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ELECTROLYTIC REDUCTION OF THORIUM OXIDE

by

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ABSTRACT

Thorium metal has been produced by electrolytic reduction of thorium oxide. Reduction was accomplished in both a KF-ThF_4 melt and a NaCl-KCl-ThCl_4 melt. A flowsheet for the complete process using the fused fluoride system is proposed.

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ELECTROLYTIC REDUCTION OF THORIUM OXIDE

INTRODUCTION

A satisfactory method for the regeneration of thorium metal from an aqueous thorium nitrate stream requires (1) a simple preparation of the feed material, (2) a successful reduction of some thorium compound to thorium metal, (3) an efficient recovery of the metal after reduction, and (4) a simple recycle of the nonrecoverable metal fines and other thorium-containing materials. Existing proposals⁽¹⁾⁽²⁾ specify electrolytic or metallothermic reduction of a thorium halide as a means of regenerating the metal. However, conversion of thorium nitrate to an anhydrous thorium halide is both a difficult and a hazardous operation. Regeneration of thorium metal through reduction of its oxide would offer the advantage of eliminating the halogenation step and substituting for it a direct calcination of thorium nitrate to thorium oxide.

This investigation was undertaken to determine the feasibility of such a process based upon reduction of the oxide. Electrolytic rather than metallothermic reduction of the oxide was selected because the latter has been reported⁽³⁾ to yield a product with an average particle size of only seven to eight microns. Other work⁽⁴⁾ indicated that electrolytic reduction should produce a metal having larger particle size and lower impurity content. The results of this experimental study form the basis for a proposed process which appears to meet all the requirements listed above for a satisfactory method of producing thorium metal.

SUMMARY

Thorium metal was prepared by electrolytic reduction of thorium oxide. The reduction was performed in two systems, a fused $KF-ThF_4$ mixture and a fused $NaCl-KCl-ThCl_4$ mixture. The average decomposition potential measured in both systems was 1.92 v. Electrolysis in the fluoride melt proved to be a superior process, the metal product having higher purity and larger average particle size than the product from the chloride melt. In addition, the recovery of thorium from recycle streams proved to be much simpler in the fluoride process than in the chloride process. The feasibility was demonstrated for all the essential steps of a complete process for production of the metal in the fluoride system.

PROCESS DESCRIPTION (FLOWSHEET)

Figure 1 is the proposed flowsheet of the complete process for the production of thorium metal in the fused fluoride system. A brief discussion of each of the steps is presented below.

Electrolysis

Electrolysis will be performed in graphite-lined cast iron cells. The liners, serving as anodes, will have to be replaced as they are consumed. An inert atmosphere chamber must be provided for removal and cooling of the cathodes following electrolysis.

Cathode Stripping

Conventional techniques and equipment are available for stripping the deposit from the cathodes.

Crushing and Screening

The gross physical separation of metal from salt is based on the fact that the salt crystals are easily reduced in size by crushing, while the metal particles are not. It is proposed that the metal in the +200 mesh (U. S. Standard Series) fraction, which contains 80 to 95 per cent metal by weight, be leached, while the -200 mesh fraction which averages only 15 per cent metal be recycled.

Leaching

The salt not removed by the physical separation can be dissolved in hot aqueous aluminum nitrate. Boiling 10 to 20 minutes in 1M aluminum nitrate gives satisfactory removal of salt.

Metal Processing

After the leaching operation, the metal is separated from the supernate by decantation. The metal is then washed with water and air-dried. The drying step will presumably be followed by a powder metallurgical forming of electrodes for subsequent arc melting.

Recycle

There are two recycle streams.

-200 Mesh Screening Fraction

The composition of this fraction averages 15 per cent thorium metal, 0.4 per cent thorium oxide, and the remainder salt. Two alternatives are available for treatment of these fines: an oxygen roast will convert the metal to thorium oxide, after which this fraction can be returned to the electrolysis cells; or, the -200 mesh fraction may be recycled directly to the cells, and a periodic oxygen sparge may be employed to re-oxidize the thorium metal. The latter alternative is favored, since an oxygen sparge will probably be necessary to re-oxidize the nonadhering metal product, which collects at the bottom of the cells during electrolysis. Any such treatment with oxygen will require careful control to prevent excessive attack on the graphite liners.

