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LANL Classification Group
MP, FSS-16, 8/28/95

[redacted]

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LA REPORT 67

This is copy [redacted] of 15 copies

March 1, 1944

This document contains 11 pages

PROGRESS REPORT ON REDUCTION BY ELECTROLYSIS

February 1944

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Classification changed to UNCLASSIFIED
by authority of the U. S. Atomic Energy Commission,
Per H. T. Carroll 3-2-56
By REPORT LIBRARY M. Miller
3-28-56

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Metallurgy; [illegible]

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ABSTRACT

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Uranium has been electrodeposited from fused salts containing approximately 16 per cent UCl_3 in a $BaCl_2$ - NaCl - KCl solvent at 600-650° C. The metal is dendritic in form and can be produced on a one-gram scale. It appears possible to strip the bath of its uranium. Current efficiency is approximately 20 per cent. The crystalline material may be melted with high recovery and is readily converted to hydride. Corrosion tests indicate that the most suitable container material is tungsten. Experiments with UCl_4 electrolytes have not been successful.

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INTRODUCTION

During the month of February experimental consideration has been given to the small scale reduction of uranium by electrolysis. Although bomb reduction of plutonium may prove satisfactory when it becomes available, it was believed that an alternative technique should be prepared. Since previous work with aqueous solutions had proved largely unsuccessful, the work was confined entirely to deposition from fused salts. In view of the small quantities of materials involved, a relatively porous container such as graphite could not be tolerated, and probable losses by volatilization indicated that low temperatures should be preferred. Because the use of pure uranium salts would involve working with fractions of a milliliter, it is obvious that extensive dilution is essential. Earlier work (LA 54, 61) had shown that fused chlorides were satisfactory solvents, but that uranium could not be deposited from such electrolytes containing small amounts of UF_4. Accordingly UCl_4 and UCl_3 were selected as the most likely sources of uranium ion.

EXPERIMENTAL

All of the salts (other than the uranium chlorides) were of C. P. or Reagent quality, and, when containing water of crystallization, were first dehydrated. Each salt was then individually fused in platinum and cast in platinum or nickel crucibles depending upon the relative ease of removal of the solid. The salts were then ground in porcelain and

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mixtures prepared and fused again in platinum and reground. The uranium chlorides were samples prepared by C. A. Kraus at Brown University. Temperatures were measured with iron-constantan or chromel-alumel thermocouples and a Thwing potentiometer.

UCl_4 Electrolytes

The tetrachloride is exceedingly hygroscopic, and mixtures for these experiments were weighed and ground in a dry box and subjected to a preliminary fusion at 600° C. in Vycor test tubes under dry HCl. Electrolyses were performed under hydrogen which had been freed of oxygen by passing over platinized asbestos at 300° C. and dried by Drierite.

One of the major causes of loss of cathode product in fused electrolyses results from reaction of the deposit with anode products such as chlorine. In the initial experiments an attempt was made to minimize such loss by separating anode from cathode through the use of cells of V shape constructed of fused silica or Vycor tubes. Successful tests of the technique were performed by depositing silver and manganese from their fused chlorides dissolved in inert chloride solvents.

Electrolyses of UCl_4 in NaCl and in a low-melting mixture of $BaCl_2$, NaCl and KCl at temperatures between 600 and 650° C., using graphite anodes, and cathodes of graphite, molybdenum, platinum, and lead, and UCl_4 concentrations of 20 per cent and 77 per cent ($2NaCl \cdot UCl_4$), resulted in thin, doubtful deposits of non-metallic appearance. These experiments were at least temporarily abandoned because of the more promising results with UCl_3 electrolytes.

