemed only to shift slightly. Actually, its diffraction data could be indexed as hexagonal. The lattice parameters $a_0 = 7.50$ Å and $c_0 = 4.25$ Å were obtained. Only one direction parallel to the a-axis seems to lengthen selectively.

4.2. $NdCl_3$–KCl system

4.2.1. Results

In this system, many invariant reactions were observed within a narrow temperature range. The transition temperatures obtained are summarized in Table 2. Several XRD patterns obtained are shown in Fig. 3. Taking these results

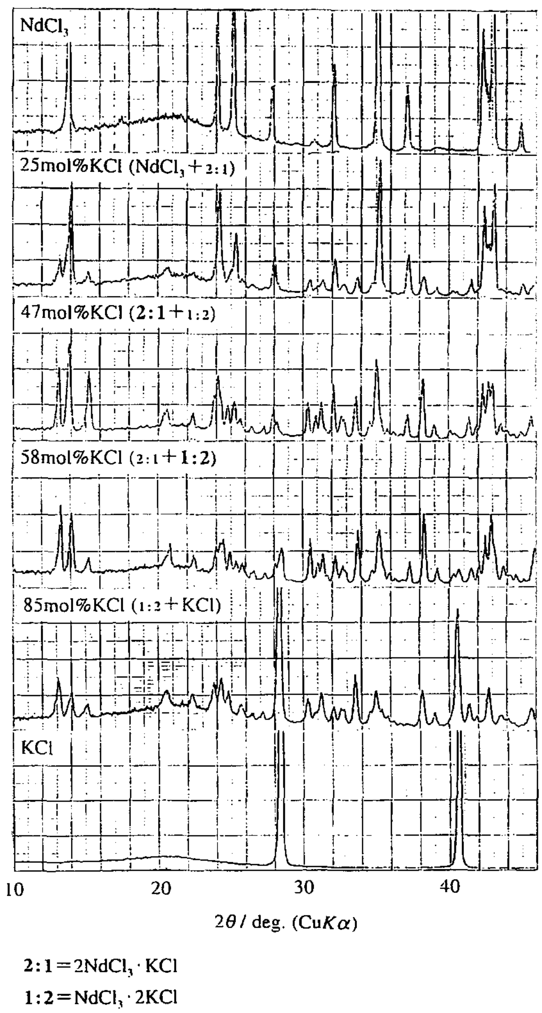

Fig. 3. Comparison of XRD patterns on the $NdCl_3$–KCl system.

Table 2
Results of DTA on the $NdCl_3$–KCl system

Composition (mol% KCl)	Transition temperature (°C)					
	decomp. [a]	decomp. [b]	eutectic	peritectic	monotectic [e]	liquidus
0.0						759
13.7		474 [c]		507		689
17.8		470 [d]	484	507		664
25.4		474 [d]	486	504		604
37.1	444	461	482			
46.7	444	474	489			564
52.3	444	464	492			590
57.8	444	474	487			612
63.4	444	474	489		604	642
73.3	439		492		606	689
76.5	444		489		610	693
79.3	444		489		632	
84.6	444		489		621	689
89.6	444		489		619	724
94.9	440		487		606	746
100						770

[a] Decomposition: 2 ($NdCl_3 \cdot 2KCl$) ⇄ 3 KCl + $2NdCl_3 \cdot KCl$.
[b] Decomposition: 3 ($2NdCl_3 \cdot KCl$) ⇄ 2 KCl + $6NdCl_3 \cdot KCl$.
[c] Synthesis: $2NdCl_3 \cdot KCl$ + 4 $NdCl_3$ ⇄ $6NdCl_3 \cdot KCl$.
[d] Decomposition reaction succeeded the synthesis described above.
[e] The 'on-set' temperature is intrinsically uncertain.

into account, it is thought that there are two intermediate compounds at room temperature in the $NdCl_3$–KCl system and that their compositions are $2NdCl_3 \cdot KCl$ and $NdCl_3 \cdot 2KCl$, respectively. Thus, the phase diagram of this system was obtained as is shown in Fig. 4; a peritectic compound of $6NdCl_3 \cdot KCl$ should exist above 474°C to make the reaction at 506°C explainable.

4.2.2. Discussion

$RCl_3 \cdot 2KCl$-type intermediate compounds (R = rare-earth elements) were reported in plural studies and the X-ray powder diffraction data for the compounds indicate

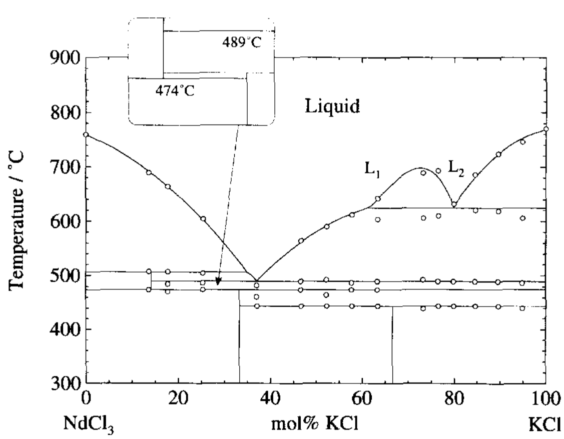

Fig. 4. The phase diagram of the $NdCl_3$–KCl system.

that they are grouped into K_2PrCl_5-type orthorhombic. In the phase diagrams [11], these were shown as peritectic compounds while $NdCl_3 \cdot 2KCl$ was found to decompose at 444°C in this work.