Leach and Wash Supernates

The leach and wash supernates contain thorium in the form of soluble Th^{+4} ion plus dispersed oxide and metal fines. The dissolved thorium can be recovered by adding KF in quantity sufficient to precipitate all the thorium as KThF_6 . Some care must be observed in order not to precipitate any of the potassium aluminum fluorides. Control is not too critical, however, since less than 80 per cent of the KF required for incipient precipitation from a blank 1M aluminum nitrate solution will precipitate essentially all of the Th^{+4} from a 1M aluminum nitrate solution saturated with KThF_6 . A well-agitated precipitation should succeed in coagulating and carrying down the dispersed particles as well. Following filtration, the precipitate will be dried and recycled to the electrolysis cells.

Waste

The only waste stream in the process is the filtrate from the KThF_6 regeneration step. Thorium concentration in this stream will be less than 10^{-5}M .

EXPERIMENTAL DETAILS

APPARATUS

Electrolysis Cells

The cells, which also served as the anodes during electrolysis, were CS-312 graphite crucibles, 18 inches high and 5 inches in diameter with 0.5-inch walls. They were obtained from the National Carbon Co. During operation the cell was inserted into a stainless steel sleeve to prevent loss of the melt in event of cell rupture.

Housing

The apparatus for the electrolytic runs was housed in a drybox-furnace assembly. Figure 5 is a photograph of the housing; Figure 6 shows the interior details and the instrumentation.

The furnace was a "Hevi-Duty Electrical Furnace", type HDT 5610, 5 kw. The axis of the furnace cavity was changed from horizontal to vertical and the supporting

legs were modified. The door and face plates were removed in order that the drybox floor could bolt directly to the furnace.

The drybox assembly consisted of a 19 x 23 x 23-inch aluminum box with a "Lucite" face, a "Transite" floor, and an enclosed superstructure on the top. The superstructure supported a ball-and-socket manipulator and two "Lucite" observation windows. The ball-and-socket joint allowed movement of a four-foot mechanical finger tong used for all internal manipulations. The windows were sealed with neoprene gaskets and held in place by aluminum studs welded to the box frame. The "Transite" floor was cut out in the center to allow access into the furnace cavity, and a "Transite" cover was provided for use with the cell in place. Racks were mounted on the walls for supporting the cathodes before and after immersion in the melt.

During operation, helium was purged through the drybox at a rate of approximately 30 cfh. At this rate a positive pressure of about 0.75 inch of water could be maintained within the box. Valved exhaust lines provided a means of purging through the furnace cavity or through the upper part of the assembly. After two hours of purging, the box atmosphere could be maintained at 99+ per cent helium.

An electrolyte entry port, consisting of three telescoping aluminum tubes pinned to the small end of a funnel, was provided so that additions could be made to the cell during operation. The entry port was sealed with a gasketed threaded plug.

Instrumentation

The electrolyzing current was provided by a 0 to 50-ampere DC power source. Other instruments included a voltmeter and a Brown recording potentiometer calibrated for direct reading of temperature from thermocouple potential. The thermocouple was housed in a stainless steel well which was immersed in the melt.

MATERIALS

Potassium Thorium Fluoride

The compound $KThF_6$ was prepared by the method of Driggs and Lilliendahl⁽⁶⁾. The anhydrous double salt precipitated upon adding an excess of aqueous potassium fluoride to aqueous thorium nitrate. The precipitation of Th^{+4} from the solution was virtually complete, the filtrate analyzing $<6 \times 10^{-6} M Th^{+4}$.

Thorium Oxide

Fisher Scientific Co. C. P. thorium oxide was used in all runs.

Cathode Metals

Six-millimeter molybdenum rod was used as cathode material in most of the electrolyses. The molybdenum and the tantalum were obtained from the Pansteel Metallurgical Corp. of North Chicago, Illinois. Titanium was obtained from Rem-Cru Titanium, Inc. of Midland, Pennsylvania; and the thorium used for cathodes was obtained from the Atomic Energy Commission.

PROCEDURES

Electrolysis

Prior to each electrolysis, the cell was filled with salt plus the desired quantity of oxide. The cathodes were hung on the racks, and all electrical connections were made. The front window was then put in place, and the helium purge and heating were started simultaneously. Two to three hours were required to reach operating temperature.

