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Electrochemical preparation of high purity uranium and neptunium metals from aqueous solutions

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Abstract

Uranium and neptunium metals were successfully produced by the thermal decomposition of electrochemically prepared amalgams from the aqueous solutions. The amalgamation rate of uranium was approximately regarded as a first-order chemical reaction and the amalgam was heated at 1250°C in vacuum. The purity of uranium metals were estimated to be about 4 N by gaseous and metallic impurity analysis. The decomposition temperature of neptunium amalgams was decided by the analysis of mercury in the lanthanum and cerium metals prepared by the above method. The neptunium amalgams were synthesized from acetate buffer solutions and bright metallic buttons of neptunium metals were obtained. As a result of this study, the proposed method is shown to be much easier and simpler than conventional ones. © 1998 Elsevier Science S.A.

Keywords: Uranium metal; Neptunium metal; Lanthanide metal; High purity metal; Amalgam

1. Introduction

Electropositive actinide metals have been prepared by metallothermic reduction of the halide, oxide and carbide and by electrolysis in a molten salt [1–3]. However, it is an enormous task to produce highly radioactive metals by conventional methods.

A mercury electrode with a large hydrogen overpotential of approx. -1.5 V in an aqueous solution is widely used to deposit elements belonging to the groups from VIa to IVb, such as Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga and Ge [4], whose reduction potentials are more positive than the overpotential. Radiopolarography [5] is an interesting technique, in which the amalgamated metal is measured by the radioactivity instead of the current. Actually, the reduction of $^{153}Gd^{3+}$ to $Hg(^{153}Gd)$ in an aqueous solution was found at $E_{1/2} = -1.91$ V, although the usual polarographic current was completely disturbed by discharge of the supporting electrolyte and hydrogen ion [6]. Electrochemical behaviors of lanthanide and actinide ions have been studied by this technique [7]. These facts suggest the feasibility of preparing electropositive metals from aqueous media by bulk electrolysis using a mercury pool electrode. The metals reduced at room temperature are expected to be of good quality, while corrosion products from reaction vessels frequently end up in the pyrochemical products.

In a previous paper [8], it was elucidated that uranium ions in acetate buffer solutions were amalgamated quantitatively; uranium metals were prepared by thermal decomposition of the amalgam at 1250°C in vacuum and the metallic impurities were much less than those of commercially available metals with ca. 99.95% pure. In this article, in order to confirm the quality of the products and to expand the applicability, the analysis of gaseous impurities in the uranium metals and the preparation of neptunium metal were investigated.

2. Experimental

An amalgamation cell (500 ml capacity) consisted of two compartments divided by a H^+-type cation exchange membrane. The mercury cathode had a surface area of 32 cm^2, a volume of 12 ml and a purity of 6 N. The platinum anode was immersed in a 1 M sulfuric acid solution. Electrolysis was performed as follows: Uranium or neptunium in 0.5 M hydrochloric acid was reduced at a lower potential to their tetravalent states. The pH was adjusted to 2.5–3.8 by the addition of acetic acid and sodium acetate or potassium acetate solutions and the solution was diluted

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to about 100 ml. The amalgamation was carried out at more negative potentials. The resultant amalgam was rinsed with water and ethyl alcohol and then was heated in a vacuum above the melting point to coalesce into a button.

Metallic impurities in the nitrate and uranium metals were analyzed by ICP–AES after the separation of uranium by a TBP extraction, where the standard solutions for the spectrometry were treated by the same extraction method, to compensate for reduction in the concentrations.

