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Electrochemical behaviors of PuN and (U, Pu)N in LiCl–KCl eutectic melts

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Abstract

Electrochemical behaviors of PuN and (U, Pu)N in the LiCl–KCl eutectic melts at 773 K were investigated by cyclic voltammetry. The electrochemical dissolution of PuN and (U, Pu)N began nearly at -0.90 ± 0.05 and -0.95 ± 0.05 V (vs. Ag^+/Ag), respectively. The rest potentials of PuN and (U, Pu)N were observed at about 0.15 V more negative potential than that of UN, in the present experimental condition. The observed rest potentials of (U, Pu)N depended on the equilibrium potential of the Pu^{3+}/PuN. In the cyclic voltammogram measured by use of (U, Pu)N as the working electrode, a steep rise of the positive current was observed at potentials more positive than -0.45 V in analogy with the cyclic voltammogram measured by use of UN as the working electrode. These indicate that UN and PuN in (U, Pu)N would be dissolved independently irrespective of forming the solid solution.

1. Introduction

Actinide nitride is a candidate material of advanced fuels and targets for fast reactors and for transmutation of minor actinides because the thermal conductivity and metal density are higher than those of actinide oxide and it has high melting temperature [1–3]. Besides above advantages, the mutual miscibility among the actinide nitrides is prospected since their crystal structures are identical with similar lattice constants [1]. However, the recycling of ^{15}N-enriched nitrogen, which is used for depression of the formation of ^{14}C, should be required in the reprocessing of nitride fuel [4]. As for the reprocessing, the aqueous process such as PUREX is not adequate for nitride fuel with ^{15}N-enriched nitrogen, because it will be diluted and dispersed by the isotopic exchange in nitric acid. Then, the application of the pyrochemical reprocessing to nitride fuel cycle has been proposed since ^{15}N can be easily recovered and the introduction of the pyrochemical process will realize more compact facilities [5,6]. In order to apply the pyrochemical reprocessing to nitride fuel cycle, the authors have investigated the individual electrode reaction of actinide nitrides such as UN, PuN and NpN in LiCl–KCl eutectic melt [7–9]. However, the electrochemical behavior of mixture of plural actinide nitrides has not been studied yet. In the present work, electrochemical behaviors of PuN and (U, Pu)N in the LiCl–KCl eutectic melt containing UCl_3 and $PuCl_3$ were investigated by cyclic voltammetry at 773 K.

2. Experimental

2.1. Sample preparation

Uranium mononitride, UN, and plutonium mononitride, PuN, were prepared by carbothermic reduction of uranium dioxide, UO_2, and plutonium dioxide, PuO_2, respectively, with graphite powder in a N_2–H_2 mixed gas stream at about 1750 K [10]. The purities of UO_2 and PuO_2 powders were about 99.9%. The products were identified by X-ray

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diffraction analysis to be single-phase UN and PuN, respectively. The impurity levels of oxygen and carbon in the nitrides were evaluated to be less than 0.1 wt%. The preparation of the solid solutions between UN and PuN, (U, Pu)N, were carried out by sintering the mixtures with the Pu/(U+Pu) molar ratios of 0.75, 0.50 and 0.25. The formation of the solid solutions was also checked by X-ray diffraction analysis.

Plutonium trichloride, $PuCl_3$, was prepared by the chlorination of the Pu–Pt alloy, which was obtained by heating the mixture of PuN and Pt metal powder, with $CdCl_2$ in Cd/LiCl–KCl system at 773 K [11]. The salt containing about 20 wt% $PuCl_3$ obtained in the above-mentioned procedure was diluted by the addition of the LiCl–KCl eutectic salt in order to obtain the adequate concentration of $PuCl_3$ for the electrochemical measurement.

Polarographic grade LiCl–KCl eutectic salt and $CdCl_2$ were obtained from the Anderson Physics Laboratory, and Cd (>99.999%) and Mo (>99.95%) used for electrode material were supplied from Soekawa Chemicals Co. Ltd.

