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Journal of Alloys and Compounds 271–273 (1998) 374–377

Journal of ALLOYS AND COMPOUNDS

Stability of UNCl in LiCl–KCl eutectic melt

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Abstract

The uranium nitride chloride (UNCl) was prepared from U_2N_3 and UCl_3. The dissolution of UNCl, UN, U_2N_3 and U_3O_8 in LiCl–KCl eutectic melt was studied. The nitrides were studied for the effects of unreacted residues in preparing UNCl; U_3O_8 for the effect of impurity oxygen. The apparent solubility of UNCl in LiCl–KCl melt was extremely low, $\sim 7\times10^{-3}$ wt% U at 773 K, but those of nitrides were even lower. Also the EMF of the cell UN(s)|UNCl, LiCl–KCl|LiCl–KCl, Ag^+|Ag was measured. At 773K, the EMF was -1.024 V with a Ag/AgCl ($x=0.091$) reference electrode at the saturation of UNCl. These data as well as thermochemical consideration preclude significant decomposition of UNCl in LiCl–KCl eutectic melt.

Keywords: Uranium nitride chloride; EMF; Eutectic melt; Molten LiCl–KCl

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1. Introduction

In the electrolytic decomposition of UN pellet in LiCl–KCl–UCl_3 molten salts at 773 K, UNCl was formed as a byproduct in addition to UCl_3. After completion of the electrolytic decomposition, bulk salt, bottom sediment, anode residue and cathode deposit were analyzed by X-ray diffraction and EPMA. Fine particles of UNCl were found as the sediment. Nitrogen in UN was either released into helium, which swept through the cell, or combined as UNCl, but their fractions were dependent on the electrolysis condition.

The ternary compound UNCl was first identified by Juza and Meyer [1]. Its structure has a tetragonal symmetry with space group *P4/nmm* [2,3]. The compound seems to decompose in vacuum to produce U_2N_3 at temperatures above 1273 K [4]. However, there has been no data on the thermodynamic stability of UNCl in molten salts. Therefore, we synthesized UNCl and studied its thermodynamic stability in LiCl–KCl eutectic melt.

2. Experimental

2.1. Materials preparation

All materials were treated in a dry box with an argon purification circuit. The typical impurities in the box were oxygen below 3 ppm and water below 2ppm. Products as prepared below were identified by X-ray diffraction analysis. Hygroscopic samples were mounted on standard glass holders with their surfaces covered with polyethylene films.

The uranium sesquinitride sample was prepared by direct nitridation of metal uranium at 1073 K in flowing nitrogen. The sesquinitride sample for the UNCl preparation had an atomic ratio of N/U=1.63 and an oxygen content of 480 ppm. That for the solubility measurement in molten salts had N/U=1.69 and 340 ppm of oxygen. The uranium mononitride sample was obtained by decomposing the latter U_2N_3 at 1273 K in a vacuum of 3×10^{-4} Pa. The sintered pellet of UN used in the EMF measurement had a density of 67% TD, and a size of 6 mm in diameter and 7 mm in height. It had a composition of $UN_{0.989}O_{0.010}$.

The uranium tetrachloride sample was made by the reaction of uranium metal powder and chlorine. A metal piece was first converted to hydride by contacting with hydrogen at 523–553 K. The hydride was decomposed to fine metal powder in a helium atmosphere at 723 K. The metal powder was reacted with chlorine at 523–553 K to produce UCl_4. The uranium trichloride was prepared by reducing UCl_4 with Zn at 723 K in a vacuum sealed pyrex-glass tube.

The uranium nitride chloride (UNCl) was synthesized by the reaction between U_2N_3 and UCl_3. The U_2N_3 and UCl_3 powders were intimately mixed in an agate motor. The sesquinitride was in excess by ~2 mol% from the equimolar composition in order to prevent the UCl_3 from remaining in the sample, which may interfere in the later

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0925-8388/98/$19.00
PII: S0925-8388(98)00092-9

measurements. The effect of residual U_2N_3 was studied in the dissolution experiments described below. The mixture was vacuum sealed in a quartz tube. The heating was made at 973 K for 23 h and then 1023 K for 2.5 h. The products contained a small amount of U_2N_3 (Fig. 1). In a preliminary study with differential thermal analysis, the starting mixture was sealed in a gold crucible and heated to 1173 K at a rate of 30 K min^{-1}. A very broad exothermic peak, whose apparent integral heat of reaction was of the order of the heat of fusion of metal chlorides, was found in a temperature range from 873 to 1073 K. The peaks corresponding to the melting/freezing of UCl_3, which are expected at about 1110 K, were absent in the succeeding heating/cooling runs between room temperature to 1173 K on the same sample. Any other additional peaks were not observed either.