$NdCl_3 \cdot 3KCl$ was not observed in this work. $RCl_3 \cdot 3KCl$-type compounds were reported by Korshunov and co-workers [11] to be stable over all temperature ranges up to their congruent melting points while Seifert et al. showed that they existed only at a higher temperature and only for R = Ce–Sm and gave their crystallographic data using high temperature XRD. Seifert [10] reported the temperature of the synthesis reaction for $NdCl_3 \cdot 3KCl$ to be 446°C, which corresponds to the decomposition temperature of $NdCl_3 \cdot 2KCl$ in this work.

$2NdCl_3 \cdot KCl$ which decomposes at 474°C was observed. $2RCl_3 \cdot KCl$-type compounds were reported for heavy rare-earths (R = Sm–Yb, Y), but Seifert et al. [10] reported that $2NdCl_3 \cdot KCl$ formed only upon heating at 467°C and decomposed at 510°C, which could be thought to correspond to $6NdCl_3 \cdot KCl$ in the present work.

4.3. Preliminary investigation for $NdCl_3$–NaCl–KCl system

For this system, only liquidus temperature was investigated preliminarily. Results of the DTA implied the existence of an intermediate ternary compound. In fact, the liquidus temperature of the $46NdCl_3$–27NaCl–27KCl sample were higher than those of surrounding composi-

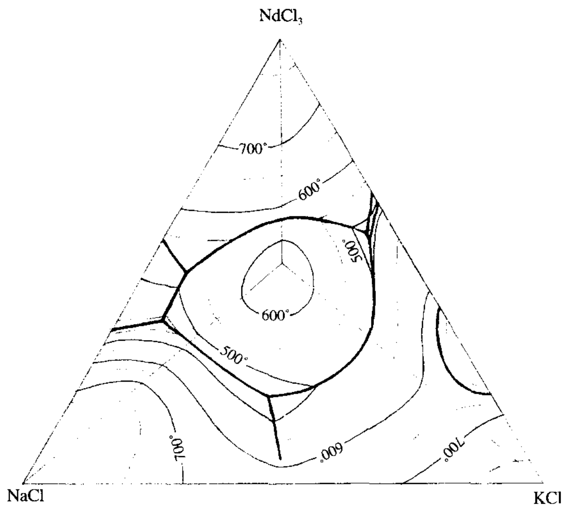

Fig. 5. The phase diagram of the $NdCl_3$–NaCl–KCl ternary system.

tions. Fig. 5 is the ternary phase diagram which could be estimated from these results and three binary diagrams constituting outlines of the diagram for this system.

It can be considered that the ternary compound is $2NdCl_3 \cdot NaCl \cdot KCl$ if it melts congruently. This compound is unfavorable to the application of a NaCl–KCl molten mixture to the diluent for FBR molten chloride fuel. If a NaCl–KCl mixture is utilized in such a system, the fraction of NaCl should be lowered.

5. Conclusion

The phase equilibria of a molten chloride mixture was investigated, using $NdCl_3$ as an imitative substance in place of UCl_3 or $PuCl_3$.

The phase diagram of $NdCl_3$–NaCl system was constructed; a compound of $3NdCl_3 \cdot NaCl$, which melts incongruently at 540°C to $NdCl_3$ and liquid and a eutectic at 437°C were found.

The phase diagram of $NdCl_3$–KCl system was also constructed; it can be thought that two intermediate compounds of $NdCl_3 \cdot 2KCl$ and $2NdCl_3 \cdot KCl$ exist at ambient temperature and decompose at 444°C and 474°C, respectively. A eutectic at 489°C, a peritectic at 506°C and a monotectic at 624°C were observed and it is thought that there should be a peritectic compound of $6NdCl_3 \cdot KCl$ above 474°C to the peritectic point of 506°C.

The ternary diagram of the $NdCl_3$–NaCl–KCl system was investigated preliminarily. A compound of $2NdCl_3 \cdot NaCl \cdot KCl$ was considered to exist in the system and it was indicated that this compound is undesirable for the fuel of molten-salt fast breeder reactors and attention should be paid to determining its composition.

References

[1] P.A. Nelson, D.K. Butler, M.G. Chasanov, D. Meneghetti, Nucl. Appl. 3 (1967) 540.
[2] M. Taube, EIR-249, 1974.
[3] F.N. T'en, I.S. Morozov, Zh. Neorg. Khim. 14 (1969) 2246.
[4] A.S. Dworkin, M.A. Bredig, J. Phys. Chem. 67 (1963) 697.
[5] I.S. Morozov, Z.N. Shevtsova, L.V. Klyukina, Zh. Neorg. Khim. 2 (1957) 1639.
[6] C.J. Barton, ORNL-2548, 1959, p. 133.
[7] C.W. Bjorklund, J.G. Reavis, J.A. Leary, K.A. Walsh, J. Phys. Chem. 63 (1959) 1776.
[8] R.A. Sharma, R.A. Rogers, J. Am. Ceram. Soc. 75 (9) (1992) 2484.
[9] T. Hattori, H. Ikezawa, R. Hirano, J. Mochinaga, J. Chem. Soc. Jpn. 6 (1982) 952.
[10] H.-J. Seifert, H. Fink, J. Uebach, J. Thermal Anal. 33 (1988) 625.
[11] Phase Diagrams for Ceramists, The American Ceramics Society, NIST, vol. I, 1964, vol. II, 1969, vol. III, 1975, vol. VII, 1989.