3. Results and discussion

3.1. Preparation of uranium metals

Amalgamations were carried out by controlled current electrolysis in acetate buffer solutions of pH 2.5–3.5 with uranium concentrations of 0.1–0.2 M. The solutions were agitated by circulation (1 l/min). The reduction rates in the sodium and potassium acetate solutions are shown in Fig. 1. The uranium was amalgamated with alkaline metals. The cathodic reactions in a sodium acetate buffer solution are $U^{3+} + 3e \rightarrow Hg(U)$, $Na^{+} + e \rightarrow Hg(Na)$ and $2H^{+} + 2e \rightarrow H_2$. The increases in pH in the catholyte were compensated by transportation of the hydrogen ions generated by the anode reaction, $H_2O \rightarrow 1/2O_2 + 2H^{+} + 2e$ through a cation exchange membrane. Most of the current was consumed for the decomposition of water and the amalgamation efficiency was calculated to be about 4%. The time dependencies of logarithmic concentration ratio $C(t)/C(0)$ were linear, except at the lower concentrations of uranium. Thus, the reductions seem to follow a first-order chemical reaction, which is characteristic of the kinetics for a controlled potential method. In fact, the working electrode was kept at −2.0–2.4 V vs. SCE.

Table 1
Analysis of gaseous impurities in uranium metals (ppm by weight)

	O	N	C
Sample A-1	6.8	0.9	3×10^1
Sample A-2	4.8	1.1	2×10^1
Sample A-3	11.6	3.6	3×10^1
Sample A-4	8.1	1.0	1×10^1
Sample A-5	7.8	2.0	1×10^1
Metal C-1	17.1	9.0	2×10^1
Metal C-2	18.6	10.1	2×10^1
Metal D			164[a]

Sample A: Uranium metal decomposed in a magnesia crucible.
Metals C and D: Commercial grade metals of ca. 99.95% purity.
[a] Analyzed by the supplier.

A bright silver button metal and a brown sponge of uranium were obtained by thermal decomposition at 1250°C. The gaseous and metallic impurities were analyzed using metals of 0.2–0.3 g and about 10 g, respectively. The results of O, N and C for bright metals and commercial grade metals of ca. 99.95% purity by metallothermic reduction followed by vacuum melting are presented in Table 1, where those for sponges are excluded due to the adsorption effect by air. The sensitivity in the carbon analysis was about 10 ppm because a large amount of uranium metal could not be covered up by the flux material in a combustion boat. The contents of oxygen and nitrogen in the prepared metal were below about 10 and 5 ppm, respectively, and the latter concentrations are especially low. It is interesting that the metal prepared from aqueous solutions is hardly contaminated by oxygen.

Metallic impurities of uranium metals and nitrate of their source material are tabulated in Table 2 with those of commercial grade metals. The major contaminating impurities in this process were found to be Al, Fe, Hg and Pt. Among them, aluminium in sample B originates from an alumina crucible used for the thermal decomposition,

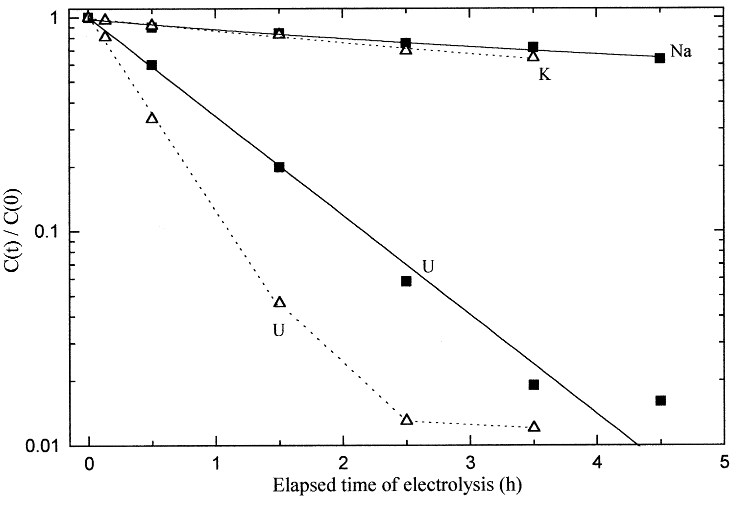

Fig. 1. Time dependence of logarithmic concentration ratios of U, Na and K. △: 215 mA cm^{-2}, pH = 3.08, [U] = 0.102 M, $[CH_3COOH] = 1.07$ M, $[CH_3COOK] = 0.44$ M, ■: 140 mA cm^{-2}, pH = 3.03, [U] = 0.102 M, $[CH_3COOH] = 1.02$ M, $[CH_3COONa] = 0.45$ M, [NaCl] = 0.46 M.