The U_3O_8 was prepared by oxidizing uranium dioxide powder in air at 873 K. The LiCl–KCl salts of eutectic composition (41 mol% KCl) of 99.99% certified purity was as-purchased from Anderson Physical Laboratory Engineered Materials.

2.2. Dissolution in molten LiCl–KCl

Dissolution of UNCl, UN, U_2N_3 and U_3O_8 in the LiCl–KCl eutectic melt was studied. The nitrides were investigated for the effects of unreacted residues from the UNCl preparation; U_3O_8 for the effect of impurity oxygen. Each powder was mixed into 10 g of LiCl–KCl, and sealed in a quartz ampoule at a vacuum-gauge reading of 10^{-3} Pa at the vacuum line. The ampoule was placed in a muffle furnace whose temperature was controlled within ±1°C. The ampoule was occasionally shaken during heating. After settling the undissolved sediment, the ampoule was taken out of the furnace and air-cooled. The freezing of the salt mixtures took place within 1 min. The cleared bulk of LiCl–KCl was analyzed for uranium content by fluorescence analysis. The technique had a sensibility of 1×10^{-4} wt% U for a sample salt weight of about 1 g, and a relative error of within 14% (one standard deviation of the mean).

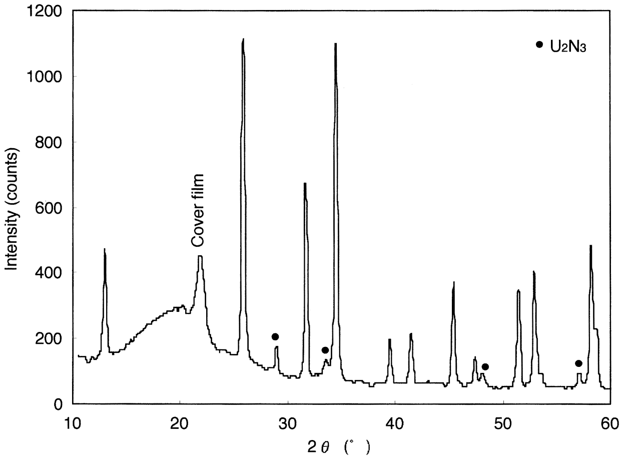

Fig. 1. X-Ray diffraction pattern on UNCl sample.

2.3. EMF measurements

The reading of electromotive force (EMF) was made with a vibrating reed electrometer having an input resistance of 10^{15} ohms. The EMF of the cell:

CELL 1:UN(s)|UNCl (x from 7.9×10^{-6} to saturation), LiCl–KCl|LiCl–KCl, Ag^+ (x=0.091)|Ag

was measured. Here the molar fraction x(UNCl) is nominal: No correction is made for the amount of residual U_2N_3 and impurity oxygen. The UN sintered pellet was held by a quartz open tube attached with a tantalum lead. The Ag/AgCl reference electrode consisted of a silver plate immersed in LiCl–KCl eutectic salt containing 9.1 mol% AgCl. The casing of the reference electrode was a mullite tube. The LiCl–KCl–(UNCl) salts were contained in a recrystallized alumina crucible, which had been degreased by heating to 1073 K in air. The whole assembly was encased in a gas-tight quartz vessel. Assembling was performed in a dry box described above. The vessel interior was swept using purified helium during the measurements.

After the measurement at each concentration of UNCl, the cell was cooled to room temperature. An additional amount of UNCl was charged in the dry box, and then the measurement with increased UNCl concentration was continued. Measurement temperature was 773 K. An attempt to observe the temperature dependence of the EMF was aborted. The apparent equilibrium was reached in about 24 h at 773 K, but it took much longer at lower temperatures. Besides, when cooling after the attainment of the apparent equilibrium at 773 K, the reading often became erratic at lower temperatures.

