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APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

Possibility of Electrochemical Refining of Uranium Alloys with Aluminum in Chloride Melts

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Abstract—Selectivity of liquid aluminum electrodes in separation of uranium from fission products was studied. The composition of a salt electrolyte and modes of electrolysis for electrorefining of uranium–aluminum alloys in molten chlorides were determined.

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Fuel elements based on alloys of uranium with aluminum are widely used in research and transport reactors. Uranium in fuel elements of this kind has a high or medium degree of enrichment in the uranium-235 isotope. The decommissioning of numerous reactors of this type poses a problem of utilization of a large number of worked-out and unirradiated fuel elements to return the fissionable material into the fuel cycle. Aqueous methods for their processing are multistage and yield a large amount of radioactive waste, and, therefore, the possibility of regeneration of fuel elements of this kind by pyrochemical methods is being studied. It has been shown that the separation efficiency of uranium and lanthanum in a metal–salt liquid system strongly depends on the nature of a liquid-metal electrode [1–3]. It would be expected that, on thallium electrodes at temperatures below 1000 K, the metallic phase would be enriched in lanthanum. For the other metals considered, this element must enrich the salt phase. Cadmium, lead, and indium electrodes show low values of separation coefficients (101–102). The coefficient θ is on the order of 102–103 for liquid zinc and bismuth, and 104–105 for gallium and aluminum electrodes. By only varying the nature of the liquid-metal solvent, the separation coefficient of uranium and lanthanum can be changed by a factor of 104–105.

In this study, the high efficiency of uranium separation from plutonium and fission products that are the closest in electrochemical behavior to plutonium on liquid aluminum electrodes was confirmed by thermodynamic calculations and experimentally, and the composition of a salt electrolyte for electrorefining of uranium–aluminum alloys was determined.

The efficiency of the separation process is commonly characterized by the separation coefficient θ, which is the quotient of the ratios between the atomic fractions of the metals being separated, M_1 and M_2, in the electrolyte (c_1, c_2) and in the alloy (x_1, x_2):

$$\theta = \frac{c_1 x_2}{c_2 x_1}. \qquad (1)$$

The expression for calculating the separation coefficients θ for metals M_1 and M_2, which form ions M_1^{n+} and M_2^{m+}, on a liquid electrode made of metal M is derived on the condition that the equilibrium potentials of the alloys M_1–M_2 and M_2–M are equal ($E_1 = E_2 = E$) and, with the conditional standard potentials of the alloys (E_1^{**}, E_2^{**}) used [1], has the form

$$\ln\theta = \frac{(n-m)FE + mFE_2^{**} - nFE_1^{**}}{RT}. \qquad (2)$$

At $n = m$, the separation coefficient is independent of the potential of the alloy and, consequently, of the amount of polarization:

$$\ln\theta = \frac{nF}{RT}(E_2^{**} - E_1^{**}). \qquad (3)$$

The separation coefficient of uranium and aluminum in the KCl–NaCl melt was estimated using the relation [4]:

$$\ln\theta = \frac{3F}{RT}(E^*_{Al^{3+}/Al} - E^{**}_{U^{3+}/U(Al)}), \qquad (4)$$

Table 1. Separation coefficients of uranium, plutonium, and main fission products on liquid aluminum electrodes in melts based on KCl–NaCl

M^{n+}	$E = a + b \times 10^{-3}T$, V		$\log \theta = c + dIT$		θ at T, K		
	$-c$	b	c	$-d$	900	1000	1100
U^{3+}	2.51	0.41	0	0	1	1	1
Pu^{3+}	2.90	0.62	3.02	5590	1550	260	115
La^{3+}	3.01	0.52	1.51	7260	3.6×10^6	5.6×10^5	1.2×10^5
Y3+	3.48	0.96	8.16	14360	6.2×10^7	1.5×10^6	7.8×10^4
Ce^{3+}	2.93	0.49	1.06	6040	4.5×10^5	9.5×10^4	2.7×10^4
Zr^{3+}	1.96	0.60	–2.72	8617	1.2×10^{12}	2.1×10^{11}	3.6×10^{10}
Zr^{4+}	2.23	0.66	–4.83	6071	3.7×10^{11}	8×10^{10}	2.2×10^{10}

