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NYO-3726

INVESTIGATION FOR THE PRODUCTION OF THORIUM METAL

Technical Progress Report – Second Quarter, August 1 - October 31, 1952

By
Merle E. Sibert
F. C. Wagner
Morris A. Steinberg

December 3, 1952

Horizons Incorporated

AEC RESEARCH AND DEVELOPMENT REPORT

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INVESTIGATION FOR THE PRODUCTION OF THORIUM METAL

Technical Progress Report—Second Quarter, August 1—October 31, 1952

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December 3, 1952

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Summary

A further report is given on progress of the investigation concerning the preparation of thorium metal by electrolytic procedures. This work has thus far been confined to electrolysis of thorium double halides in alkali halide media.

The electrolysis of $KThF_5$ in NaCl has been successful, but the salt bath has a limited life. The use of $NaThCl_5$ has also been successful but not consistently so. This latter procedure is of considerable interest due to its possibilities for use as a continuous process. Operating data for these and other systems are given in this report.

Work has been initiated on obtaining decomposition potentials of salts which show promise as source materials. Preliminary results are included herein.

Some physical metallurgical evaluation of the metal produced has also been accomplished. This is reported along with pertinent analytical data.

INVESTIGATION FOR THE PRODUCTION OF THORIUM METAL

(Second Quarter - August 1 to October 31, 1952)

A. Introduction

Further investigation on the preparation of thorium metal by the electrolysis of fused salts has been carried out following the lines of attack as given in the report for the First Quarter. This has principally entailed an investigation of the conditions of electrolysis using two compounds as sources of thorium.

The process as developed to date is essentially an inert atmosphere electrolysis utilizing a fused sodium chloride bath. The two most promising sources of the metal to date appear to be potassium thorium pentafluoride and sodium thorium pentachloride. The latter offers particular promise for reasons to be discussed later. Other sources have been preliminarily studied, including ammonium thorium pentafluoride and thorium oxychloride but these have been inferior to the sodium and potassium salts.

Operational variables such as temperature, current density, concentration of thorium salts and purity of these salts have been investigated.

In addition, work has been started on certain physico-chemical measurements dealing with these fused salt baths. This will consist principally of decomposition potential and electrical conductivity measurements on the more promising electrolytic baths. Some of the decomposition potential data is complete and reported herein.

The process as its present stage of development is capable of producing a ductile grade of thorium metal from either the sodium or potassium double halide salt. Some work has been done on the physical metallurgical evaluation of the metal produced, and this data is included in the present report.

B. Equipment

1. Electrolytic Cell

The electrolytic cell employed in this work has been completely described in the report for the First Quarter. There have been no significant changes in this design. Thus far the cathode cooling chambers have not been used in this work, and all work has been on a single run basis wherein the bath and deposit is allowed to cool in the cell atmosphere over night.

2. Decomposition Potential Apparatus

The decomposition potential work is being done utilizing a small electrolytic cell with the same principles of operation as the larger one previously described. It is heated by a graphite resistance element and employs an argon atmosphere. The crucible holds a 50 g. salt charge and serves as the anode, comparable to the larger cell. A 12 volt, 15 ampere selenium rectifier serves as a DC power source for this unit.

Conductivity measurements will be made using a standard Wheatstone bridge apparatus. A 1000 cycle AC oscillator will be used as a power source. The cell itself will be an induction heated unit consisting of a graphite crucible in a gas tight alumina tube. This will fit inside a silica tube suitably insulated from the alumina. Adjustable platinum wire electrodes will be used. The measurements will be done in an argon atmosphere.

C. Electrolytic Work

As previously mentioned, there have been two principal salt baths investigated, one an $NaCl-KThF_5$ mixture, and the other $NaCl-NaThCl_5$. Both have produced ductile thorium metal, and in both cases, the baths are reusable at least within limits, as many as six runs having been made on a given bath.

Of the two materials used as a metal source, the sodium salt may not be a true compound, but is properly represented by the assigned formula in respect to composition. Both source materials have been prepared in our laboratories and are essentially completely stable at room temperature. Both have some tendency to retain moisture however, and all thorium salt charges have been vacuum dried at 100-120°C. before use. In most cases this vacuum drying has been done in lieu of a pre-electrolysis at low voltage to remove excessive moisture. The sodium chloride used has been a high purity analytical reagent grade.

The run procedure has been well standardized and is essentially unchanged from that previously reported. The cell is heated to 900°-950°C., the salts charged and melted under purified argon. After the desired temperature of equilibrium is obtained, a steel cathode with graphite protective sleeve for the lead, is inserted into the molten bath. The electrolysis is carried out under the desired conditions, the cathode raised out of the bath, and allowed to cool in the argon cell atmosphere.

