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Electroformation of Uranium Hemispherical Shells

by S. L. Marshall, L. Redey,
G. F. Vandegrift, and D. R. Vissers

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ELECTROFORMATION OF URANIUM HEMISPHERICAL SHELLS

by

S. L. Marshall, L. Redey, G. F. Vandegrift, and D. R. Vissers

ABSTRACT

This effort was directed at developing an electrochemical process for forming uniform and dendrite-free deposits of uranium from molten salts. This process is to be used for the electroformation of free-standing hemispherical shells of uranium for nuclear applications. Electrodeposition of uranium onto a substrate was accomplished with a fused chloride mixture containing 42 wt % UCl_3 and a fused chloride-fluoride mixture containing 4 wt % UF_4 . Under pulsed potential control at 504°C , the chloride-fluoride mixture yielded the widest range of plating conditions for which dendrites could be avoided. Bipolar current pulse plating with both electrolytes gave good results, and successful application of this technique to a large tubular cathode has been demonstrated.

EXECUTIVE SUMMARY

The objective of this effort was to develop the base technology required for the electroformation of free-standing hemispherical shells of uranium for nuclear applications. To meet this objective, we focused our work on the development of an electrochemical process for forming uniform and dendrite-free deposits of uranium from molten salt. The primary problem in the process is that the reversible deposition kinetics of uranium results in a strong tendency toward formation of dendritic (irregular, tree-like) deposits. Consequently, our efforts have been focused on developing plating processes that permit preparation of dendrite-free deposits.

We initially determined conditions for pulse potential electrodeposition of uranium from a molten salt mixture (A) consisting of 20 wt % UCl_3 in LiCl-KCl eutectic onto various metal substrates (Ta, Ni, Al, Fe, Cu, and stainless steel). Next, we determined the dendrite-free plating conditions on nickel using both the potential-pulse and the bipolar current-pulse techniques in two more electrolytes, which had the compositions (in wt %): (B) 42.1 UCl_3 -13.5 LiCl -44.4 KCl and (C) 4.5 UF_4 in 43.3 LiCl -55.1 KCl -1.6 LiF .

The results of these studies indicated that near-dendrite-free coatings can be prepared by using either the potential-pulse or bipolar current-pulse plating regimes. Plating rates of nearly 1 mil/h were achieved with both plating techniques. The potential-pulse plating regime for dendrite-free deposits had the widest range of operating parameters with electrolyte (C), while the bipolar current-pulse regime appears to give excellent results in both electrolytes (B) and (C) [electrolyte (A) was not evaluated with this plating regime].

Because a bipolar current-pulse technique requires only simple, inexpensive galvanostats with polarity reversal capabilities rather than the expensive potentiostat and a stable reference electrode required by the potential-pulse technique, it seems appropriate that future effort should focus on the former technique and be expanded to the all-fluoride-ion electrolyte systems using either nickel or uranium plating surfaces.

I. INTRODUCTION

The objective of this research effort was to develop the base technology required for electrochemical formation of thick, metallurgically sound uranium bodies of specified geometries with acceptable mechanical properties for nuclear applications. The effort was directed primarily toward determining how the electrolyte composition and plating regime affected the quality of the uranium plate formed on substrate material.

The plating regimes evaluated in this effort were the potential-pulse technique, developed last year, and the bipolar current-pulse technique. The latter utilizes a very short cathodic current pulse to deposit a monolayer or so of uranium followed by an anodic current pulse to dissolve the major part of that which was plated. The thought here was that any irregularities in the deposit would be removed during the anodic pulse, and thus, irregularities and/or dendrite formation in the uranium coatings would be avoided.

The compositions of the electrolyte mixtures (in wt %) investigated were as follows: electrolyte (A), 20 UCl_3 in LiCl-KCl eutectic; electrolyte (B), 42.1 UCl_3 -13.5 LiCl-44.4 KCl; and electrolyte (C), 4.5 UF_4 in 43.3 LiCl-55.1 KCl-1.6 LiF eutectic mixture. The objective of this study was (1) to determine how the higher level of uranium trichloride in the chloride-ion molten salts affected the deposits relative to the 20 wt % UCl_3 in LiCl-KCl eutectic and (2) to determine whether good coatings could be prepared from melts containing both the chloride and fluoride ions. In the latter case, we felt that we might be able to develop a bath which is similar in plating properties to the all-fluoride-ion bath but which would not require the high plating temperature and the difficult electrolyte purification regime of the all-fluoride-ion bath.