After thermal equilibrium at the desired temperature had been attained, the cathode was immersed in the melt and electrolysis started immediately. At the conclusion of the electrolysis, the cathode was withdrawn slowly to allow maximum drainage of the molten salt. The cathode with its metallic deposit was hung on the rack. A second cathode could then be immersed and the process could be repeated. A helium atmosphere was maintained throughout the cooling period to prevent oxidation of the

deposited metal. Figure 7 is a photograph of a typical cathode deposit.

Metal Recovery

Fluoride System

The procedure for recovery of the metal produced by electrolysis in the fluoride system consisted of stripping the deposit from the cathode, crushing, screening, and leaching. After the deposit was crushed, 20 to 40 per cent passed a 200-mesh screen. This fraction, containing from 5 to 14 per cent of the metal, was not processed further. The +200 mesh fraction was leached for 10 to 20 minutes in boiling aqueous aluminum nitrate (~1M). A white or grey near-colloidal dispersion formed in the supernate during the leaching operation. This dispersion, which consisted of finely divided thorium oxide and thorium metal, could be coagulated and precipitated by centrifugation. After the leaching operation, the metal was visibly free of salt, as shown in Figure 8.

Chloride System

The recovery scheme following electrolysis in the chloride melt differed from that for the fluoride system. The procedure consisted of stripping the deposit from the cathode, crushing, and leaching with water. Screening yielded no effective separation of metal from salt due to the very small average particle size of the metal. Leaching was accomplished easily, since the chloride salts of the melt are all highly soluble in water.

Cathode Pretreatment

During the course of the experimentation, it was found that the physical properties of the metallic deposit were somewhat improved by pretreating the cathode. This pretreatment consisted of sanding to roughen the surface, degreasing with trichloroethylene vapor, and pickling for three to five minutes with an agent suitable for the cathode material (see Table III). Following the pickling, the cathodes were washed in distilled water and dried in air.

RESULTS

Electrolysis of Thorium Oxide

The composition of the anode gas evolved during electrolysis in both the fused fluoride and the fused chloride systems established thorium oxide as the compound undergoing decomposition. The oxygen resulting from decomposition of the oxide was liberated at the graphite anodes as carbon dioxide and carbon monoxide. The large increase in the oxide content of the gas surrounding the anode during electrolysis is evident from the analyses listed in Tables I and II. No gases containing fluorine or chlorine were found. The presence of these gases would have been observed had the halides been decomposed during the electrolysis.

Decomposition Potential

The decomposition potential of thorium oxide in both systems was determined in the conventional manner from current-voltage graphs. A typical plot is shown in Figure 2. A variation from 1.67 to 2.15 v was found over fourteen independent determinations in the fused fluoride system, yielding a value of 1.92 ± 0.11 v. Ten determinations in the fused chloride system gave a value of 1.92 ± 0.27 v.

Solubility of Thorium Oxide

The solubility of thorium oxide in a KF-ThF_4 melt, 70 per cent ThF_4 by weight, was found to be approximately one per cent. No reliable result was obtained for the solubility of thorium oxide in the NaCl-KCl-ThCl_4 melt.

Leaching Agents

A solvent was required for the constituents of each of the melts in order to leach the occluded salt from the metal. No problem was encountered in the chloride system, since all the salts in the melt are water soluble. Thorium fluoride and its

double salts with potassium fluoride are insoluble in water, but dissolve satisfactorily in boiling aqueous aluminum nitrate.

Product Purity

The product was identified as thorium metal by X-ray diffraction. Determination of the HCl-insoluble content yielded the amount of dissolved or occluded thorium oxide, which averaged 0.63 per cent in the product from the fluoride process, but ran as high as 12.2 per cent in the product from the chloride process. One complete spectroscopic analysis of the metal produced by electrolysis in the fluoride melt is listed below:

600 ppm Al	35 ppm Mg
9 ppm B	40 ppm Mn
90 ppm Ca	300 ppm Ni
<0.5 ppm Cd	400 ppm Si
700 ppm Cr	<1 ppm U
250 ppm Cu	80 ppm Zn
1000 ppm Fe	<50 ppm Zr
Remainder Th	

The source of impurities was assumed to be the fluoride salt.