When the deposit is at room temperature, it is broken off the cathode, crushed to +35 mesh or less and washed in cold water. The pH is kept at 5-6 to prevent undue hydrolysis. After the material is salt-free, it is washed with successive baths of cold water, decanted each time until a clear supernatent liquid is obtained. It is essential that the washing procedure be carried out in a minimum time, preferably two hours or under. The metal powder is then filtered and dried with acetone or ether. It is then stored in sealed containers under argon until melted into an ingot.

A list of thorium compounds included in this electrolytic series is given in Table I together with their metal content and bath concentration ranges used.

A summary of runs made is given in Table II, III and IV. Table II includes all runs made from $KThF_5$, Table III those made from $NaThCl_5$ and Table IV, other miscellaneous runs.

In the foregoing tabulated runs, all thorium salts were thoroughly vacuum dried before use. Concentrations were varied from about 13 to 27 per cent with the exception of $ThOCl_2$ where a limited amount of material was available.

Current densities were varied from 170-675 Amps/dm^2. The average operating voltage of the bath at 150-200 Amps was about 4.5 V. Average temperature of operation has been about 850°C. All cathodes were made of 1/2" mild steel rod welded to nickel shafts.

D. Discussion of Electrolytic Results

Of the five salts investigated, three have given acceptable thorium metal deposits. The two materials listed in Table IV were not satisfactory. The NH_4ThCl_5 fumed violently and considerable available thorium is lost because of this. The current efficiency is

TABLE I

Thorium Salts Investigated

Salt	Th Content %	Salt Content in Bath %	M. P. °C
NH_4ThCl_5	54.3	12.5	Decomposes
$NaThCl_5$	53.7	12.9-25	---
$KThCl_5$	51.9	13.0-16.5	---
$KThF_5$	63.4	13.7-27	906
$ThOCl_2$	72.9	9.0	---

TABLE II

Electrolysis of $KThF_5$

Run No.	Cell Charge	I Amps.	E Volts	t hrs.	T °C	Amp. hrs.	C.D. Initial	g.	Yield %	Apparent C.E. %	Remarks
97-7	2025 g. NaCl	150	4.3	1.25	808-21	187	205	118.5	58	27	Polarization at 187 A. hrs.
	320 g. $KThF_5$	100	4.5	.25	810	13 200	135				
97-9	97-7 bath + 900 g. NaCl 270 g. $KThF_5$	150	4.2	1.75	807-17	263	205	100	58	18	
97-11	97-9 bath + 450 g. NaCl 280 g. $KThF_5$	150	4.2	1.75	860	260	255	115	63	20	
97-13	97-11 bath + 450 g. NaCl+ 300 g. $KThF_5$	150	4.5	1.75	855-68	260	310	130	68	23	Na observed end of run
97-15	97-13 bath + 600 g. $KThF_5$	150	4.6	3	852-59	450	310	150	40	15	Na observed, heavy fuming after 300 A hrs.
97-17	97-15 bath + 300 g. $KThF_5$	150	4.7	2.3	853-60	340	310	70	37	9	Loss of metal in washing.
97-25	2025g. NaCl 320 g. $KThF_5$	300	5.8-6.2	1	852-68	300	675	163	80	25	Fuming after 225 A. hrs. Some Ni in bath
97-27	2025 g. NaCl 320 g. $KThF_5$	75	3.5-3.7	3.25	847-71	263	170	166	81	29	
97-29	2025 g. NaCl 320 g. $KThF_5$	150	3.2-4.5	2	937-54	300	335	---	---	---	At 150 A. hrs. heavy fuming and V drop to 3.2

TABLE III
Electrolysis of Double Chloride Salts

Run No.	Cell Charge	I Amps	E Volts	t hrs.	T °C.	Amp. Hrs.	C.D.	Yield g.	Yield %	Apparent C.E.%	Remarks
97-33	2025 g. NaCl 400 g. $NaThCl_5$ Lot No. 1	150	4.7	2	854-62	300	370	133	62	20	Some Na at end of run
97-35	2025 g. NaCl 300 g. $NaThCl_5$ Lot No. 1	75	3.6-3.9	3.25	855-67	263	185	---	---	---	Mod. fuming after 150 A. hrs. and on melting.
97-37	97-35 bath + 900 g. NaCl 300 g. $NaThCl_5$ Lot No. 2	150	4.5-4.8	2.5	848-95	375	370	47	29	6	Heavy fuming after 225 A. hrs. and on melting. Deposit stuck in bath, loss of part of deposit.
97-41	1800 g. NaCl 600 g. $NaThCl_5$ Lot No. 2	200	4.8-5.0	2.25	846-63	450	490	80.6	25	8	Heavy Na deposit, h. fuming on melting.
97-43	97-41 bath + 600 g. $NaThCl_5$ Lot No. 2	200	4.6-5.0	1.75	856-64	350	490	94.5	29	13	Deposit fell in salt bath, h. fuming during melting.
97-45	1900 g. NaCl 600 g. $NaThCl_5$ Lot No. 2	150	4.6-4.7	1	846-58	150	370	43.9	14	14	Na metal and polarization at 150 A. hrs. h. fuming
97-19	2025 g. NaCl 400 g. $KThCl_5$	150	4.7	2	855-61	300	335	66.7	32	10	Na metal, end of run, heavy fuming on melting. Loss metal in recovery.
97-31	2025 g. NaCl 400 g. $KThCl_5$	150	4.3-4.6	2	851-68	300	370	130.7	63	20	Heavy fuming after 225 A. hrs. and on melting.
97-39	2025 g. NaCl 300 g. $KThCl_5$	150	4.7	2	858-64	300	370	---	---	---	Heavy fuming before current applied, after 185 A. hrs. and on melting.