2.2. Electrochemical measurements

Electrochemical measurements were carried out in a type of cell described previously [7]. A Mo net cage (o.d.: about 8 mmø, depth: about 15 mm, 1 mm mesh) was used as a working electrode, and one PuN or (U, Pu)N pellet of 9.5±0.5 mm in diameter and 3.5±0.5 mm in thick was placed in the cage. The counter electrode used was a Mo wire of 1 mmø in diameter. The reference Ag^+/Ag electrode consisted of an Ag wire (1 mmø, >99.99%) immersed in the LiCl–KCl eutectic salt containing 1.00 wt% of AgCl. A porous tube made of sintered aluminosilicate was employed for the casing of the reference electrode. Temperature of the salt phase was measured by a calibrated Chromel–Alumel thermocouple. Cyclic voltammograms were obtained using a voltammetric analyzer, Potentiostat/Galvanostat Model 273A (Seiko EG&G), at a scan rate of 0.005 V s^{-1}. The concentrations of UCl_3 and $PuCl_3$ in the LiCl–KCl eutectic were determined by ICP-AES after the voltammetric measurements.

The electrolysis and potentiometric measurements were performed by using the above voltammetric analyzer, a potentiometer, HA-501 (Hokuto Denko Co. Ltd), and an X-T recorder (Yokogawa Co. Ltd). The preparation of electrodes and assembly of the cell were carried out in gloveboxes with Ar gas atmosphere purified to the levels of 0.5–2 ppm oxygen and 2–5 ppm moisture. Then, the electrochemical cell was continually flushed with high purity He gas at the flow rate of 0.3 L min^{-1} and the inner pressure was controlled at about 1.0 atm during the voltammetric measurements and electrolysis. The N_2 concentration in the He carrier gas was measured by gas chromatography, GC-8A (Simadzu Co.).

3. Results and discussions

3.1. Electrochemical studies on PuN in LiCl–KCl melt

The rest potential on the surface of PuN at 773 K was −0.90±0.05 V vs. the Ag^+/Ag reference electrode, when the salt phase contained 0.55 wt% $PuCl_3$ and partial pressure of N_2 gas in the atmosphere was 10^{-5}–10^{-6} atm (1–10 ppm). Here, the small amount of N_2 gas was generated at the anode equipped with the nitrides during the electrochemical measurement. This potential is considered to correspond to the equilibrium between PuN, $PuCl_3$ and N_2 gas in the molten salt:

$$\mathrm{PuN} \rightleftharpoons \mathrm{Pu}^{3+} + 3e^- + 1/2\mathrm{N}_2.(\mathrm{Pu} \rightleftharpoons \mathrm{Pu}^{3+} + 3e^-, \\ \mathrm{Pu} + 1/2\mathrm{N}_2 \rightleftharpoons \mathrm{PuN}) \tag{1}$$

The equilibrium potential of PuN against the Ag^+/Ag reference electrode, $E_{\mathrm{PuN-Ag^+}}/\mathrm{Ag}$, is described as Eq. (2) by the same procedure as in the previous work [7–9].

$$\begin{aligned} E_{\mathrm{PuN-Ag^+/Ag}} &= \Delta G^0/3F - \Delta G^0/3F - \Delta G^0/F \\ &\quad + (RT)/(3F)\ln \gamma_{\mathrm{PuCl_3}} c_{\mathrm{PuCl_3}} \\ &\quad + (RT)/(6F)\ln p\mathrm{N_2} \\ &\quad - (RT)/F\ln \gamma_{\mathrm{AgCl}} c_{\mathrm{AgCl}}, \end{aligned} \tag{2}$$