Table 2
Analysis of metallic impurities of uranium metals (ppm by weight)

Elements	Nitrate	Sample A	Sample B	Metal C[a]	Metal D[a]
Al	7	10	350	15	20
Ca	38	4	5	25	
Cd	<1	<1	<1	25	
Co	<1	2	1		
Cr	<1	5	3	25	<30
Cu	<1	1	2	25	<30
Fe	10	39	10	50	90
Hg	<1	11	10		
La	<1	<1	<1		
Mg	7	1	1	50	
Mn	<1	<1	<1	25	<20
Na	68	27	10	25	35
Ni	1	6	1	50	<30
Pb	<1	1	3	50	
Pt	<1	3	4		
Si	5	8	7	50	<90
Ti	<1	2	1	25	
Zn	<1	1	1	25	50

Nitrate: Source material of Sample A and Sample B.
Sample A: Uranium metal decomposed in a magnesia crucible.
Sample B: Uranium metal decomposed in an alumina crucible.
Metals C and D: Commercial grade metals of ca. 99.95% purity.
[a] Analyzed by the supplier.

mercury from the amalgam and platinum from its wire, which was used for electric contact to the cathode. Iron in sample A may be attributed to a magnesia crucible or an accidental contamination. In addition, sodium comes not only from the source material but also from the amalgamation of ions mentioned above. Impurities with a high vapor pressure, such as mercury and sodium, can be removed by prolonged decomposition at higher temperatures. It was confirmed that the purity of uranium metals prepared from aqueous solutions is much higher than 99.95% and is estimated to be about 4 N.

3.2. Preparation of neptunium metals

Some properties associated with the amalgamation and thermal decomposition of uranium, neptunium and related elements are summarized in Table 3 [9]. The chemical and electrochemical behaviors of neptunium in aqueous solutions are similar to those of uranium, and the amalgamation was carried out in the same way as mentioned above. However, the melting point was much lower. In addition, the phase diagram of Np-Hg system has not been reported. The temperature of the thermal decomposition should be decided in terms of not only coalescing into a button but also removing the mercury. For this purpose, the preparation of lanthanum and cerium metals was examined. Their melting points are approximately similar to that of neptunium and, moreover, some compounds in the La–Hg system exist at temperatures beyond the melting point of lanthanum, while all of the compounds in the Ce–Hg system decompose into cerium and gaseous mercury at low temperature [10]. Therefore, these metals are appropriate for use in preliminary examinations of the thermal decomposition of neptunium amalgam.

Table 3
Standard reduction potentials, half wave potentials and melting points of U, Np, Pu, La and Ce

	U	Np	Pu	La	Ce
$E^0(\mathrm{M}^{3+}/\mathrm{M})$ (V)	-1.66	-1.79	-2.00	-2.52	-2.43
$E_{1/2}[\mathrm{M}^{3+}/\mathrm{Hg(M)}]$ (V)	-1.65	-1.78[a]	-1.99[a]	-1.75	-1.84
Melting point (°C)	1132	637	640	920	795

[a] Estimated value.

The amalgamation rates of lanthanum and cerium are illustrated in Fig. 2. The kinetics of the reaction appear to differ from those of a first-order reaction, in spite of quasi-controlled potential electrolysis. Although their reduction potentials are more negative than that of uranium, the half wave potentials are similar, as is shown in Table 3. The characteristic current–time behavior for the controlled potential method would be expected on the basis of the reported half wave potentials, since the reductions were carried out at potentials corresponding to the limiting current regions. Further investigations, including those of the half wave potentials and the kinetics of the electrode reactions of lanthanum and cerium, are indispensable for solving the anomaly.