II. BACKGROUND

The electrochemistry of uranium in fused salts has been of technological importance since the early days of the nuclear industry. Preparation of uranium powder by electrolysis was first described by Driggs and Lilliendahl.¹ Electrolytic preparation was also performed during the Manhattan Project² and subsequently adapted to the refinement of uranium produced by nonelectrochemical methods³ and nuclear fuel reprocessing.⁴ While several potentiometric studies of U/U^{3+} (Refs. 5-7) and U^{3+}/U^{4+} (Refs. 8 and 9) half-cells have appeared, relatively little attention has been devoted to the kinetics of these reactions. The first application of transient techniques was described by Caligara et al.,¹⁰ who used chronopotentiometry to investigate the kinetics of oxidation of U^{3+} to U^{4+} . Very recently, cyclic voltammetry experiments were conducted by Poa et al.¹¹ on the reduction of UCl_3 to U in a molten $LiCl-NaCl-CaCl_2-BaCl_2$ mixture. In this paper, we describe aspects of the transient behavior of uranium electrodeposition that are relevant to the development and application of pulse-plating techniques.

Since the uranium objects for applications require high standards of surface uniformity, the most important problem to be addressed was that of avoiding the well-known tendency of uranium to form dendritic¹² or powdery^{1,2} deposits. Broc¹² has reported that smooth uranium coatings about 4 mil (100 μm) in thickness can be electrodeposited from molten fluoride mixtures (UF_3 , UF_4 in FLINAK). This work required high operating temperatures (about 800°C) and extensive purification of the fluoride electrolyte materials. We chose instead to work with the $LiCl-KCl-UCl_3$ and the $LiCl-KCl-LiF-UF_3$ systems at temperatures between 440°C and 560°C.

In view of the importance of dendrite formation in relation to metal electrodeposition in general and to our work in particular, some introductory remarks are in order on what constitutes a dendrite. Electrodeposition of metals is well known to result in a wide variety of structures, from essentially smooth surfaces to highly branched crystals. The term "dendrite," usually applied to the latter extreme, literally suggests a tree-like structure, but within this general category various forms are possible. These have been described by Wranglén¹³ and rationalized by him on the basis of the crystal structure of the various metals concerned. More recently, dendritic electrodeposits have been described as fractal structures, characterized by a fractional dimensionality.¹⁴

Unfortunately, there is no term in common use that satisfactorily describes metallic deposits lying between the above two extremes, in which the crystals are obviously discrete but are not highly branched and do not possess the scale-invariance characteristic of a fractal structure. An obvious common characteristic of the dendrites described in Wranglén's paper¹³ is their elongation. This observation suggests that elongation of crystals may be identified as a tendency toward dendritic growth. Several theoretical treatments¹⁵ of dendritic electrodeposition are also based on this concept. Although elongated crystals are not necessarily dendritic, in the present report we apply the term "dendrite" to crystals in which the height is noticeably greater than the diameter.

III. EXPERIMENTAL

A. Cell Assembly

Molten alkali halide salts, in general, are characterized by an extreme sensitivity to moisture. Solutions of uranium salts in alkali halide melts also exhibit a pronounced reactivity toward oxygen. Reaction with oxygen and water vapor leads to formation of oxychlorides, the presence of which has been shown to lower the quality of electrodeposited specimens.^{2,12} For this reason, the experiments were carried out in a glove box (Vacuum Atmospheres Corporation) under purified helium, with the oxygen and moisture content maintained below 1 ppm.

The electrolytes used in this work were as follows.

Electrolyte (A). A 20 wt % solution of UCl_3 was prepared by reaction of excess uranium metal with a solution of CdCl_2 in molten LiCl-KCl eutectic at 450°C . The reaction proceeded according to the equation:

This reaction has been used extensively in experiments conducted in this laboratory in connection with the Integral Fast Reactor program¹¹ and is known to be quantitative.