TABLE IV.

Electrolysis of Other Salts

Run No.	Cell Charge	I Amps.	E Volts	t hrs.	T °C	Amp hrs.	C.D.	Yield g.	Yield %	Apparent C.E. %	Remarks
92-21	2025 g. NaCl 290 g. NH_4ThCl_5	150	4.7	1.75	864-67	260	335	34.7	22	6	Na in deposit, heavy fuming throughout melting and electrolysis.
97-23	2025 g. NaCl 200 g. $ThOCl_2$	150	4.9	1.25	852-67	190	335	19	13	5	Na metal, attack on graphite. Doubt on purity of Th salt.

very low, $\cong 5\%$.

The $ThOCl_2$ was equally unsatisfactory, but this is not conclusive since there was some doubt as to the purity and homogeniety of this starting material. The indications of sodium metal production suggest that the Th concentration was either exhausted or that the decomposition voltage of the $ThOCl_2$ is higher than that of NaCl.

The $KThF_5$ has given consistently successful deposits with metal yields up to 80% of theoretical. Current efficiencies are not high however, not having exceeded 30% . It is indicated (Run 97-15) that higher concentrations (ca. 15%) give even lower current efficiencies. Such figures are not completely accurate due to loss of fines in the recovery process. This is also reflected in the figures for total recoverable metal yields.

Temperature variations over about 150°C from 800-950°C. (Runs 97-7, 29) gave no appreciable change in either operating characteristics or type of deposit. Likewise, variance in current density from 170-675 Amps/dm^2 (Runs 97-25, 27) showed no appreciable changes. In fact the maximum yields of metal were obtained at these two extremes of current densities.

Work with the double chlorides has been as satisfactory as that with the fluorides insofar as quality of the metal produced is concerned. However, yields and current efficiencies have generally been lower than corresponding runs with the fluoride. It is noted that fuming was observed in all of these runs, and losses of available thorium may be involved therein. These salts have not been established as true compounds of thorium, either, being simple melts of $ThCl_4$ + KCl or NaCl.

It is also true that considerable more work has been done using the fluoride and optimum conditions have not been fully ascertained in the chloride process. The presence of excessive moisture in these baths may be indicated, as well as evidenced, by the heavy fuming and also by the fact that several of the deposits did not stay on the cathode rods on removal from the bath. This may be due to hydrogen being evolved simultaneously with metal during the initial stages of the deposition causing a loose spongy contact with the cathode.

Here again, as with the fluoride, a higher concentration of thorium salt seems undesirable (Runs 97-41, 43, 45), giving the lowest current efficiency values. We are discounting runs where part of the deposit was lost by other means.

Present emphasis is on the chloride process due to several inherent advantages to this bath. There is little difference in behavior of the sodium and potassium salts. With such a bath, the opportunity for a continuous process immediately is apparent. With a completely chloride system, only NaCl and reducible chlorides of thorium are involved, and the bath can theoretically be reused indefinitely. Thus far, only two runs have been made on a given bath.

There is also an additional advantage to a NaCl-$KThCl_5$ or $NaThCl_5$ bath in that there is no accumulation of NaF or KF, both of which are relatively insoluble and present some washing difficulty in recovery of the metal powder from the cathode deposits. Deposits from the all-chloride baths wash up extremely readily as opposed to those from the fluoride.

This chloride electrolytic bath shows considerable promise as an industrially feasible process providing satisfactory efficiency can be obtained. There is little reason to believe that this should not be possible under proper operating conditions.

E. Analysis of Electrolytic Thorium

Representative samples of electrolytic thorium have been analyzed for common impurities. This has included material from all types of baths and conditions. Generally, analyses were run for oxygen, nitrogen, and carbon. Methods employed have been described in the previous report.

Analytical data are shown in Table V.

F. Determination of Decomposition Potential - $KThF_5$

The decomposition potential for $KThF_5$ has thus far been determined as a 25% concentration in NaCl at 850°C and 1000°C. A value in the vicinity of 2.7 V is indicated at 850°C and 2.4 V at 1000°C. A value of ca. 1 volt is also indicated by the type of curve obtained. This may be the breakdown of the $KThF_5$ to the trivalent thorium state, and the higher value, the reduction to metal. Alternatively the lower value may be the point where $KThF_5$ is reduced to metal and the higher figure the decomposition of NaCl. This point will be clarified in future runs.

