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Technical Progress Report for Fourth Quarter, February 1 to April 30, 1953

By
Merle E. Sibert

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DEVELOPMENT REPORT

May 25, 1953

Horizons Incorporated

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METALLURGY AND CERAMICS

INVESTIGATIONS FOR THE PRODUCTION OF THORIUM METAL

By
Merle E. Sibert

May 25, 1953

Horizons Inc.
Cleveland

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INVESTIGATIONS FOR THE PRODUCTION OF THORIUM METAL
(Technical Progress Report for Fourth Quarter, February 1 to April 30, 1953)

By Merle E. Sibert

SUMMARY

The investigation has been continued to explore the possibilities for thorium production by fused salt electrolysis. Further work has been done on the electrolysis of NaThCl_5 . For comparison a review of former work with KThF_5 has been done. Several pounds of metal have been produced from the two processes and are now being evaluated.

Metal, as produced by either process, is of approximate equivalent quality with respect to purity, hardness and workability. Current efficiencies of the two processes are also comparable when the starting materials are of equivalent quality.

The chloride process is still to be preferred over the fluoride however, because of its potentiality for continuous operation and also the simpler procedure for preparation of the source electrolyte.

Material of Rockwell E 75-80 hardness has been consistently produced by both the fluoride and chloride methods. Current efficiencies of 40-50% are normal, and recoveries of 80% or better can be expected.

A. Introduction

The final phase of this present contract period has consisted of a review and substantiation of data for both the fluoride and chloride processes for electrolytic production of thorium metal. Source materials for both methods have been prepared by previously established optimum conditions and subjected to electrolysis according to described methods. (Reports 2 and 3) Some new facts have been brought to light regarding the KThF_5 material.

Procedures are now well defined for electrolysis of both salts on the 5-lb. cell scale. Exact chemical and physical methods should now be applied to ascertain the required specifications on the raw materials used in the processes.

One larger scale run was made using the fluoride material, and it appears that scaling up of the operation should not present any new major problems of an electrochemical nature.

B. Preparation of Thorium Salts

The fluoride material was prepared from the nitrate-hydrate of thorium. The $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ (450 g.) is put up in water (2500 ml.) and a solution of $\text{KF} \cdot 2\text{H}_2\text{O}$ (320 g. in 500 ml.) added to it (a 1 to 5 mole ratio). The KThF_5 then precipitates, is filtered and thoroughly washed in water. The precipitate is quite gelatinous and difficult to filter. Elimination of the washing step was tried, but did not give a satisfactory electrolytic source material. The KThF_5 is subject to air oxidation, and must be either vacuum dried or air dried at a low temperature.

The double chloride used was prepared from ThOCO_3 . This was put into solution in HCl giving a clear yellow liquid. NaCl and NH_4Cl were then added to this solution with vigorous stirring. Ratios used were ThOCO_3 - 2 mols, NH_4Cl - 2 mols, NaCl - 2.2 mols and HCl - 22 mols.

This solution was then evaporated to near dryness over approximately 5 hours. It was then placed in graphite crucibles in a semi-fluid form.

The mixture was then heated to 300°F and held so for 2 hours. The temperature was then raised to 600°F and held for 14 hours. It was then allowed to cool yielding a dense gray colored material. This was ground to a fine powder and stored in air-tight containers.

C. Electrolytic Preparation of Thorium Metal Powder

1. Electrolysis of NaThCl₅:

Several additional runs have been made to verify previous conclusions regarding preparation of the NaThCl₅. This material was prepared from ThOCO₃ as before and gave consistently good results.

A series of three runs made on the same bath is shown in Table 1, and is typical of the successful operation of this process. There is no apparent limit to the extent to which a bath may be recharged and electrolyzed since no extraneous bath products are produced. Likewise, no loss in current carrying capacity is experienced. Current efficiencies run from 50-60%. In run 2, part of the deposit was mechanically lost. Both yield and current efficiency data would run even higher if the weights of discarded fines are included.

Metal produced from the chloride is extremely easy to recover being deposited with only NaCl and a small amount of ThCl₄.

It is doubtful that a pre-electrolysis to remove moisture and/or oxides is really a requirement of the process. An air or vacuum drying step may be adequate. This is currently being investigated.

Important criteria toward successful operation of the process are dry oxide-free electrolyte materials, an inert atmosphere, and cell operation at 3 volts or less to minimize formation of free sodium.