Electrolyte (B). A ternary eutectic with composition 12.0 mol % (42.4 wt %) UCl_3 , 29.5 mol % (12.8 wt %) LiCl , and 58.5 mol % (44.8 wt %) KCl was prepared by melting together 182.80 g FeCl_2 (Anderson Physics Laboratory), 221.75 g KCl (Alpha), and 227.76 g LiCl-KCl eutectic (Anderson Physics Laboratory) and allowing this mixture to react with 228.78 g uranium metal. This resulted in the formation of UCl_3 according to the equation:

Thermodynamic data suggest that this reaction is quantitative. The literature value¹⁶ of 335°C for the melting point of this eutectic was verified by measurement of a cooling curve, but cooling of the molten electrolyte from 500°C to 450°C resulted in precipitation of solids to the extent that insufficient liquid remained for the experiments. To lower the liquidus temperature, a further 6.4 g LiCl was added, resulting in a final electrolyte composition only slightly different from that of the ternary eutectic: 11.8 mol % (42.1 wt %) UCl_3 , 30.8 mol % (13.5 wt %) LiCl , and 57.4 mol % (44.4 wt %) KCl .

Electrolyte (C). A solution of U^{3+} was prepared by reaction of excess uranium metal with a 4.5 wt % solution of UF_4 (supplied by the Y-12 Plant of Oak Ridge National Laboratory) in a ternary eutectic with composition 56.0 mol % (43.3 wt %) LiCl , 40.5 mol % (55.1 wt %) KCl , and 3.5 mol % (1.6 wt %) LiF . Trivalent uranium was formed by the reaction¹²:

The anodes used in the experiments were rods or discs of pure uranium metal, with stainless steel rods serving as current collectors.

In exploratory electrodeposition experiments, the cathode consisted of a disc (0.178 cm² area) made from a 3/16-in. (0.48 cm) dia nickel rod with an insulating sheath of boron nitride covering the cylindrical surface. Larger-scale plating experiments used cylindrical nickel coupons of 7.74 cm² total area. Coupons of copper, tantalum, and aluminum were also tested.

The reference electrode consisted of a 3/8-in. (0.95 cm) dia uranium metal rod. The potentials in this report are quoted with respect to the uranium electrode in the same electrolyte as the cathode. Changing the position of the reference electrode relative to the working electrode was observed not to exert a significant effect on the observed current. This indicates that uncompensated solution resistance effects are negligible.

The temperature of the electrolyte was monitored with a Chromel-Alumel thermocouple and maintained thermostatically to $\pm 1^\circ\text{C}$.

A diagram of the cell assembly is shown in Fig. 1.

Fig. 1.

Diagram of Cell Assembly. A: mild steel crucible; B: stainless steel support rods/electrode leads; C: threaded stainless steel stud for cathode; D: alumina tube insulator; E: cathode coupon; F: uranium disk anode; G: uranium rod reference electrode surrounded by boron nitride insulator; H: electrolyte level; I: tube-tube couplings (Parker-CPI).

B. Tubular Cathode Plating Assembly

To demonstrate the feasibility of electrodepositing uranium on the inner surface of a large tube, a special two-electrode cell was developed. Electrolyte (B) was contained in a 1-1/2 in. (4 cm) ID alumina crucible surrounded by a stainless steel secondary crucible. The cathode (101 cm² area) was made

from a 5 in. (12.70 cm) length of nickel tubing, 1 in. (2.54 cm) ID and 1-1/4 in. (3.18 cm) OD, with opposing external grooves cut in the wall to facilitate separation of the tube into halves after the experiment for examination of the electrodeposit. Nickel tubing, 1/8 in. (0.32 cm) ID and 1/4 in. (0.64 cm) OD, welded to the upper rim of the cathode, served as the current collector and thermocouple gland.

A 5/16 in. (0.79 cm) dia uranium rod was positioned coaxially with the cathode by use of a boron nitride insulator with center hole, lying on the bottom of the alumina crucible. The entire assembly, with the heat reflectors for the furnace well, is shown in Fig. 2.

Fig. 2. Photograph Showing Cell Components (a) and Assembled Cell (b). The cell components in Fig. 2a are, from left to right: cell hanger, steel crucible, Al₂O₃ crucible, BN insulator, Ni tube cathode, heat shield assembly, Al₂O₃ insulator sleeves, and a 5/16-in. dia rod in front of the other components.