These measurements were determined using the small 50 g. electrolytic cell described ~~under~~ Equipment (B). The desired temperature is obtained and the salt mixture melted. The purest available salts are used. These are then pre-electrolyzed at 1.0-2.0 volts using a graphite cathode; this step removes any occluded moisture and small amounts of iron and silicon. A pure graphite cathode of measured area is then inserted into the bath and DC power supplied. Voltages are accurately set using a rectifier regulated by a variable transformer, and corresponding

TABLE V.

Analysis of Electrolytic Thorium

Run No.	Oxygen %	Nitrogen %	Carbon %	Remarks
97-9	.037	.0022	.210	Typical $KThF_5$ Run
97-23	C Interference	.0065	>6	$ThOCl_2$ run graphite sleeve shattered
97-41	1.65	.0027	.673	$NaThCl_5$ runs Lot No. 2 Material unsatisfactory
97-43	1.83	.0043	.316	
97-45	1.26	.0035	.227	
97-19	---	---	.902	$KThCl_5$ run

current readings taken. A Simpson millivoltmeter is used, and a Weston milliammeter. Connections are made directly to the electrodes.

The current readings are then converted to current density, and these values plotted against voltage. The straight line portion of the curve is extrapolated to zero current, thus giving the indicated decomposition voltage.

These data are given in Table VI and a plot of the values are shown in Figure 1. Similar work is now being taken using varying temperatures and also using the $NaThCl_5$ and $KThCl_5$ baths.

G. Physical Properties of Electrolytic Thorium

To evaluate the quality of the electrolytic thorium produced from $KThF_5$ during the last quarter, samples of a number of runs were arc-melted under 1/5 atm. of purified argon. The resulting 20-30 gr. buttons were tested for hardness and cold-rolled to sheet if possible. In addition to arc-melted buttons, a larger amount of thorium powder was induction melted in vacuo to produce a small ingot. Attempts to cold-roll a section from this ingot were not successful, as extensive cracking occurred on the first pass through the rolls. Another section of the ingot was therefore "canned" in a steel sheet and hot-rolled at 800°C to 50% of the original thickness. The steel covering was then removed and the thorium was reduced cold to .040" in thickness.

Hardness

The hardnesses of the arc-melted buttons varied from 15 to 90 R_b for the lots of thorium tested. This means that the impurity content of the metal varied considerably from batch to batch. The impurities responsible for the high hardness may be either carbon or oxygen, and

TABLE VI.

Decomposition Potential Data

75% NaCl ; 25% $KThF_5$

T = 850°C			T = 1010°C		
Voltage	Current	C.D. Amps/dm²	Voltage	Current	C.D. Amps/dm²
0.35	.020	.197	0.37	.090	.886
0.53	.040	.394	0.73	.135	1.33
0.83	.045	.443	1.07	.195	1.92
1.05	.060	.590	1.27	.240	2.36
1.40	.080	.788	1.50	.340	3.35
1.72	.115	1.13	1.70	.490	4.82
1.88	.170	1.67	2.13	.630	6.20
2.05	.240	2.36	2.46	.820	8.08
2.15	.300	2.95	2.57	.950	9.35
2.34	.435	4.28	2.77	1.30	12.8
2.50	.510	5.02	3.00	3.10	30.5
2.83	.550	5.42	3.25	4.10	40.4
3.10	.620	6.10	3.50	5.10	50.2
3.25	.830	8.18			
3.35	1.000	9.85			