Operating and Performance Data

Fused Fluoride System

Table III lists the operating and performance data for seventeen electrolyses carried out in the fused fluoride system. Runs with a common numeral were made in the same salt bath. The recovery efficiency listed in the table is the per cent recovery of the metal theoretically deposited by the passage of the given charge. The HCl-insoluble content indicates the quantity of oxide dissolved in the metal.

Examination of the data reveals that the first electrolysis with each salt bath resulted in poor yields. This effect is ascribable to impurities in the salt, the presence of which decreases the mean particle size^(s) and consequently the recovery efficiency. The first electrolysis with each bath apparently served as a scavenging run, after which performance improved.

From the data in Table III the superiority of molybdenum as a cathode material over the other metals tested is apparent. If the results of the scavenging runs are discounted, the recovery efficiency for the electrolyses with molybdenum cathodes varied from 8.2 to 41.0 per cent, averaging 18.3 per cent.* The weight ratio of the recovered metal to the deposit averaged 39.3 per cent, with a total variation from 18.2 to 67.9 per cent. An average of 61.7 per cent of the recovered metal exceeded 40 mesh in size, and the amount of metal fines in the -200 mesh fraction ranged from only 2 to 7 per cent of the total deposit. The HCl-insoluble content varied from 0.10 to 2.30 per cent averaging 0.63 per cent. Performance with thorium, titanium, and tantalum cathodes was much less satisfactory. In particular, the particle-size distribution of the product was less favorable than with the molybdenum cathodes, since much larger fractions of the thorium metal were produced as irrecoverable fines with the other three cathode materials tested. Figure 3 illustrates the differences in particle-size distributions for the four cathode materials.

Current density was varied from 35 to 380 amperes per square decimeter for the electrolyses listed in Table III. No good correlation was observed, however, between current density and any of the performance criteria. This was probably due to lack of adequate control of other operational variables. Figure 4 shows the particle-size distributions for electrolyses run at different current densities.

Beginning with Run 3A, the cathodes were given a pretreatment with a pickling agent in an attempt to improve the adherence of the deposit. Improvement was not pronounced; however, the metal particles plated on pickled electrodes had a firmer

* A sizable loss resulted from lack of proper equipment to strip the tightly adhering thorium deposit efficiently from the cathodes.

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structure, which facilitated separation of the metal from the salt.

Fused Chloride System

Fourteen electrolyses were performed in the chloride system. Recovery efficiency varied from 13.9 to 55.0 per cent, averaging 27.2 per cent. The weight ratio of the recovered metal to the deposit averaged 22.5 per cent, ranging from 10.9 to 43.3 per cent. The HCl-insoluble content was high, 1.92 to 12.2 per cent. The particle-size distribution was considerably less favorable than that resulting from the electrolyses in the fluoride system. In only one of the fourteen runs did any of the metal particles exceed 80 mesh in size. Virtually all the product was -100 mesh, with sizable fractions in the 10 to 50-micron range.

Comparison of Processes in the Fluoride and Chloride Systems

The experimental results indicate that the production of thorium metal by electrolysis of thorium oxide in the fused fluoride system is superior to the analogous process in the chloride system. The chloride melt has a lower fusion temperature ($\sim 800^{\circ}\text{C}$) than the fluoride system ($\sim 1000^{\circ}\text{C}$), plus a high water solubility of the bath constituents, which facilitates the leaching operation. However, these advantages are inadequate to compensate for the lower purity and smaller particle size of the product. Moreover, there is no simple technique for recycling the occluded chloride salts that are removed with the cathode deposit. Unless methods can be found for depositing larger metal particles from the chloride melt, electrolysis of thorium oxide in this system does not appear to be competitive with the fluoride process.