C. Instrumentation

Electrical control of the cell was provided by a potentiostat (Princeton Applied Research, model 173) fitted with a digital coulometer (Princeton Applied Research, model 179) and an electronic function generator (Princeton Applied Research, model 175). In the experiments with the large coupons, application of nucleation pulses and preanodization of the substrate electrodes was effected by switching control of the cell from the potentiostat to a 25 A constant-current power supply (Sorensen, model SRL 20-25). For plating experiments with the tubular cathode, a reverse-pulse plating machine (Dynatronix, model DPR 20-100-400) was used.

IV. RESULTS AND DISCUSSION

A. Potential-Step Current Transients

Potentiostatic transient experiments were performed to examine the relaxation behavior of the current as a function of time at constant potential and to determine the steady-state polarization curve. Information of both kinds was of interest to us in the design of electroplating experiments.

Potential-step transients for electrodeposition of uranium from electrolyte (A), onto a nickel disc electrode of 0.178 cm^2 area, are characterized by maxima in the current which occur progressively earlier as the deposition potential V_2 becomes progressively more negative (see Fig. 3).

Fig. 3.

Current Transients Resulting from Potential Steps from V_1 to V_2 in Electrolyte (A) at 444°C .
 $V_1 = 300 \text{ mV}$.

Such maxima were observed to correspond to the formation of dendrites, and similar results were obtained in experiments in different electrolytes. The most reasonable explanation for these current maxima is that they result from the enlargement of the electrode surface area associated with dendrite formation. This is consistent with the strong tendency of uranium to form dendrites, as already reported in the literature.^{2,4,12,17}

The construction of an empirical representation of the electrodeposition current as a function of time is difficult, since the transient currents do not obey the exponential or inverse power decay laws usually associated

with the potential-step technique. Construction of a steady-state current/potential curve is also difficult, since limiting steady values of the current are not reached. Although the usual steady-state kinetic method is evidently not strictly applicable, a crude polarization curve may be constructed by considering the maximum current attained before surface enlargement effects start to predominate. The variation of these maximum currents (I) with the deposition potentials (V) is empirically represented by the equation

$$I = I_0[\exp(\alpha_a F(V - V_r)/RT) - \exp(-\alpha_c F(V - V_r)/RT)] \quad (4)$$

The quantities V_r , I_0 , α_a , and α_c represent the apparent values of the reversible potential, exchange current, anodic transfer coefficient, and cathodic transfer coefficient, respectively. Least-squares curve fitting yields $i_0 = I_0 \times 5.61 \text{ cm}^{-2} = 240 \text{ mA cm}^{-2}$, $V_r = 10 \text{ mV}$, $\alpha_a = 0.590$, and $\alpha_c = 1.773$ at $T = 440^\circ\text{C}$ in electrolyte (A). The value of i_0 , which is to be regarded as only a rough estimate, is somewhat lower than typical values (about 1 A cm^{-2}) expected for exchange current densities of metal dissolutions in molten salts;¹⁸ nevertheless, it suggests a considerable degree of reversibility on the nickel substrate. The association of a high exchange current density with a strong tendency toward dendrite formation is in agreement with general observations¹⁹ and theoretical predictions²⁰ by Landau and Shyu.

B. Application of Pulsed Potential

Electrodeposition under the influence of periodically pulsed potentials was also of interest, in view of the well-known usefulness of pulse plating as a means of avoiding dendrite formation.²¹ The results are typified by Fig. 4, in which both the applied potential signal and the current response are shown.

In a typical experiment using the small disk working electrode (area of 0.178 cm^2), the pulsed potential signal was applied for 20 min, during which the charge accumulation was measured continuously, and the currents developed in the plating pulse and rest period were measured with an oscilloscope at intervals of 5 min. The extent of dendrite formation was assessed by measurement of the length, d (in mm), of the largest dendrite present, and the average current density was calculated from the total charge accumulated during the experiment. Measurement of the current pulses provided an additional method of identifying appreciable dendrite formation, since, under potential control, the resulting increase in the surface area of the electrode manifests itself in an increase in the current. The formation of dendrites was associated with the observation of a change in current of about 10% over 20 min.