$E_D(1) = 1.7$ V, $E_D(2) = 2.7$ V $E_D(1) = 1.0$ V, $E_D(2) = 2.4$ V

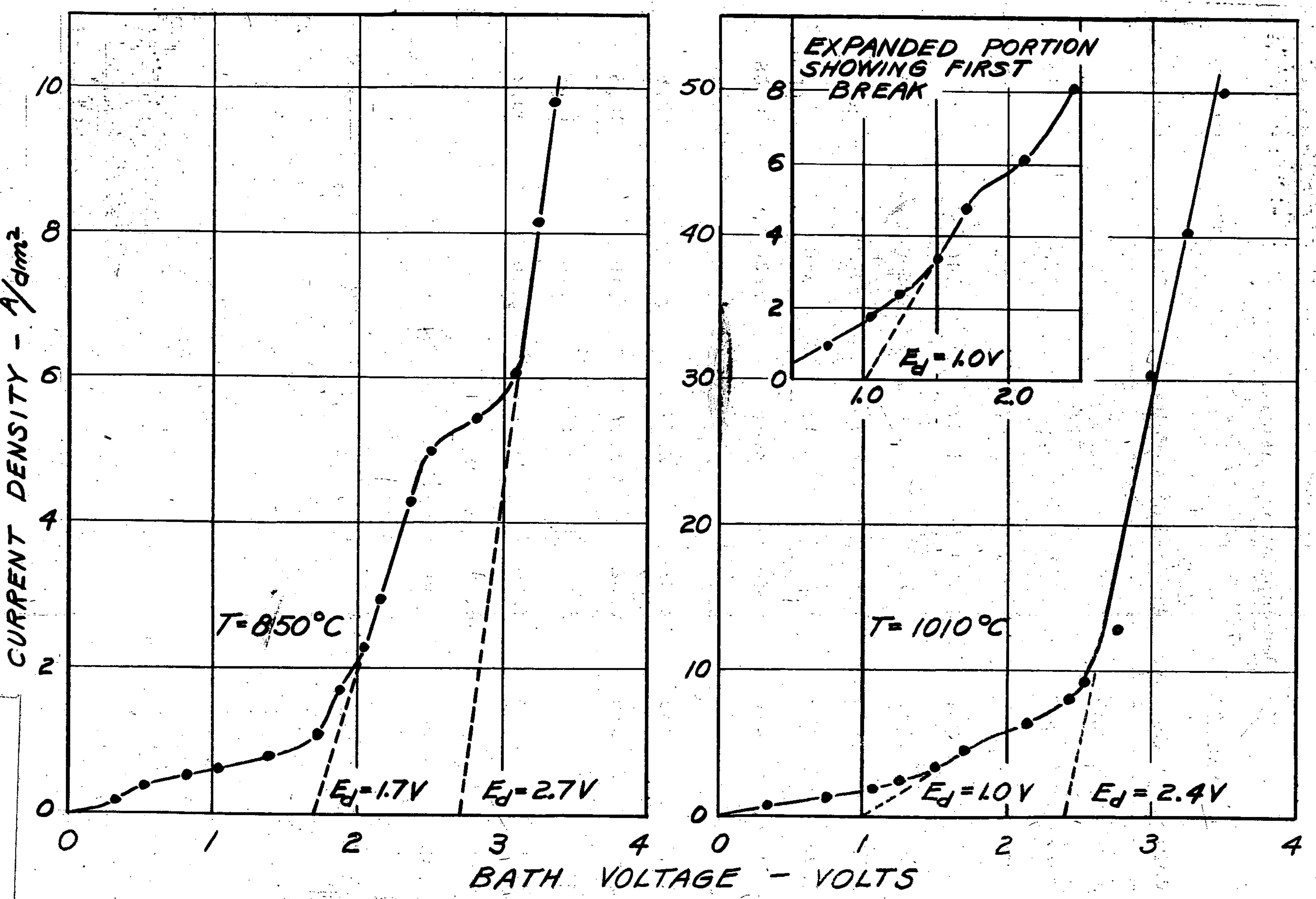


Fig. 1 Decomposition Potential Curves - 25% $KThF_5$ - 75% NaCl

chemical analyses of the electrolytic thorium are being made to determine the cause of this condition.

Tensile Properties

Two tensile specimens were prepared from thorium sheet of .040" thickness and tested to fracture. The sheet was rolled from a small ingot of thorium which was induction melted in a berylia crucible under vacuum. The ingot was sealed in a steel jacket and hot-rolled to a thickness of 1/8" which represented a reduction of about 50%. This sheet was then cold-rolled to .040" thickness for the tensile tests. The specimens were vacuum annealed at 600°C for one hour prior to testing. The average values of ultimate tensile strength, yield point (0.2%), and %elongation in a one inch gage length are as follows:

UTS	Y.P. (.2%)	%Elong. (1")
52,235 psi	41,675 psi	11.2%

A stress strain curve for this material is shown in Figure 2.

Pole Figure Determination

The cold-rolled and cold-rolled + recrystallized textures of thorium sheet were determined from X-ray diffraction photograms using MoK α radiation with Zr filter. Four reflection patterns were used for each pole figure determination, corresponding to rotation of the specimen about axes 0°, 30°, 60°, and 90° from the rolling direction. Laue transmission photograms were also taken normal to the rolling plane. These photograms are shown in Fig. 3. The stereographic plots of the 110 and 100 poles are shown in Figs. 4 and 5, for cold-rolled and cold-rolled + recrystallized thorium respectively.

The principal textures developed in cold-rolling were (100)[001]