where $E^{**}_{U^{3+}/U(Al)}$ is the conditional standard potential of U–Al alloys in the KCl–NaCl melt (V) [1],

$$E^{**}_{U^{3+}/U(Al)} = -2.51 + 0.41 \times 10^{-3} T; \quad (5)$$

and $E^{**}_{Al^{3+}/Al}$, conditional standard potential of aluminum in the KCl–NaCl melt (V) [5],

$$E^{*}_{Al^{3+}/Al} = -2.568 + 0.602 \times 10^{-3} T. \quad (6)$$

Substitution of expressions (5) and (6) into Eq. (4) gives

$$\ln \theta = \frac{3F}{RT}(0.188 \times 10^{-3}T - 0.068), \quad \theta_{973\,K} = 61. \quad (7)$$

The purification coefficient θ* is related to the separation coefficient θ by the expression [1]

$$\theta^{*} = \theta \frac{x_1}{x_2}, \quad (8)$$

where x_1 and x_2 are the concentrations of the metals being separated in the final alloy.

The value of θ is also close to the ratio of currents consumed for the dissolution of metals M_1 and M_2 from the alloys.

The body of data on the conditional standard potentials of aluminum alloys, accumulated in the literature [1–3], made it possible to calculate the temperature dependence of the separation coefficients by Eqs. (2) and (3). First of all, yttrium and rare-earth elements (REE) were considered, whose yield is the highest among the fission products and whose recovery potentials are the closest, among the electronegative fission elements, to those of uranium and plutonium. Therefore, the coefficients of separation of uranium from these elements give a clear notion of the possibility of electrochemical regeneration of worked-out uranium–aluminum fuel elements in molten halides. A more negative element, e.g., uranium in the case of the U–Zr pair, is always considered as metal M_1.

It can be seen from the results of the calculations (Table 1) that, depending on temperature, the coefficients of separation on a liquid aluminum electrode in the NaCl–KCl melt are 10^4–10^7 for U–REE pairs, 10^{10}–10^{12} for U and Zr, and 10^2–10^3 for U and Pu. Comparison with the known data [1] shows that liquid aluminum electrodes show the highest selectivity in molten chlorides with respect to both electronegative and electropositive fission products.

In [6], the following distribution coefficients of elements in extraction from 3 M HNO_3 with a 30% TBP solution in synthine were reported: U(IV) 8.1, Pu(IV) 1.55, Pu(VI) 0.62, Zr 0.02, Pu(III) 0.008, and REE 0.002. Calculation of the separation coefficients from these data gives for the following pairs the values: U(IV)–Pu(IV) 5.2, U(VI)–Pu(VI) 13, U(IV)–Pu(III) 1013, U(VI)–Zr 405, and U(VI)–REE 4000. It can be seen that single-stage electrochemical processes in a liquid system constituted by aluminum and a chloride melt compare well with aqueous extraction. Use of bipolar electrodes makes it possible, in principle, to achieve any required degree of uranium purification to remove fission products.

EXPERIMENTAL

The distribution of uranium and plutonium among the salt (KCl–NaCl–UCl_3–$PuCl_3$) and metallic (Al) phases was studied at 690°C. Experiments were performed in beryllium oxide crucibles in the atmosphere of purified argon at a constant initial content of plutonium ions

in the melt (4 wt %) and several times varied content of uranium (2.2 to 10 wt %). An analysis of the alloys upon keeping for 3 h (Table 2) demonstrated that the content of plutonium in these alloys is not high (0.06–0.15 wt%), which is approximately 10 times smaller than that in experiments with melts containing only plutonium trichloride. The content of uranium in the alloy is substantially higher and increases with the content of its ions in the electrolyte.

According to a calculation by Eq. (1), the separation coefficient θ is within the range 102–274, which enables effective separation of uranium and plutonium in electrochemical processes with liquid aluminum electrodes and is in satisfactory agreement with the results of thermodynamic calculations (Table 1).

The polarization of liquid-metal electrodes composed of pure aluminum and uranium–aluminum alloys was studied during their anodic dissolution in a NaCl–KCl melt. The anode potential relative to the chlorine reference electrode was measured at the instant of switching-off the current. The results obtained are shown in the figure.