The pulsed potential signal used in these experiments involved application of a plating potential V_2 for time τ , followed by a potential V_1 for time $r\tau$, where $r > 1$. Each of these parameters was found to exert an influence on the formation of dendrites. These influences for electrodeposition from electrolyte (A) were determined in a two-level factorially designed sequence

Fig. 4. Pulsed Applied Potential Signal and Transient Current Response of Nickel Test Electrode in Electrolyte (C) at 558°C. ($V_2 = -100$ mV, $\tau = 1.0$ ms, $r = 4.0$; all three symbols are defined in the text)

of experiments in which V_1 was maintained at 0 mV. In this case, the quantity r is equivalent to an off: on time ratio. The independent variables were assigned the following pairs of values, which also define the permissible limits of variation:

Plating potential, V_2 :	-25 mV and -250 mV
Off: on time ratio, r :	1 and 11
Plating pulse duration, τ :	0.1 ms and 1.0 ms

The dependent variable was the dendrite length, d , defined in the previous paragraph.

Analysis of the data resulted in a linear equation expressing the main effects of each variable:

$$d = 0.339 + 22.222|V_2| + 0.556\tau - 0.2r \quad (5)$$

For a specific value of τ , the condition for avoidance of dendrites ($d = 0$) corresponds to a linear relation between $|V_2|$ and r . For the experimentally accessible values of τ , viz., 0.1, 0.2, 0.5, and 1.0 ms, these linear relations are graphed in Fig. 5. As $|V_2|$ increases, the plating current increases, but larger values of r are required. These two variables thus exert opposing influences on the overall current density attainable with this technique. Coulometric measurement of the plating yield over 20 min, with values of r and $|V_2|$ selected according to Fig. 5, shows that the plating potential exerts the dominant effect. In other words, the gain in overall deposition rate resulting from the use of a larger cathodic overvoltage $|V_2|$ offsets the loss resulting from the requirement of larger r values for avoidance of dendrite formation.

Fig. 5.

Predicted Relation between Potential-Pulse Plating Parameters Corresponding to the Absence of Dendrites

A disadvantage of the approach used in this early work is that it implies an assumption concerning the effects exerted by each independent variable. In other words, the linear relations between r and $|V_2|$ are artifacts of the two-level experimental design, representing only a crude approximation to the actual situation. In the work on electrolytes (B) and (C), it was decided to avoid this assumption of linearity and to determine the desired relation between r and V_2 for a constant value of τ (1 ms) by application of the same experimental technique. If the conditions of each experiment are again represented as points with coordinates r and V_2 , the corresponding values of the dendrite parameter d may be considered to define a surface above the r - V_2 plane. From such a representation of the data, it is possible to determine the boundary of the "dendrite-free" region in this plane.

The results of this procedure are shown in Fig. 6 for electrolytes (B) and (C) at several temperatures. The largest dendrite-free region was

Fig. 6. Boundaries of Dendrite-Free V_2 - r Regions for Electrolyte (B) at 509°C (curve 1), Electrolyte (C) at 455°C (curve 2), Electrolyte (C) at 504°C (curve 3), and Electrolyte (C) at 550°C (curve 4). Regions below the curves are dendrite free; above the curves, dendrites form.

observed in electrolyte (C) at 504°C (curve 3) and the smallest in electrolyte (B) at 509°C (curve 1). Comparison of curves 2 and 3 shows that elevation of the temperature from 455°C to 504°C results in an enlargement of the range of accessible values of r and V_2 . Further increase of the temperature, to 550°C, has only a slight effect on the maximum allowable deposition potential, as shown by comparison of curves 3 and 4.

In general, the formation of dendrites in metal electrodeposition reflects the extent to which the natural surface irregularities of the substrate are amplified. This tendency is, in turn, determined by a balance of curvature and surface tension effects on the free energy of the deposit, and the effect of concentration polarization produced by the reaction in the vicinity of the surface.¹⁵ The concentration polarization tends to promote growth of dendrites, while the surface free energy associated with small radii of curvature tends to suppress it. For intrinsically fast reactions such as metal dissolution and deposition in molten salts, concentration polarization is particularly pronounced. Thus, in the experiments described above, the off: on time ratio (r) most probably exerts its influence by determining the time available for the relaxation of a locally nonuniform concentration profile.