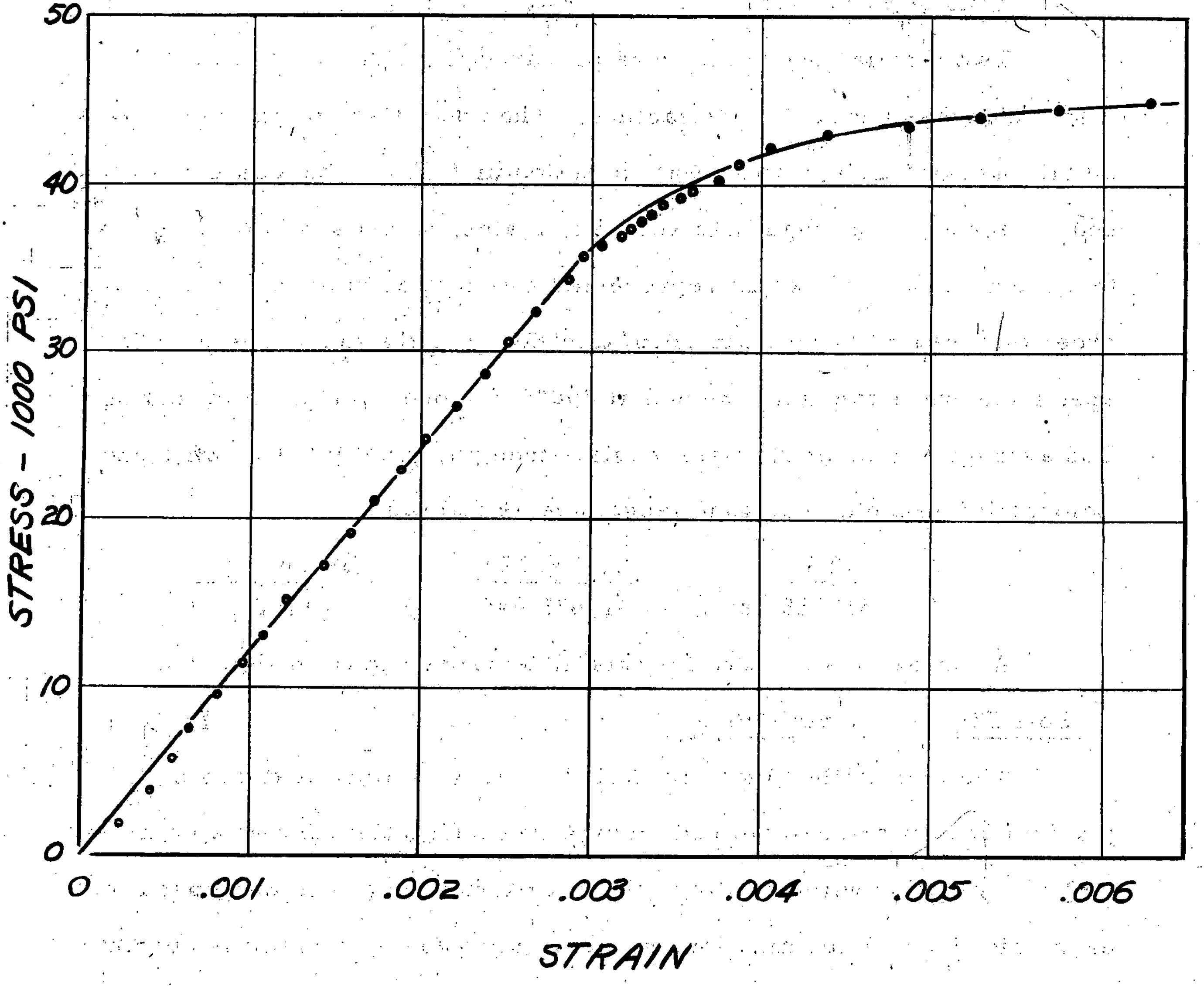
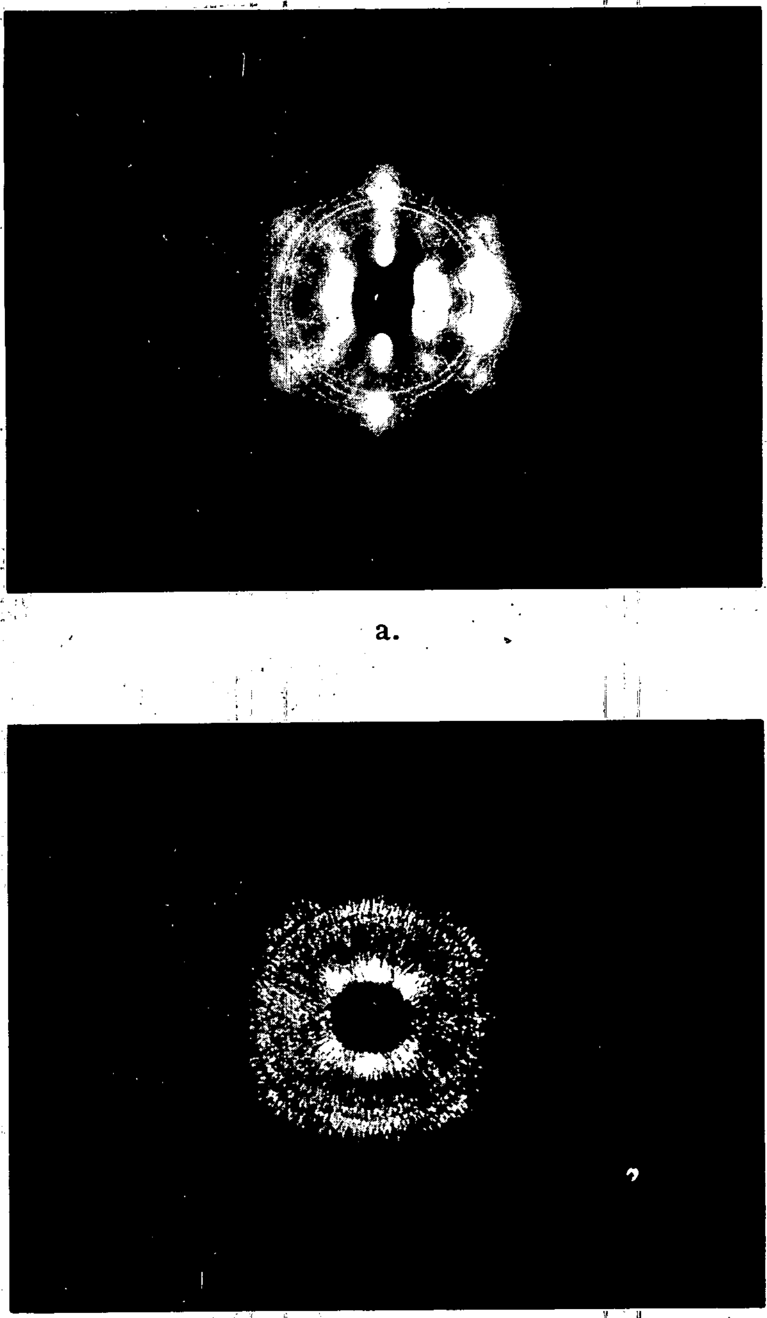