Heat treatments for coalescence and the contents of mercury in the resultant metals are shown in Table 4. The buttons could be obtained by prolonged heating even at lower temperatures. The quantities of mercury found in the products, however, are strongly dependent on the tempera-

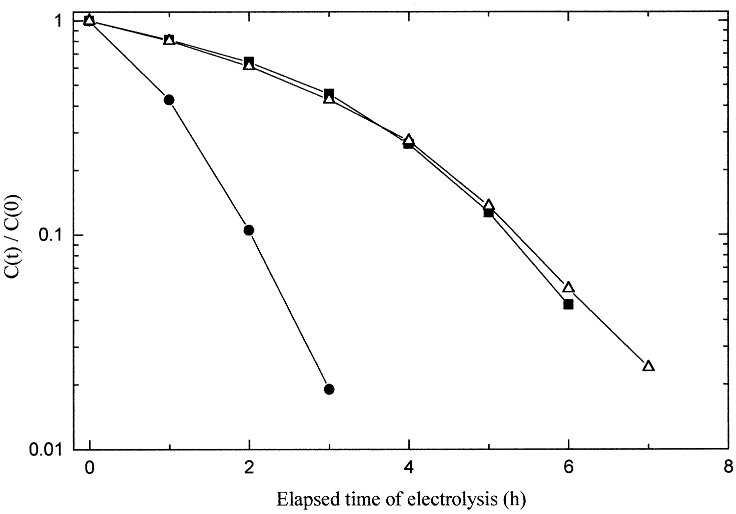

Fig. 2. Time dependence of logarithmic concentration ratios of La and Ce. △: 215 mA cm^{-2}, pH=3.67, [Ce]=0.210 M, [CH_3COOH]=1.05 M, [CH_3COONa]=0.66 M, ■: 215 mA cm^{-2}, pH=3.68, [La]=0.218 M, [CH_3COOH]=1.06 M, [CH_3COONa]=0.60 M, ●: 140 mA cm^{-2}, pH=3.66, [La]=0.109 M, [CH_3COOH]=1.11 M, [CH_3COONa]=0.38 M.

Table 4
Heat treatment of the amalgam and the analysis of mercury

Element	Decomposition of the amalgam		Quantity of Hg in the product
	Temperature (°C)	Time (h)	
La	1000	2	17%
La	1050	2	8%
La	1250	1	17 ppm
Ce	900	1	38%
Ce	950	3	34%
Ce	1000	4	14%
Ce	1250	1	31 ppm

ture and are as much as 30% below 1000°C, regardless of the differences in their phase diagrams. Thus, the temperature of neptunium amalgam was decided at 1250°C.

Amalgamations of neptunium were carried out in acetate buffer solutions of pH 3.4–3.7, where the electrolytic current was varied to prevent the temperatures of the solutions from rising in the glove box. The amalgamation rate is shown in Fig. 3 and was retarded in comparison with that of uranium. It would be attributed to slow agitation of the catholyte magnetic stirrer.

The amalgam in a magnesia crucible was decomposed in a vacuum at 400°C for 1 h, at 700°C for 30 min and at 1250°C for 1 h. A metallic silver button without a sponge was obtained, which was confirmed to be α-neptunium by density measurement. The density at 25°C was found to be 20.4_5 g cm^{-3}, which is in good agreement with the literature [11]. A photograph of a 1.02 g sample of neptunium metal is shown in Fig. 4. Unfortunately, the instruments for impurity analysis of highly radioactive