Several characteristic parts can be distinguished in polarization curve 1. At low current densities, the anode potential is invariable and close to the steady-state potential of aluminum. In this part of the polarization curve, the anode current densities are comparable with currents of spontaneous dissolution of aluminum in corrosion. At $i_a > 5 \times 10^{-3}$ A cm^{-2}, the anode potential starts to shift in the positive direction because the concentration of aluminum ions in the near-electrode layer of the melt begins to exceed the corrosion-related steady-state value. The anode polarization plotted in the coordinates log i_a–φ is linear:

$$\varphi = -2.066 + 0.071 g i_a \quad (700^\circ C). \qquad (9)$$

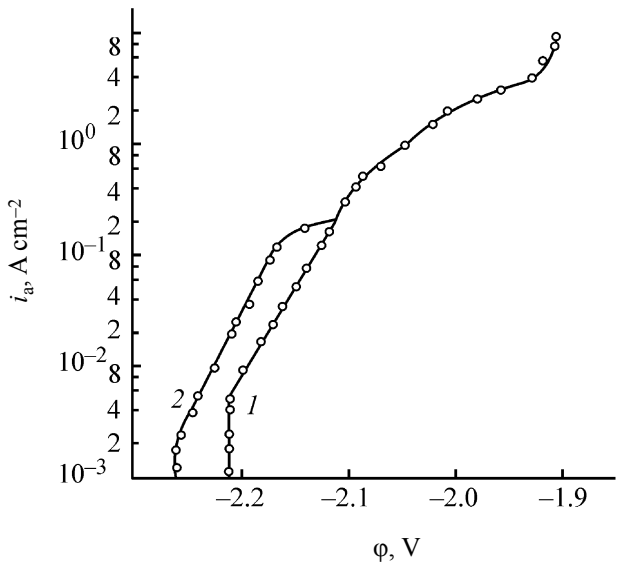
The valence of aluminum ions, calculated from the prelogarithmic coefficient in Eq. (9), is close to three.

At current densities of 0.4–0.5 A cm^{-2} and potentials of about –2.075 V, the slope of polarization curves changes because of the increase in the concentration of aluminum chloride in the near-electrode layer to values at which its behavior in the melt ceases to be described by laws for dilute solutions. Above 2–3 A cm^{-2}, the anode potential sharply shifts in the positive direction to values corresponding to the potential of aluminum in a melt of an intrinsic individual chloride. Calculation of the standard electrode potential of aluminum [5] gives a value of –1.88 V for 700°C. The experimental values of $E^\circ_{Al^{3+}/Al}$ (see figure) almost coincide with those calculated, which confirms the adequacy of interpretation of processes occurring at the anode in the portion of the polarization curve considered here.

Table. 2. Results of equilibrium distribution of plutonium and uranium among the $KCl–NaCl_3–UCl_3–PuCl_3$ melt and liquid aluminum alloy

Equilibrium concentration, wt %				θ_{Pu-U}
in the melt		in the alloy		
U^{3+}	Pu^{3+}	Pu	U	
2.8	0.92	0.06	5.4	274
2.8	1.74	0.15	9.5	102
3.1	3.54	0.06	15.4	225

Introduction of uranium into aluminum shifts the initial potential of the anode toward electronegative values. However, the preferential dissolution of uranium from the alloy occurs only at low current densities. The ratio between the currents consumed for dissolution of uranium and aluminum remains constant up to the limiting current density of uranium dissolution from the alloy and is in good agreement with the value of θ, calculated by Eq. (8) for the alloy under study [61 (4.63/95.37) = 3].



Anodic polarization of (*1*) aluminum and (*2*) uranium–aluminum alloys containing 4.63 mol % uranium in the KCl–NaCl melt at 973 K at the instant of switching-off the current. (i_a) Current density and (φ) potential.