A more specific conclusion that may be drawn from these results is that the mixed chloride-fluoride electrolyte (C) provides a wider range of accessible operating conditions under the type of pulsed-potential control used

here. To interpret this result in terms of the differences in composition between electrolytes (B) and (C), it would be necessary to conduct an additional series of experiments in which the concentration effects of each electrolyte component, in turn, were determined. In molten salt systems, a difficulty that arises with studies of this kind is that the range of concentration changes that can be examined is limited by the dependence of the liquidus temperature on composition. However, in connection with the possible effect of fluoride on the tendency toward dendrite formation, Broc¹² reported that dendrite-free coatings of uranium could be deposited from all-fluoride melts under rigorously anhydrous conditions.

C. Coulombic Efficiency

The coulombic efficiency of uranium electrodeposition from electrolyte (B) was also determined during the series of potential-pulse experiments just described. This was achieved by measurement of the charge recovered by anodization of the electrodeposited uranium at a potential of 400 mV (after examination to determine the dendrite length d). The coulombic efficiency of the electrodeposition process was then computed by expressing this recovered charge as a percentage of the total cathodic charge consumed in the course of the plating experiment.

The coulombic efficiency thus defined is represented as a function of r and V_2 (as was done above for the dendrite parameter, d) in Fig. 7. Inclusion of the boundary of the dendrite-free region pertinent to this electrolyte shows that the formation of dendrites is correlated with the observation of coulombic efficiencies significantly less than 50%.

Fig. 7. Coulombic Efficiency for Potential-Pulse Plating as Function of V_2 and r in Electrolyte (B) at 509°C. Numbers next to data indicate coulombic efficiency. Curve defines the boundary of the dendrite-free region.

The discrepancy between the consumed and recovered charges in these plating experiments indicates the presence of a parasitic electrode reaction, which becomes progressively more important as the cathodic overvoltage reaches more negative values. This is in agreement with results obtained by Niedrach and Glamm,⁴ who observed a decrease in current efficiency with increasing current under galvanostatic conditions. The explanation proposed by these authors was that the parasitic reaction is the reduction of UCl_4 to UCl_3 at the cathode. In view of the high purity of the electrolyte starting materials and the glovebox atmosphere used in our work, this indeed seems the most reasonable explanation. The application of a cathodic overvoltage to the working electrode requires the occurrence of an anodic process at the counter electrode, namely, the dissolution of uranium into the molten salt. As the cathodic polarization of the working electrode increases, the resulting increase in the anodic polarization of the counter electrode could result in the further oxidation of UCl_3 to UCl_4 . Diffusion of this UCl_4 through the electrolyte, followed by its reduction to UCl_3 at the working electrode, would consume some of the charge that would otherwise result in the deposition of uranium.

Interpretation of the observed correlation between dendrite formation and low coulombic efficiency would require a detailed study of the electrode kinetics of uranium in molten chlorides, which was beyond the scope of the present investigation. An additional complication peculiar to this system is that U , UCl_3 , and UCl_4 can be interconverted by the reverse disproportionation reaction (3), as well as by electrode processes. Although UCl_3 is the thermodynamically preferred species,⁴ an assessment of the role of UCl_4 in electrodeposition would require knowledge of the rate of this non-electrochemical reaction, in addition to the kinetic parameters of the U/U^{3+} and $\text{U}^{3+}/\text{U}^{4+}$ electrode reactions.

It is interesting that the coulombic efficiency with electrolyte (A) and (C), while not carefully studied, was much higher than that with electrolyte (B). In the cursory studies that were conducted in these two electrolytes, the efficiencies appeared to be in the 80 to 100% range. Why the efficiency is so much better in these systems is not completely understood, but it is probably associated with the lower concentrations of U^{3+} in the respective electrolyte systems.

D. Potential-Pulse Plating Experiments with Large Coupons

The results of the above investigations were applied to long-time-scale plating experiments with 5/8 in. (1.6 cm) dia cylindrical nickel, copper, tantalum, and aluminum cathodes, 7.74 cm² in area. The bottom circular faces of these coupons were polished with diamond paste to a 1 μm finish. In the first experiments, coupons were also etched to remove oxide films and expose crystal faces so that epitaxial growth of the electrodeposit would be enhanced. The etchant used was either a mixture of nitric acid, acetic acid, and water (for nickel and copper) or concentrated sulfuric acid (for tantalum). Since this etching step did not exert an appreciable effect on the resulting coating, it was subsequently discontinued. The same effects were achieved instead by anodic dissolution, to be discussed below.