2. Electrolysis of KThF₅:

A review of the previously disclosed fluoride process for thorium powder production has been made for comparison with the chloride procedure. Some investigation has been made with grades of starting KThF₅. Continuous operation of a bath has been attempted, and the effect of pre-electrolysis investigated. Effects of temperature have also been confirmed.

Typical work on the fluoride process is shown in Table 2. Difficulty is encountered in re-using a bath more than twice. They generally become contaminated with graphite after two runs. Current carrying capacity is also reduced after two runs on a bath.

Most of the runs were made at 850-870°C. It is seen by runs 97-129 and 97-131 that the efficiency is diminished by operation at lower temperatures. The conditions of operation for this process are not highly critical, however.

It is of interest that the average efficiency of runs made without a pre-electrolysis was higher than those run with a purification electrolysis, 37 to 34%. Hardness results of metal show no improvement as a result of a pre-electrolysis cycle, nor were improvements in particle size noted. The last 7 runs reported in Table 2 were all done without a low voltage electrolysis.

It is of some interest that a cladding of the steel cathode was obtained in a number of runs with the fluoride material. In all cases this was produced in runs where evolution of moisture was noted on charging of the KThF₅ to the cell indicating inadequate drying of the salt, or presence of room temperature stable thorium hydrates or oxy-halide hydrates.

Several types of starting double fluorides have been tried as source materials. These are listed in Table 3 together with results produced. It is evident that thorough washing and drying of the KThF₅ improves the quality of thorium produced.

3. Electrolysis of KThF₅, 10 lb. Scale:

In order to ascertain the ease of scaling up an electrolytic thorium operation, one run was made on a larger scale. A cell of a 35 lb. salt capacity was used. This cell is similar in design to the smaller cell used for this program; a crucible 7" in diameter by 17" deep is used.

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Table 1—Electrolysis of NaThCl₅

Run No. Series No.	T °C	E Volts	I Amps	t Mins	A Hrs.	C.D. A/dm ²	Yield g %		Current Efficiency, %	Remarks
97-97(1)	870	2.0	2	360	12P*	6				Mod. coarse
	855	4-4.2	50	132	110	150	136.5	64	59	
97-113 (2)	875	2.2	2	190	6 P	6				
	855	4	50	150	125	150	81	50	31	Lost bottom of deposit giving low yield
97-115 (3)	875	1.4	10	75	12P	30				
	855	4.2	50-47	150	120	150	110	84	43	Coarse deposit

* P—Purification Electrolysis

Table 2—Electrolysis of KThF₅

Run No. Series No.	T °C	E Volts	I Amps	t Mins	A Hrs.	C.D. A/dm ²	Yield g %		Current Efficiency, %	Remarks
97-117(1)	865	2-2.2	2	160	5 P*	6				Coarse deposit; dendrites. Some plating of steel
	855	4.3-4.0	40-34	195	115	100-120	81.1	42	33	
97-119(1)	870	2	2	90	3 P	6				
	850	6	90	75	112	270	62.8	33	26	Part of deposit lost
97-121(2)	865	2	2	150	5 P	6				Moisture in salt; deposit coarse, cladding of cathode
	835	6.3	90	120	180	270	169.3	88	44	
97-123(1)	840	6.3	93	120	186	280	166.3	87	42	No pre-electrolysis; cladding; coarse cryst. deposit; wet salt
97-125(2)	850	6.5	90	105	157	270	136.6	72	41	No pre-electrolysis; cladding
97-127(1)	835	6-6.2	90	120	180	270	160.5	82	42	No pre-electrolysis; cladding
97-129(1)	800	6.1-7.0	90	137	205	270	171	71	39	No pre-electrolysis; cladding
97-131(2)	760	6.4	90	125	187	270	118	46	30	No pre-electrolysis; transite in bath. Deposit in crucible
97-133(1)	850	5.8-6.0	90	120	180	270	88	35	23	No pre-electrolysis; NO ₂ given off on charging salt; deposit in bath
97-137(1)	850	5.6	90	107	160	270	134	53	40	No pre-electrolysis

* P—Purification Electrolysis

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Table 3—Effect of KThF_5 Source Material

Run No. Series No.	Material Description	Yield %	Current Efficiency, %	R_H
97-117(1)	pptd. from $\text{Th}(\text{NO}_3)_4$, not washed (120-59)	42	33	B 93
97-119(1)	120-59 Vacuum dried-pre- electrolyzed, not washed	33	26	E 95.5 (B 64)
97-121(2)	120-59 Vacuum dried-pre- electrolyzed, washed	88	44	E 79
97-123(1)	120-59 Vacuum dried, washed, no pre-electrolysis	87	42	E 82
97-125(2)	120-59 Vacuum dried, washed, no pre-electrolysis	72	41	E 81
97-127(1)	120-59 Washed, Vacuum dried no pre-electrolysis	82	42	E 84
97-133(2)	Like 97-127 except further vacuum dried at 150°C	35	23	E 78

The heating element is assembled from $\frac{3}{4}$ " graphite rod and machined connector links. A 32 KVA Hobart Welding Transformer is used as an AC heating source. A 1500 Amp Selenium rectifier serves as a DC source.