where F is the Faraday constant. The standard Gibbs energy for formation of PuN at 773 K, $\Delta G^0{}_{\mathrm{PuN}}$, is −232.2 kJ·$mol^{-1}$ [12], and that of AgCl, $\Delta G^0{}_{\mathrm{AgCl}}$, −86.22 kJ mol^{-1} [13]. The concentration of $PuCl_3$ in the melt and that of AgCl in the reference electrode, $c_{\mathrm{PuCl_3}}$ and c_{AgCl}, were 0.55 wt% (0.088 mol.%) and 1.00 wt% (0.390 mol.%), respectively. The activity coefficient of AgCl in the reference electrode, γ_{AgCl}, is assumed to be unity [13]. The standard Gibbs free energy for formation of $PuCl_3$ in the LiCl–KCl eutectic melt phase at 773 K, $\Delta G^0{}_{\mathrm{PuCl_3}}$ in LiCl–KCl, is evaluated as −767.8 kJ mol^{-1} [14]. $\Delta G^0{}_{\mathrm{PuCl_3}}$ in LiCl–KCl is made up by the sum of the standard Gibbs free energy for formation of $PuCl_3$, $\Delta G^0{}_{\mathrm{PuCl_3}}$, and the solvation energy of $PuCl_3$ in the LiCl–KCl eutectic melt. The solvation energy is expressed by $RT \ln \gamma_{\mathrm{PuCl_3}}$, where $\gamma_{\mathrm{PuCl_3}}$ is the activity coefficient of $PuCl_3$ in the LiCl–KCl eutectic melt. Therefore, the equilibrium potential at 773 K derived from Eq. (2) is expressed as follows:

$$\begin{aligned} &E_{\mathrm{PuN-Ag^+/Ag}}(\text{at 773 K}) \\ &\quad = -0.5883 + 0.02221 \ln c_{\mathrm{PuCl_3}} + 0.0111 \ln p\mathrm{N_2} \end{aligned} \tag{3}$$

Therefore, the equilibrium potential of PuN at 773 K under the present experimental condition is expected as −0.872 to −0.898 V. This value is comparable with the equilibrium potential obtained by the measurement of electromotive force.

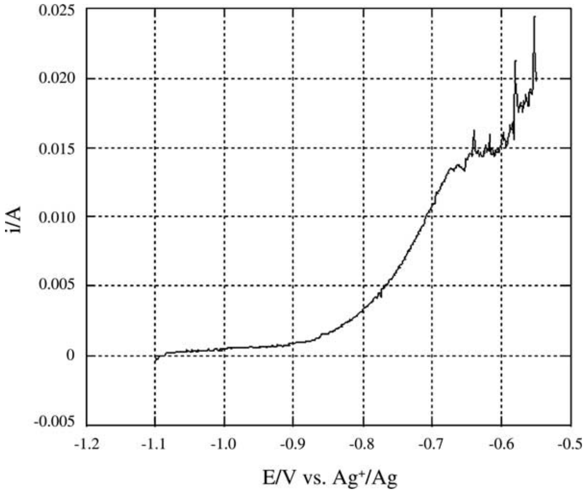

Fig. 1. Linear sweep voltammogram of PuN in $PuCl_3$–LiCl–KCl melt at 773 K. Working electrode: PuN pellet in an Mo cage. $PuCl_3$ concentration: 0.55 wt%. Scan rate: 0.005 V s^{-1}.

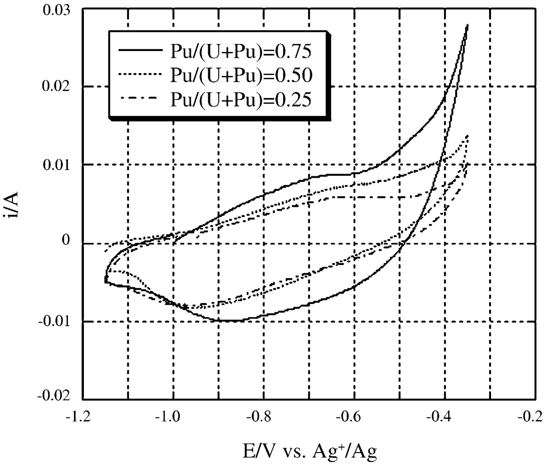

Fig. 2. Cyclic voltammograms of (U, Pu)N in $PuCl_3$–LiCl–KCl melt at 773 K. Working electrode: (U, Pu)N pellet in an Mo cage. $PuCl_3$ concentration: 0.55 wt%. Scan rate: 0.005 V s^{-1}.