Pulse-plating parameters, selected from Fig. 5, were $\tau = 0.1$ ms, $V_2 = -75$ mV, and $r = 10.3$, and the average current density achieved with this technique was between 3 and 5 mA cm⁻². Plating times were usually 21 h, corresponding to an average deposit thickness of approximately 5 mil (130 μ m).

On the nickel and tantalum coupons, the deposits were in all cases dendrite free and well bonded to the substrate. An example of uranium plated onto nickel is shown in Fig. 8. The uniformity of the deposit increased markedly when a nucleation pulse (current density -706 mA cm⁻² for 2 s) was applied before commencement of the potential signal. The deposits on copper coupons were also dendrite free but tended to become less uniform when a nucleation pulse was applied.

Fig. 8. Potential-Pulse Plated Uranium Deposit on Nickel Coupon (5/8 in. dia) in Electrolyte (A) at 450°C. Preanodization: 5 coulombs passed at 1.35 V. Nucleation pulse: -706 mA cm⁻² for 2 s.

In some experiments, anodization of the coupons was carried out immediately prior to imposition of the nucleation pulse. For nickel and tantalum substrates, this resulted in a slight improvement of the deposit uniformity and a significant improvement in the adhesion of the crystals. In the case of nickel, this latter effect is probably due to the deposition of a uranium-nickel alloy during the nucleation pulse and in the early stages of pulse plating. In principle, an improvement in adhesion could also result from interdiffusion of nickel and uranium. This interdiffusion has been studied by Lebedev et al.²² by means of chronopotentiometric measurements on a uranium-plated nickel electrode in a molten KCl-NaCl- UCl_3 mixture at temperatures between 800°C and 900°C. Considering that the time required for formation of UNi_5 by interdiffusion at 800°C was observed by these authors to be about 8 h, it is unlikely that interdiffusion would occur to an appreciable extent at the temperature of our experiments (450°C). A similar explanation probably applies to the tantalum coupons, but in this case the uranium-tantalum system forms a continuous range of solid solutions,²³ and kinetic data for interdiffusion do not appear to be available.

The adhesion of electrodeposited uranium to copper coupons was not significantly improved by anodic pretreatment.

In the case of aluminum coupons, alloy formation was observed. The alloy coating was quite smooth but readily became detached from the substrate; chemical analysis and X-ray powder diffraction identified it as UAl_3 .

E. Current-Pulse Plating Experiments with Large Coupons

The potential-pulse technique described in the preceding sections was the most convenient technique for screening current-pulse plating parameters for dendrite formation. To obtain a closer correspondence between our work and the procedures usually used in industrial electroplating, we carried out a series of experiments under controlled-current conditions. Of particular interest to us was the application of current-pulse techniques, which are known, in some cases, to provide electrodeposited coatings of finer grain size and superior coherence.²¹

A bipolar current-pulse technique was applied by Cohen²⁴ to the electrodeposition of niobium from molten fluorides. This involves alternate application of cathodic current density i_c for time t_c and anodic current density i_a for time t_a , which results in the removal of a fraction of the material deposited during each cathodic pulse. The reciprocal of this fraction is given by

$$q = i_c t_c / i_a t_a \quad (6)$$

In terms of q , the ratio of pulse lengths $R = t_c/t_a$, and the time-average current density $\langle i \rangle$, the values of i_a and i_c are given by

$$i_a = \langle i \rangle (1 + R) / (1 + q) \quad (7)$$

$$i_c = i_a q / R \quad (8)$$

In these equations, the cathodic and anodic currents retain their signs (negative and positive, respectively) so that q is a negative quantity. In this respect our notation differs somewhat from that of Cohen,²⁴ who characterized his experiments in terms of the absolute value of this pulse charge ratio.