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TABLE I

ANODE GAS ANALYSES DURING ELECTROLYSIS OF ThO_2 IN A KF-ThF_4 MELT*

Constituent	Before Start	8 Min After Start	18 Min After Start	3 Min After Conclusion	16 Min After Conclusion
He	95.4	70.0	72.1	94.1	96.6
CO	1.77	22.2	25.8	4.62	2.33
CO ₂	0.17	7.02	1.23	0.10	0
N ₂	0.15	Trace	Trace	Trace	Trace
O ₂	0.03	0	0	0	0
H ₂ **	2.45	0.69	0.88	1.10	1.10
F-containing gas	0	0	0	0	0

* All figures given in mol per cent
 ** The presence of H₂ as yet unexplained

TABLE II

ANODE GAS ANALYSES DURING ELECTROLYSIS OF ThO_2 IN A NaCl-KCl-ThCl_4 MELT*

Constituent	Before Start	5 Min After Start	20 Min After Start	Immediately After Conclusion	10 Min After Conclusion
He	98.4	71.6	73.2	93.8	98.0
CO	0	5.33	6.96	2.53	0.15
CO ₂	0.10	20.4	17.8	1.78	0.24
N ₂	0.10	0.41	0.51	0.22	0.09
O ₂	0	0.05	0	0	0
H ₂ **	1.35	2.10	1.55	1.64	1.56
Cl-containing gas	0	0	0	0	0

* All figures given in mol per cent
 ** The presence of H₂ as yet unexplained

TABLE III

OPERATING AND PERFORMANCE DATA FOR THE ELECTROLYSES OF ThO_2 IN A KF-ThF_4 MELT

Run	Cathode Material	Cathode Pretreatment	Temperature °C	Current Density a/dm^2	Per Cent Recovery Efficiency	Wt. Metal Recovered Wt. Deposit	Wt. % Recovered Metal +40 mesh	Wt. % Deposit -200 mesh	Wt. % Metal in -200 mesh Deposit	Per Cent HCl- Insolubles
1 A	Mo	None	990	160	2.5	0.025	0	-	-	-
1 B	Mo	None	1000	280	9.6	0.221	38.7	-	-	2.30
1 C	Mo	None	980	56	14.7	0.328	16.7	-	-	-
1 D	Mo	None	950	63	8.2	0.276	69.0	-	-	1.10
1 E	Mo	None	940	103	24.6	0.583	95.0	-	-	0.43
1 F	Mo	None	960	280	10.3	0.210	63.4	-	-	0.14
2 A	Mo	None	1000	193	0	-	-	-	-	-
2 B	Mo	None	1000	380	18.5	0.182	32.4	-	-	0.44
2 C	Mo	None	990	380	21.5	0.473	69.0	34.3	6.9	0.94
3 A	Mo	8M HNO_3	950	174	12.0	-	1.5	-	18.8	2.70
3 B	Mo	8M HNO_3	965	104	7.8	0.478	63.5	39.2	-	0.32
3 C	Mo	8M HNO_3	970	35	19.1	0.596	65.1	27.2	-	0.26
3 D	Mo	8M HNO_3	980	174	41.0	0.679	91.4	18.8	-	0.10
3 E	Mo	8M HNO_3	1010	182	25.8	0.400	74.1	31.4	20.7	0.23
3 F	Th	6M HCl	1000	53	8.2	0.129	2.0	66.7	21.8	0.21
3 G	Ti	6M HCl	1000	136	10.2	0.084	0	80.6	39.0	2.60
3 H	Ta	8M HNO_3	1000	167	12.3	0.058	0	88.0	40.0	0.25

FIGURE 1

PROPOSED FLOWSHEET FOR PRODUCTION OF THORIUM METAL
IN FUSED FLUORIDE SYSTEM

FIGURE 2

CURRENT-VOLTAGE CURVE FOR ELECTROLYSIS
OF ThO_2 IN A KF-ThF_4 MELT

FIGURE 3

PARTICLE-SIZE DISTRIBUTION FOR ELECTROLYSES
WITH VARIED CATHODE MATERIAL

FIGURE 4

PARTICLE-SIZE DISTRIBUTION FOR ELECTROLYSES
AT VARIED CURRENT DENSITIES

FIGURE 5

DRYBOX-FURNACE HOUSING

FIGURE 6

DRYBOX-HOOD ASSEMBLY SHOWING INTERIOR DETAILS
AND ASSOCIATED INSTRUMENTATION

FIGURE 7

TYPICAL CATHODE DEPOSIT OBTAINED BY ELECTROLYSIS
OF ThO_2 IN A KF-ThF_4 MELT

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FIGURE 8

THORIUM METAL PARTICLES (+ 10 MESH) PRODUCED BY ELECTROLYSIS
OF ThO_2 IN A KF-ThF_4 MELT, FOLLOWING LEACH WITH HOT AQUEOUS
ALUMINUM NITRATE