Linear sweep voltammograms of PuN were obtained in the LiCl–KCl eutectic salt containing with 0.55 wt% $PuCl_3$ at 773 K. The typical voltammogram is indicated in Fig. 1. Anodic current, which corresponded to the reaction (1), was observed in the voltammogram. The reaction (1) seemed to be irreversible, because N_2 gas generated by the electrolysis, which might exceed the solubility of N_2 gas in the salt phase, was liberated to the outer atmosphere.

3.2. Electrochemical studies on (U, Pu)N in LiCl–KCl melt

The rest potentials of (U, Pu)N with the Pu/(U+Pu) molar ratios of 0.75, 0.50 and 0.25 at 773 K were -0.90 ± 0.05, -0.95 ± 0.05 and -0.95 ± 0.05 V, respectively, vs. the reference electrode, when the salt phase contained 0.02–0.05 wt% UCl_3, which was generated during the electrolysis, and 0.46–0.50 wt% $PuCl_3$ and partial pressure of N_2 gas in the atmosphere was 10^{-5}–10^{-6} atm (1–10 ppm). These potentials are considered to correspond to the equilibrium between PuN and $PuCl_3$ in the molten salt. Fig. 2 shows voltammograms for the dissolution of (U, Pu)N with the Pu/(U+Pu) molar ratios of 0.75, 0.50 and 0.25 in the LiCl–KCl eutectic salt containing 0.02–0.04 wt% UCl_3 and 0.46–0.50 wt% $PuCl_3$ at 773 K. In the voltammograms, two anodic current waves were observed in some cases, though the wave form was not clear. The anodic current wave observed around -0.8 V decreased with decreasing the Pu/(U+Pu) molar ratio. Then, the anodic current increased as the potential of the working electrode was scanned from about -0.7 V to the positive direction. In addition, a steep rise of the positive current was observed at more positive potential than -0.45 V in analogy with the cyclic voltammogram measured by use of UN as the working electrode [9]. These indicate that UN and PuN in (U, Pu)N would be dissolved independently irrespective of formation of the solid solution. Kobayashi et al. proposed that the steep current rise should be attributable to formation of UNCl and U_2N_3 in the salt or the adsorbates on the surface of UN [15]. On the other hand, the authors suggested that insoluble UNCl was formed directly at the surface of UN in the salt because the redox reaction of the U^{4+}/U^{3+} couple occurred at about -0.4 V, as Eq. (4) [9].

$$UN + Cl^- = UNCl + e^- \tag{4}$$

Here, UN^+ is considered to be formed by oxidation of UN, since U behaves trivalent ion in solid UN. However, it is thought that UN is formed immediately since the dissociation coefficient of UNCl ($UNCl \rightleftharpoons UN^+ + Cl^-$) is very low. In the present experimental condition, the contribution of oxidation from U^{3+} to U^{4+} in the salt to the anodic reaction might be small since the concentration of UCl_3 was very low.

3.3. Recovery of U and Pu by the electrolysis using (U, Pu)N as the anode

The recovery of U and Pu as alloy was tried by the electrolysis using (U, Pu)N as an anode. By using the potential-controlled method, the constant potential of -0.5 V was applied on the working electrode in which (U, Pu)N was placed, and U and Pu were recovered as alloy at the Mo cathode. Fig. 3 shows typically time-courses of electric current, cathodic potential and concentration of N_2 gas in the carrier He gas during the electrolysis. As the working electrode (U, Pu)N with the Pu/(U+Pu) molar ratio of 0.75 was used and -0.5 V was applied between (U, Pu)N and the reference electrode. The deposits consisted of Pu metal and a small amount of U metal. The electric current was 0.020–0.036 A. When the electrolysis was initiated, potential of the Mo cathode changed from -1.1 to -2.3 V. A few minutes later,