Experiments with this technique were performed with electrolyte (B) and cylindrical nickel coupons (area of 7.74 cm^2). The bipolar pulsed currents were preceded by a nucleation pulse, involving application of about -1 A cm^{-2} for 2 s, which was intended to ensure uniform coverage of the substrate with crystal nuclei. The coupon shown in Fig. 9 was plated with $i_c = -74.9 \text{ mA cm}^{-2}$, $t_c = 4.17 \text{ ms}$, $i_a = 107.0 \text{ mA cm}^{-2}$, and $t_a = 2.08 \text{ ms}$, for which $R = 2$, $\langle i \rangle = -14.3 \text{ mA cm}^{-2}$, and $q = -1.400$. The values of i_c and t_c correspond to the

Fig. 9.

Bipolar Current-Pulse Plated
Uranium Deposit on Nickel Coupon
(5/8 in. dia) in Electrolyte (B)
at 504°C. $R = 2$, $\langle i \rangle = -14.3$
mA/cm², $q = -1.4$, $t_c = 4.17$ ms.

deposition of about a monolayer of uranium per plating pulse, of which $1/1.4 \times 100 = 71.4\%$ is removed in the following dissolution pulse. Plating time in this case was about 8 h, so that the average thickness was about 7 mil (180 μm).

In general, the coherence and uniformity of the deposits were found to be improved by values of q approaching -1. This is similar to the conclusion reached by Cohen²⁴ from his experiments on electrodeposition of niobium from fluoride melts. From Eqs. 7 and 8, it is clear that, for such values of q , large pulse current densities are required. Large current densities in the plating pulse can offset the beneficial effects of q being close to -1, unless the plating pulse length is adjusted so that the amount deposited in each pulse is small. In a series of experiments involving q values progressively approaching -1 and plating pulse lengths adjusted to correspond to the deposition of a monolayer, the quality of the coating was observed to be approximately constant.

F. Tubular Cathode Plating Experiment

The plating conditions of the coupon shown in Fig. 9 were applied to the 101-cm² tubular cathode in electrolyte (B). A nucleation pulse was not used in this case because the large currents required (about 100 A) exceeded the DC output capacity of the power supply. The net charge consumed in the experiment was about 10 Ah, corresponding to a nominal coating thickness of 6 mil (150 μm). (Uranium electrodeposition requires about one ampere-minute per square centimeter per mil.) After plating, the cathode was halved longitudinally, rinsed with deionized water, dried with methanol, and photographed (Fig. 10).

Fig. 10. Bipolar Current-Pulse Plated Uranium Deposit on Nickel Tubular Cathode. Conditions as for Fig. 9.

With the exception of some dendrites, the quality of the deposit on the nickel tubular cathode was as good as, or slightly better than, that obtained with the small coupons. Although our earlier experiments indicated that nucleation pulses tend to improve the uniformity of deposition, their omission in this experiment did not seem to exert much effect. Differences in the anode-cathode separation [$1/8$ in. (0.3 cm) and $11/32$ in. (0.9 cm), respectively] and in the current distribution were probably more important. Another potentially important factor is the surface preparation. The inner surface of the tube was used as-received, with no further mechanical or chemical pretreatment except degreasing with acetone, while the smaller coupons were polished to a $1\text{ }\mu\text{m}$ surface finish.

The fact that the dendrites are concentrated on the side opposite the current collector suggests that the temperature distribution in the cell could have been nonuniform. Heat conduction along the heavy-walled current-collector tube could have caused a temperature gradient, resulting in electrolyte convection, uranium concentration gradients, and thermogalvanic effects. Such a nonuniform temperature distribution would have been compounded by the radiative, rather than conductive, heating of the crucible in the furnace well.

V. CONCLUSIONS

In this report, it is shown that a potential-pulse plating technique, involving deposition pulses separated by zero-potential rest periods, can be used to produce dendrite-free deposits of uranium on various substrates. A technique for determining the optimal plating conditions is described, and it is shown using this technique that the widest range of accessible operating conditions is found in the molten chloride-fluoride electrolyte (C) at 504°C. In experiments on large coupons, positive effects of preanodization and nucleation pulses on the adhesion and uniformity of deposits have been observed. Our best results, however, have been obtained with a bipolar current-pulse technique involving alternate deposition and dissolution pulses. Overall current densities of about 14 mA cm⁻² have been achieved, and the application of this technique to a large tubular cathode has been demonstrated.

If future work is to be carried out on this project, we recommend that it be done with an all-fluoride ion electrolyte and the bipolar current-pulse technique.

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