In the identical arrangement, the EMF of the cell:

CELL 2:U(s)|UCl_3 (x from 3.5×10^{-4} to 5.1×10^{-3}), LiCl–KCl|LiCl–KCl, Ag^+ (x=0.091)|Ag

was measured [5] in order to check the accuracy of the data in the present arrangement. A metal uranium rod was suspended by a tantalum rod. The EMF at temperatures 723–773 K, which was corrected for the difference in the AgCl concentration of the reference electrodes, was 3–7 mV lower than that measured by Knacke [6]. The difference of about -3 mV was found to be due to the mullite casing of the reference electrode, which was used in these measurements for its robustness compared with a pyrex-glass membrane. The maximum difference of -7 mV in EMF translates to that of ≤ -2 kJ mol^{-1} in the partial molar free energy of formation of UCl_3. In the correction for the AgCl concentration, the activity coefficient of AgCl(l) in the LiCl–KCl eutectic melt is assumed to be independent of its concentration for the narrow range of $x(\mathrm{AgCl})=0.0378$ (Knacke)–0.091 (this study).

3. Results and discussion

3.1. Dissolution in LiCl–KCl eutectic melt

The dissolved amounts of UNCl, UN, U_2N_3 and U_3O_8 in the LiCl–KCl eutectic melt are summarized in Table 1. The dissolved amount is represented by weight percent of uranium, since we do not know real chemical forms of species which dissolve in the molten salts. All these compounds showed very limited dissolution. The undissolved residue was identified by X-ray diffraction as identical with those originally added to LiCl–KCl.

Johnson [7] reported the solubility of UO_2 in the LiCl–KCl eutectic melt at 1073 K as 5×10^{-3} wt% U. No experimental detail is given. The author also mentioned that U_3O_8 initially forms a soluble phase, which slowly decomposes to insoluble UO_2. The present result of 5×10^{-3} wt% U for U_3O_8 at 773 K is, therefore, consistent with their data.

Both UN and U_2N_3 dissolved to less than 2×10^{-4} wt% U. The amount was less than that expected from their oxygen contaminations and the dissolution of U_3O_8. This could be ascribed to slower kinetics of dissolution of oxygen-bearing species in these nitrides.

From these observations, overestimation of the dissolution of UNCl due to the oxygen impurity and residual nitrides is considered to be negligible, if any. It is not certain, however, whether the dissolved amount represents the solubility. Uranium in UNCl could dissolve into the molten salts either by the dissociation of UNCl into ions or by its decomposition to a solid nitride (U_2N_3 or UN) and the dissolved UCl_3. Dissolution of UCl_3 into the molten salts can reduce its partial molar free energy to make the partial decomposition of UNCl thermochemically possible. This point is further discussed below.

3.2. EMF

The EMF of CELL 1 at 773 K is shown in Fig. 2 as a function of the nominal uranium amount added as UNCl to the LiCl–KCl eutectic melt. Apparent half-cell reaction is:

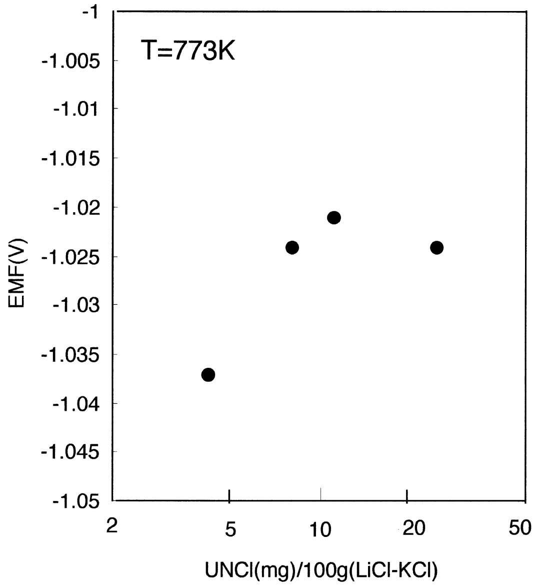

Fig. 2. EMF of CELL 1 as a function of nominal UNCl concentration.

$$\mathrm{UN(s)} + (1/2)\mathrm{Cl_2(g)} = [\mathrm{UNCl}], \tag{1}$$

where [UNCl] denotes the nitride chloride dissolved in the molten salts. A saturation level of $E=-1.024$ V was almost reached at a nominal concentration of 7.9×10^{-5} wt% U (or $x(\mathrm{UNCl})=1.5\times10^{-5}$).