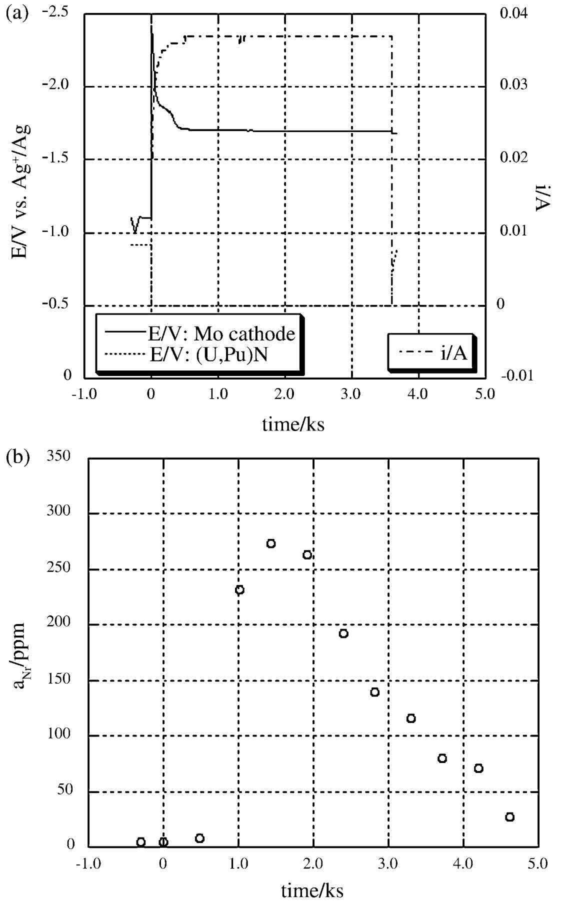

Fig. 3. Time-courses of (a) potentials of the working electrode (U, Pu)N, and the counter Mo electrode, electric current and (b) concentration of N_2 gas in He carrier gas during the potential-controlled electrolysis in LiCl–KCl eutectic salt at 77.

the Mo cathode potential showed almost constant value, -1.70 ± 0.05 V. When the electrolysis was completed, $t = 3.6$ ks, the working electrode was picked up from the salt. The concentration of UCl_3 in the melt increased slightly (ca. 0.01 wt%) and that of $PuCl_3$ decreased slightly (ca. 0.01 wt%) during the electrolysis according to the results of ICP-AES analysis. During the electrolysis, production of N_2 gas was identified by gas chromatography as shown in Fig. 3(b). Accordingly, the recovery of U and Pu from (U, Pu)N by the controlled-potential electrolysis was successful in this condition.

The recovery of U and Pu was tried under the controlled-potential electrolysis by applying -0.45 V for 3600 s on the (U, Pu)N, of which U/Pu ratio was 1, in the melt containing 0.13 wt% UCl_3 and 1.19 wt% $PuCl_3$. The anodic current increased up to -180 mA until 200 s, and that flowed at 180–195 mA from 200 s to 3.6 ks. After the electrolysis, the concentrations of UCl_3 and $PuCl_3$ were 0.05 and 0.75 wt%, respectively. During the electrolysis, about 0.42 g of U and Pu was lost in the melt. The reason would be because the formed UNCl was precipitated and the circulated current, which occurred by the reduction of U^{4+} to U^{3+} at the cathode and the oxidation of U^{3+} to U^{4+} at the anode at the same time, in the melt. Although the precipitate was observed in the salt, the precipitate could not be analyzed since too small amounts of the precipitate could be recovered. Taking into account the voltammetric understanding and information on the electrolysis, the electrolysis using (U, Pu)N as an anode by applying more negative potential than -0.45 V should be performed in order to diminish the loss in the recovery process.

4. Conclusion

Electrochemical behaviors of PuN and three kinds of (U, Pu)N with different Pu/(U + Pu) ratios were investigated in the LiCl–KCl eutectic melt at 773 K, and U and Pu were recovered at the Mo cathode by potential-controlled electrolysis. The rest potential of (U, Pu)N in UCl_3–$PuCl_3$–LiCl–KCl melt depended on the equilibrium potential of PuN in the melt. UN and PuN in (U, Pu)N were dissolved as U^{3+} and Pu^{3+} with the evolution of N_2 gas at potentials more positive than -0.70 and -0.90 V, respectively. On the other hand, UN was not dissolved as U^{3+} and the electrolytic efficiency was lowered when the applied potentials on the surface of (U, Pu)N were more positive than -0.45 V. In order to recover U and Pu efficiently, we should apply the potential between -0.45 and -0.70 V on (U, Pu)N.

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