Table 3. Conditions and results of electrorefining of uranium–aluminum alloys in the NaCl–KCl–AlF_3 melt at 730–750°C

Run no.	Initial conditions				Electrolysis mode			
	cathode mass, g	mass of anode components, g			τ, h	i_a	i_c	Q,, A h
		U	A1	uranium mole fraction		A cm^{-2}		
1	10.995	2.502	5.400	0.050	13.2	0.7	0.1	13.74
					10.8	0.05	0.005	
2	9.569	2.994	5.529	0.056	10.2	0.7	0.1	13.81
					3.0	0.45	0.06	
					6.0	0.25	0.03	
3	10.660	3.354	5.310	0.065	2.76	3.3	0.5	13.83
4	12.981	3.243	5.499	0.063	12.0	0.7	0.1	14.31
					7.8	0.25	0.03	
	Results of electrolysis							
	anode				cathode			
	mass loss, g	Q_U	Q_{Al}	share of current for uranium	mass gain, g	Q_U	Q_{Al}	share of current for uranium
		A h				A h		
1	6.570	0.747	12.993	0.054	6.430	0.693	13.047	6.570
2	6.870	0.852	12.954	0.062	6.834	0.830	12.970	6.870
3	6.018	0.525	13.302	0.034	5.895	0.480	13.35	6.018
4	6.594	0.684	13.623	0.040	6.381	0.603	13.704	6.594

At 0.2 A cm^{-2}, the limiting current of uranium dissolution from the alloys is observed, above which the share of the current consumed for aluminum dissolution increases.

The electrorefining of U–Al(Zr) alloys was performed in a melt containing potassium and sodium chlorides and aluminum fluoride at 730–750°C in the atmosphere of argon. The mass of the electrolyte was 60 g, and that of the aluminum cathode, 10–13 g; the zirconium content of the alloy was 2 wt %. The concentration of aluminum fluoride in the melt was sufficiently high (10 wt %) for ruling out any possibility of reduction of alkali metals even at high cathode current densities. Molten aluminum was used as the cathode. In the chloride-fluoride melt, the potential of aluminum is strongly shifted in the negative direction because of the formation of stable fluoride complexes and is close to the potential of uranium. This leads to joint ionization of uranium and aluminum. The conditions and results of the experiments are listed in Table 3.

The amount of uranium and aluminum dissolved from the anode and passing into the cathode, and the corresponding quantities of electricity, were calculated from the mass loss and gain of the electrodes during electrolysis with a knowledge of the quantity of electricity passed.

It can be seen from Table 3 that joint ionization of uranium and aluminum and their joint deposition onto the cathode occur under any of the conditions studied. The relative amounts of the dissolving metals depend on the anode current density. At its high values (run no. 3), aluminum is preferentially ionized, as it also occurs in a purely chloride melt. By lowering i_a, it is possible to provide preferential ionization of uranium (run no. 2), but this can be done to a lesser extent, compared with the chloride solution. The electrolysis mode in run no. 1 provides dissolution of uranium and aluminum at the anode and their transfer into the cathode product in the same relative amounts as those in the anode alloy. Accordingly varies the completeness of uranium recovery from the anode: it increases as the current density becomes lower at the same amount of passed electricity. In the stage of cathodic deposition, 88–98% of uranium passes from the electrolyte into the cathode alloy. The direct recovery of uranium into the cathode at 80% dissolution of the anode is as high as 82.9%. In the process, 1.4–6.4% of uranium remains in the electrolyte, and 11.6–15.7%, in the anode. A chemical analysis of the electrolyte and cathode demonstrated that they contain no zirconium. The whole amount of this element remained in the anode alloy.

CONCLUSIONS

(1) Liquid aluminum electrodes in chloride solutions show high selectivity in electrochemical processes

of uranium separation from plutonium and fission products.

(2) The ratio between the current densities consumed for dissolution of uranium and aluminum under anodic polarization from aluminum and its alloys with 30% uranium in a KCl–NaCl melt remains constant up to the limiting current density of uranium dissolution from the alloy and is in good agreement with thermodynamic estimates.

(3) At the chosen electrolyte compositions and electrolysis modes in electrorefining of uranium–aluminum alloys, uranium and aluminum dissolve at the anode and pass into the cathode product in the same relative amounts as those in the anode alloy, being effectively freed from fission products in the process. This can be used for repeated fabrication of fuel elements.

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