With this saturation EMF, the equilibrium among UNCl, UN,U_2N_3 and UCl_3 in a closed system corresponding to the condition of dissolution measurement described above, can be discussed. In addition to Eq. (1), two reactions can be written:

$$3\mathrm{UNCl(s)} = 2\mathrm{UN(s)} + [\mathrm{UCl_3}] + (1/2)\mathrm{N_2(g)}, \tag{2}$$

$$3\mathrm{UNCl(s)} = \mathrm{U_2N_3(s)} + [\mathrm{UCl_3}], \tag{3}$$

where $[UCl_3]$ denotes uranium trichlorides dissolved in the molten salts. In Eqs. (2) and (3), it is implicit that UNCl in the melt is in saturation: its activity is unity. In the closed system, the partial pressure of nitrogen by Eq. (2) would become sufficiently high to convert UN to U_2N_3. Therefore, the reaction (3) is considered below.

We introduce the free energy, ΔG_r, of the reaction:

$$\mathrm{UN(s)} + (1/4)\mathrm{N_2(g)} = (1/2)\mathrm{U_2N_3}. \tag{4}$$

Table 1
Results of solubility measurements in the LiCl–KCl eutectic melt

Sample	Sample weight[a] (g)	T (K)	Time (h)	Dissolved U (wt% U in LiCl–KCl)
UNCl	0.300	773	68.5	7.2×10^{-3}
UNCl	0.365	633	23[b]	1.5×10^{-2}
UN	0.069	773	99.5	$<1\times10^{-4}$
$UN_{1.69}$	0.144	773	110.5	1.2×10^{-4}
U_3O_8	0.089	773	110.5	5.0×10^{-4}

[a] Charged into 10 g LiCl–KCl.

[b] Preceded by heating at 500°C for 68.5 h.

Combining Eqs. (1), (3), (4), we write:

$$\begin{aligned} RT\ \ln[x(\mathrm{UCl_3})] &= 96.483\ (\mathrm{kJ\ mol^{-1}})\cdot(3E) \\ &\quad + \Delta G_f{}^\circ(\mathrm{UN(s)}) - 2\Delta G_r - \Delta G_f{}^\circ(\mathrm{UCl_3(l)}) \\ &\quad - RT\ln\gamma(\mathrm{UCl_3}), \end{aligned} \tag{5}$$

where $\gamma(\mathrm{UCl_3})$ is the activity coefficient of $\mathrm{UCl_3(l)}$ and $x(\mathrm{UCl_3})$ is the molar fraction of dissolved $\mathrm{UCl_3}$. The $\Delta G_f{}^\circ(\mathrm{UCl_3(l)})$ is the free energy of formation of the super-cooled $\mathrm{UCl_3(l)}$. The E is the EMF of the CELL 1 converted to the $\mathrm{Cl_2/Cl^-}$ reference at the saturation of UNCl. The EMF with the Ag/AgCl reference is converted to the $\mathrm{Cl_2/Cl^-}$ reference by translating by -1.055 V: $E(\mathrm{vs.\ Cl_2/Cl^-}) = -2.079$ V.

Then, the equilibrium $x(\mathrm{UCl_3})$ can be estimated with the following data at 773 K:

$\Delta G_f{}^\circ(\mathrm{UN(s)}) = -227.6\ \mathrm{kJ\ mol^{-1}}$ (Barin [8])

$\Delta G_r = -32.9\ \mathrm{kJ\ mol^{-1}}$ (Tagawa [9]])

$\Delta G_f{}^\circ(\mathrm{UCl_3(l)}) = -679.4\ \mathrm{kJ\ mol^{-1}}$

(estimated from Barin [8])

$RT\ \ln\gamma(\mathrm{UCl_3}) = -31.6\ \mathrm{kJ\ mol^{-1}}$

(estimated from Knacke [6] with $\Delta G_f{}^\circ$ $(\mathrm{UCl_3(l)})$ above).

With the combined errors in the pertinent thermochemical data in Eq. (5), which would not be smaller than ±15 kJ $\mathrm{mol^{-1}}$, $x(\mathrm{UCl_3}) = 3\times10^{-5}$–$3\times10^{-3}$ is expected. The dissolved uranium at 773 K in Table 1 corresponds to $x(\mathrm{UCl_3}) = 1.6\times10^{-5}$, if the dissolved species is assumed mainly $\mathrm{UCl_3}$. Therefore, a partial decomposition of UNCl, which is at saturation in the LiCl–KCl molten salts, to a solid nitride (UN or $\mathrm{U_2N_3}$) and dissolved $\mathrm{UCl_3}$ cannot be refuted in view of the existing thermochemical data of related substances. Further study is needed in order to ascertain the true dissolved species. A spectrophotometric study is planned.

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