This run (133-65) was made using KThF_5 in 33 weight percent concentration. A charge of 20 lbs. NaCl and $9\frac{3}{4}$ lbs KThF_5 was melted in the usual manner. No purification electrolysis was used in this run since it has been demonstrated that this of little or no benefit to the final product.

For the electrolysis, a 1" diameter $\times$ $2\frac{1}{2}$ " long steel cathode with nickel support shaft was used. The electrolysis was run at 840°C and 500–600 Amperes. The voltage was 5.2–5.0. A 4 hour run gave a total of 2300 Ampere hours, and sodium was observed toward the end of the run indicating substantial depletion of the bath thorium content. The deposit was cooled above the bath, crushed and recovered per standard procedures.

A deposit 5" in diameter by 8" long was produced. A total of 1080 g. thorium metal powder was recovered from this deposit. Considerable loss was experienced in the recovery of the metal due to the large quantity involved. The source material was not of the desired purity and some oxide was noted in the deposit. A hardness of R_E -91 was obtained on this metal. A run on the same source material in the small cell (97-137) gave an R_E -84 hardness.

Considering a greater chance for atmospheric contamination in the larger cell, this can be termed a successful run. Although the indicated recovery is only 1080/2580 or 42%, the actual recovery was considerably higher.

D. Hardness Evaluation, Electrolytic Thorium

For each run completed, a 20-30 g. sample was taken for arc melting. These samples were melted by the previously described procedure using a water cooled copper hearth and a tungsten electrode. Melting is done under a quarter atmosphere of purified argon.

Hardness values for the runs listed in Table 1 and 2 are shown in Table 4. From this standpoint, it is seen there is little choice between the two source materials. Neglecting runs where a factor was present to yield a high hardness value, the average hardness seems to lie in the region Rockwell E-75-80 (B 30-39).

E. Conclusions and Recommendations for Further Work

Two electrolytic processes have been evolved, both capable of producing high purity thorium metal powder. Both operate under variations of the same conditions and in the same type of inert atmosphere cell.

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Table 4—Hardness Evaluation-Electrolytic Thorium

Run No.	Series No.	Source Material	R _H	Remarks
97-97	1	NaThCl ₅	E-81	
97-113	2	NaThCl ₅	E-76	
97-115	3	NaThCl ₅	E-90	
97-117	1	KThF ₅	B-93	KThF ₅ not washed
97-119	1	KThF ₅	E-95.5	KThF ₅ not washed
97-121	2	KThF ₅	E-79	
97-123	1	KThF ₅	E-82	
97-127	2	KThF ₅	E-81	
97-127	1	KThF ₅	E-84	
97-129	1	KThF ₅	E-78	
97-131	2	KThF ₅	E-91	Transite in bath
97-133	1	KThF ₅	E-78	
97-137	1	KThF ₅	E-84	

The electrolytic reduction of NaThCl₅ offers considerable potential advantage over KThF₅, principally with respect to its possibilities for operation as a continuous process. Because only NaCl and Cl₂ are obtained as by-products, no difficulties are experienced in respect to polarization or conductivity of the bath. The preparation of the source material is also much simpler than the fluoride providing such material can be consistently prepared of acceptable purity.

Purity limits of the source material is the principle unknown factor of the process. Work should be initiated to determine accurately what moisture, oxide and other major impurities can be tolerated to yield acceptable metal. Work of this nature is planned for the next phase of the program.

It is recommended that future work should emphasize the chloride process due to the aforementioned advantages. A future program should stress those details which will enable the achievement of consistently equivalent results.

In light of the larger scale run made with the fluoride, there is no reason to believe that the chloride method cannot be readily scaled up. This would follow as a logical second step in a future program. Some emphasis should be devoted to design of larger size cells specifically adapted to the method of preparation.

From the work of the past contract year, the nuclei of two feasible electrolytic thorium production methods have been evolved. It is believed that with nominal development, either could result in a competitive commercial method with respect to both quality and production cost.

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