Fig. 2 Stress Strain Plot for Annealed Thorium



a.

b.

Fig. 3 Laue Transmission Photograms of Thorium Sheet: (a) Cold Rolled, (b) Recrystallized

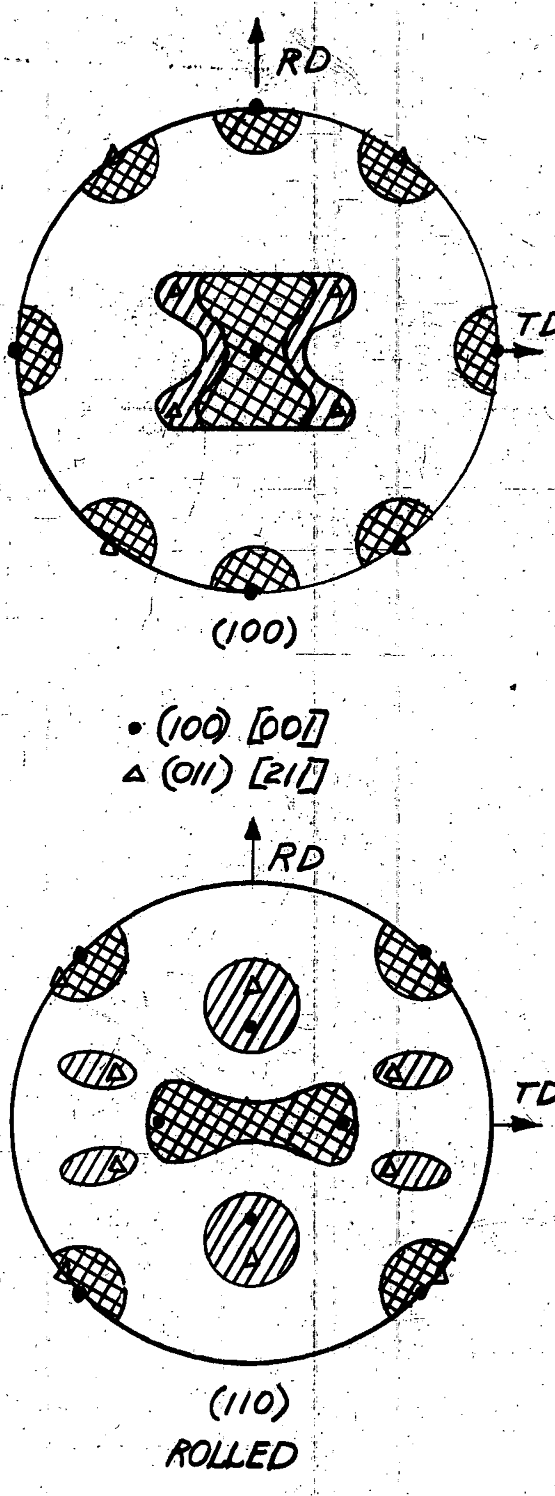


Fig. 4 Pole Figures Showing Preferred Orientation in Thorium Due to Cold Rolling.