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UCl$_3$ Electrolytes

It was found that satisfactory yields of uranium could be obtained from UCl$_3$ electrolytes without resorting to cell division and, therefore, straight tubes of fused silica, Vycor, or Pyrex were employed as cells. Furthermore, in the exploratory experiments described below, it was not found necessary to employ a dry box for UCl$_3$ weighings, provided they were made rapidly. In all tests in which the cell was open to the air, a brick-red powder was precipitated, but this was prevented by an atmosphere of dry, oxygen-free hydrogen. Heating of the cells was effected by a small wire-wound furnace, manually controlled. The anodes were 1/4 in. diameter commercial graphite or graphite of special spectroscopic purity. Current densities are not specified because the metal was deposited in dendritic form, so that the effective cathode area increased continously. Current efficiencies are based on the reduction of uranium from the trivalent state, although it is likely that considerable quantities of U^{4+} were present by virtue of anodic oxidation. The actual efficiencies are, therefore, probably higher than stated. In all of the electrolyses the solvent (designated as #1161) consisting of 48 per cent BaCl$_2$, 21 per cent NaCl, 31 per cent KCl, with a melting point slightly over 500° C., was melted first and the UCl$_3$ added. When hydrogen was passed through the cell, the effluent gases appeared to consist largely of HCl which was absorbed in soda-lime. The cathode product was washed with cold water followed by alcohol or acetone, and air-dried. Typical results are summarized in Table I. It was found that in conformity with general

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experience, the crystal size decreases with increased current density. At low currents, or with longer deposition periods, crystals over a centimeter in length were produced. A photograph of a typical growth on a platinum wire (Run #1248) is shown in Figure I, on a one-inch scale.

The most suitable container material would appear to be tungsten although no data are available on silicon contamination resulting from the use of glass tubes. Based on the evidence of one run, it appears possible to strip the bath completely of its uranium content by electrodeposition. The current efficiencies, which appear to be in the neighborhood of 20-30 per cent, are low when compared with commercial fused salt electrolysis on a large scale, but are relatively high for such small scale operation.

Only one temperature range and one solvent composition have been investigated, but it is hoped to extend the study to other conditions.

Melting of Crystalline Uranium

Several one-gram scale melts of the electrolytic uranium have been made. A. U. Seybolt has succeeded in melting the uncompacted crystals in a beryllia crucible using a conducting liner in a 0.5 megacycle induction furnace. Compacts approximately 1/8 in. in diameter, pressed at 3,000 pounds, melt readily in beryllia by self-conduction. However, a reddish film appears to form on the exterior of the melts which prevents perfect agglomeration. As-melted recoveries in these cases are about 99.5 per cent, falling to 97 per cent after pickling to remove the film. One such compact was melted under fused barium chloride at 1300° C. with a final recovery of 98.5 per cent after cleaning.

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Hydride Formation

Approximately 0.1 gram of crystalline uranium prepared by electrolysis has been converted to hydride by J. E. Burke with a resultant formula, based on hydrogen absorption, of $UH_{3.00 \pm 0.02}$. Hydride formation was rapid.

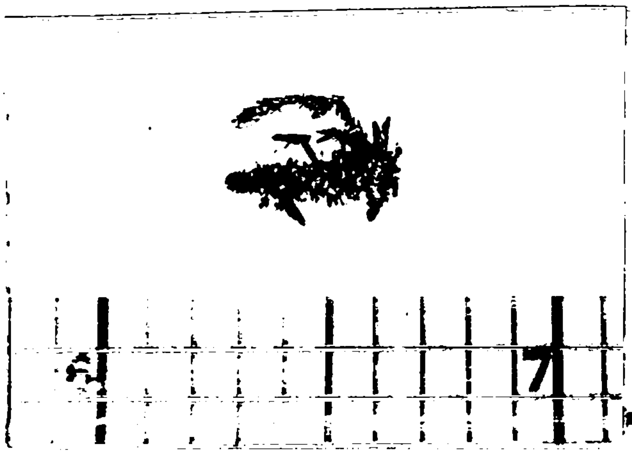

Fig. 1

Crystalline Uranium

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TABLE I. ELECTROLYSIS OF URANIUM TRICHLORIDE

(#1161 = 48% $BaCl_2$; 21% NaCl; 31% KCl)

Run	Bath Composition Weight Percent	Operating Conditions	Results
1203	20 UCl_3; 80 #1161	25 g charge. Vycor tube 22 x 200 mm, 1/4" graphite cathode; 3/4" immersion; 600° C; 1.3 amp; 5 minutes.	Small dendritic uranium crystals.
1213	Continuation of 1203	Same as 1203; 640-680° C; 15 minutes.	Small uranium crystals
1214	Continuation of 1213	Same as 1213; 670-680° C; 3 amp; 7 minutes.	Very small uranium crystals.
1215	Continuation of 1214	Same as 1214; 665-680° C; 1.0 amp; 10 minutes.	Fairly large uranium crystals.
1216	Continuation of 1215	Same as 1215; 665-680° C; 0.85 amp; 6 minutes.	Crystals larger than any above.
1227	25 UCl_3; 75 #1161	4 g. charge; 8 mm. Vycor tube; 0.020" platinum wire cathode, 1 cm. long at base; 650° C; 0.35 amp. 15 minutes.	Fairly large, silvery crystals of uranium.