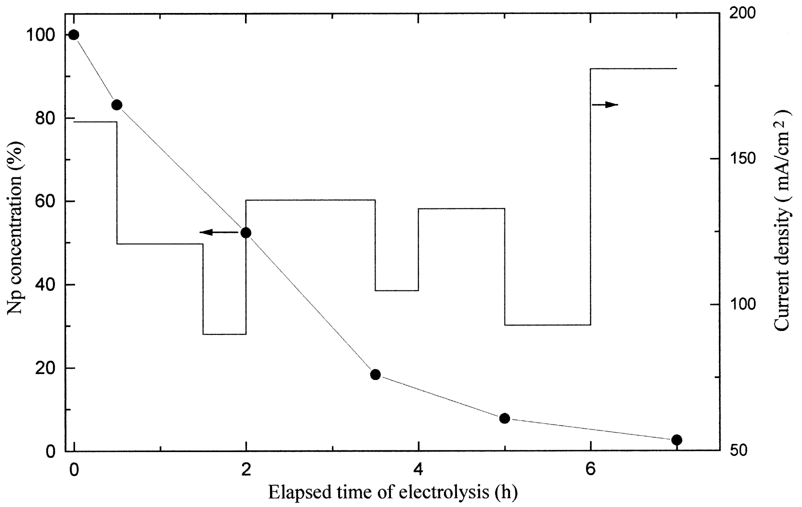

Fig. 3. Amalgamation rate of Np and the electrolytic current density. ●: pH=3.50, [Np]=0.05 M, [CH_3COOH]=1.02 M, [CH_3COONa]=0.30 M.

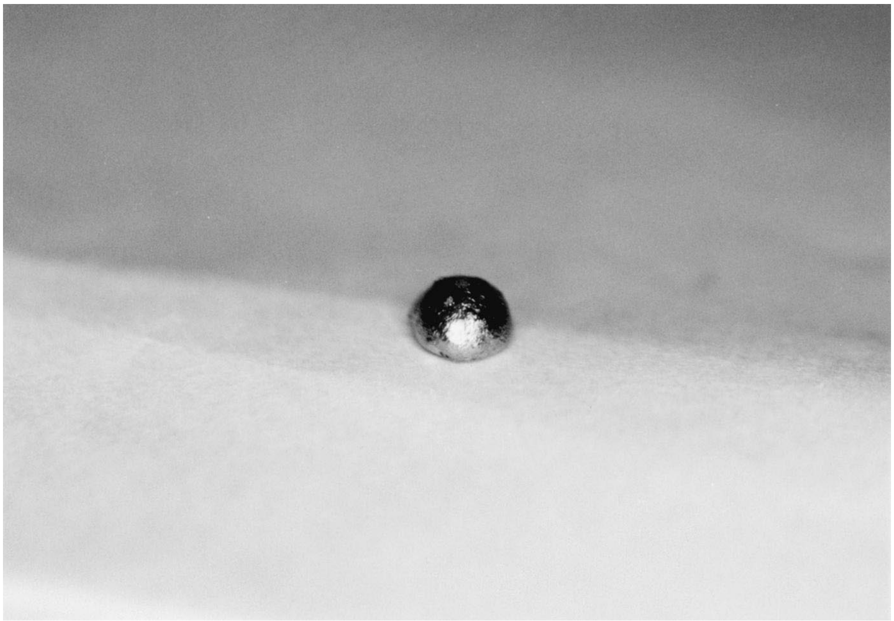

Fig. 4. A 1.02 g sample of neptunium metal.

neptunium are not available in our laboratory. The neptunium metals, however, were presumed to be of excellent quality, based on the purity of uranium metals prepared by the same procedure.

High purity uranium and neptunium have been prepared by electrorefining following direct oxide reduction. It is, however, exclusively applicable to large scale productions [1]. The proposed electrochemical method is easy and simple and is suitable for laboratory scale preparation of these metals, yielding excellent quality. Moreover, the preparation of plutonium metals will be feasible by this technique, once careful consideration is given to the reduction potential, the estimated half wave potential, the melting point (as is shown in Table 3) and to the vapor pressure [1].

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