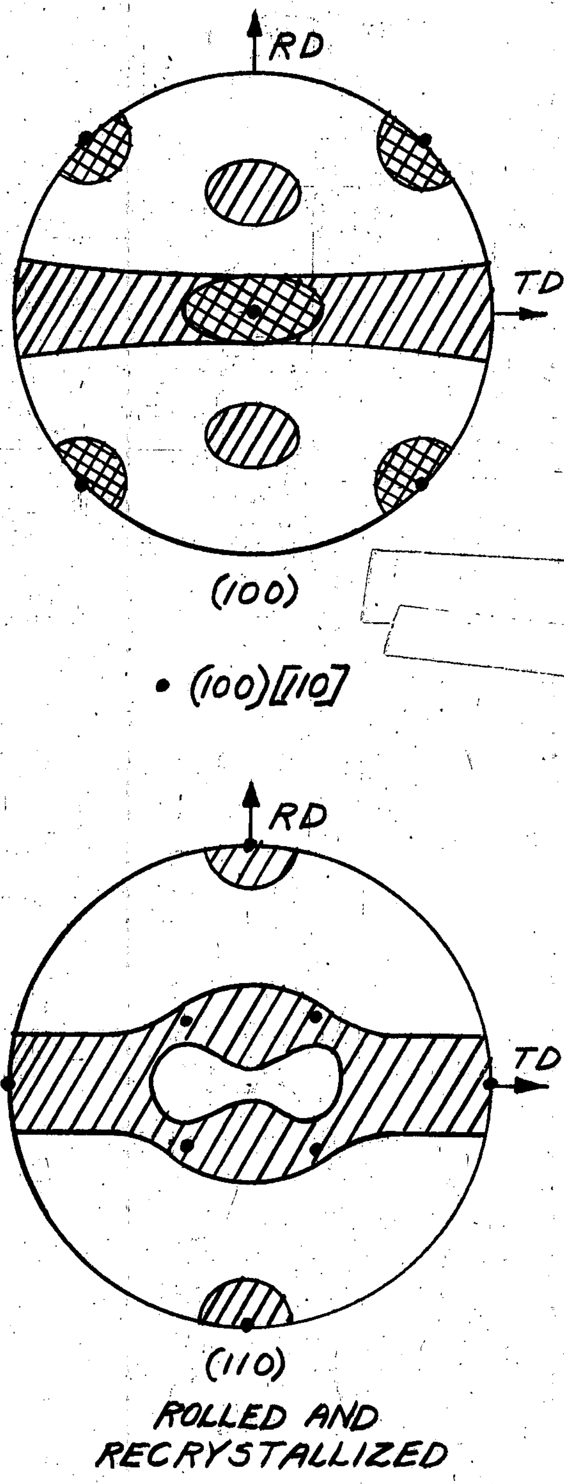


Fig. 5 Pole Figures Showing Preferred Orientation in Thorium Due to Cold Rolling and Recrystallization

and (011)[211]. Such duplex rolling textures are not uncommon in face-centered cubic metals, having been found in most pure metals and alloys having the F.C.C. crystallographic structure.

The recrystallization textures were somewhat more difficult to define in terms of ideal textures. A considerable tendency toward randomness existed in the recrystallized sample. There were evidences, however, of a (100)[110] preferred orientation, and, in addition an indication of 111 planes in the rolling plane. However, this latter condition did not seem to be associated with a definite crystallographic orientation in the rolling direction.

H. Tentative Research Program

It is anticipated that the current program of electrolytic research will be continued along the same lines as followed to date. The process utilizing $NaThCl_5$ will be thoroughly investigated with particular emphasis on its manifestation as a continuously operative process. The source material itself must be standardized on and specifications set up in light of the variance of results from three lots so far investigated. A survey of operating conditions will also be made.

Some further work will be done to either credit or discredit other salts as possible thorium source materials, e.g., $KThCl_5$, NH_4ThF_5, NH_4ThCl_5, $ThOCl_2$, etc. It may be advisable to survey the possibilities of alkaline earth-thorium double halides as well.

A number of measurements on the physical nature of these baths are planned. Decomposition potentials will be measured for $KThF_5$, $NaThCl_5$ and $KThCl_5$, plus any other promising source materials, at two or three temperatures within the normal range of operation. Likewise, electrical conductivities of these and other acceptable baths will be measured by techniques mentioned under (F).

A continued program of metal evaluation is planned utilizing chemical and metallurgical techniques. This will include analysis for carbon, nitrogen and oxygen, and any other significant impurities encountered. A continuing check will be made on physical properties of the metal by arc-melting, hardness evaluation, tensile properties and its workability.

As a given process approaches resolution, the yield per run will be increased and the cell operated semi-continuously for a period of 6-8 runs in order to completely validate the process as a means of obtaining pure thorium metal. When it is felt that a satisfactory grade of metal can be consistently obtained, samples of the material will be submitted to both the Oak Ridge and Ames Laboratories for testing and evaluation. The process utilizing $KThF_5$ is essentially at this point now, but this does have the disadvantage of limited bath life and a more difficult raw material preparation. For this reason a higher priority will be given the work with the $NaThCl_5$ salt.

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