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TABLE I. ELECTROLYSIS OF URANIUM TRICHLORIDE (CONTINUED)

Run	Bath Composition Weight Percent	Operating Conditions	Results
1228	16.7 UCl_3; 83.3 #1161	12 g. charge; 18 x 150 mm. Pyrex tube; 0.020" platinum wire cathode, 1 cm. long at base; 650-670° C; 0.35 amp; 13 minutes.	Similar to 1227.
1229	16.7 UCl_3; 83.3 #1161	12 g. charge; 25 x 200 mm. Vycor tube; platinum cathode 8 x 15 mm.; 650-670° C; 0.9 amp; 20 minutes.	Fine dendritic uranium in flaky form. Platinum markedly attacked at liquid line.
1236	16 UCl_3; 84 #1161	9.5 g. charge; 18 x 150 mm. Pyrex tube; 0.040" platinum wire cathode, 1 cm. long; 640-652° C; 0.2 amp; 45 minutes.	Substantial dendritic growth of uranium on the platinum wire.
1248	16 UCl_3; 84 #1161	Same as 1236; 630-636° C; 0.1 amp; 63 minutes.	Coarse crystals adherent to platinum.
1256	16 UCl_3; 84 #1161	9.5 g. charge; 18 x 150 mm. Pyrex tube; 0.020" platinum wire. 1 cm long at base of tube; 630-635° C; 0.1 amp; 180 minutes.	Coarse dendritic crystals as well as growth of uranium foil following contours of tube.

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TABLE I. ELECTROLYSIS OF URANIUM TRICHLORIDE (CONTINUED)

Run	Bath Composition Weight percent	Operating Conditions	Results
1262	16 UCl_3; 84 #1161	37 g. charge; 22 x 175 mm. Pyrex tube; 0.040" platinum wire, 2 mm. long sealed in base; 626-635° C; 0.3 amp; 197 minutes.	Substantial and fairly thick dendrites in a shell of uranium foil following contour of tube. C.E. 43%; metal produced = 1.26 gm.
1266	27 UCl_3; 73 #1161	22 g. charge; 18 x 150 mm. Pyrex tube; 0.040" tungsten wire, 1 cm. long sealed in base; 626-636° C; 0.3 amp; 3.5 volts; 420 minutes.	Silver-white crystals, fairly adherent to tungsten. C.E. 18%. Metal produced = 1.05 gm.
1279	27 UCl_3; 73 #1161	Same as 1266; 635-650° C; 0.89 amp; 3.5 volts; 353 minutes.	Long, silver-white crystals. C.E. 19%; m metal produced = 2.88 gm.
1280	16 UCl_3; 84 #1161	19 g. charge; 22 x 175 mm. Pyrex tube; silver cathode 1/8" x 0.010", 3/4" immersion; 633-642° C; 0.35 amp; 2.5 volts; 318 minutes.	Small silvery crystals of uranium. Silver cathode coated with thin white film above liquid line, but not visibly attacked. C.E. 21%; metal produced = 1.16 gm.

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TABLE I. ELECTROLYSIS OF URANIUM TRICHLORIDE (CONTINUED)

Run	Bath Composition Weight Percent	Operating Conditions	Results
1288	16 UCl_3; 84 #1161	Same as 1280; 0.040" tungsten wire cathode; 3/4" immersion; 635-640° C; 0.35 amp; 2.3 volts; 450 minutes.	Short thick crystals. Bath stripped of UCl_3 and all metal recovered within limits of error. Tungsten not attacked above liquid line. C.E. 25%; metal produced = 1.97 gm.
1296	35 UCl_3; 65 #1161	48 g. charge; 26 x 150 mm. Pyrex tube; all glass cell; 0.040" tungsten wire cathode, 1 cm. long sealed in base; 635-645° C; 2.05 amp; 300 minutes.	Long thin silvery crystals. C.E. 29%; metal produced = 8.74 gm.

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