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AEC RESEARCH AND DEVELOPMENT REPORT

THE TECHNOLOGY OF THORIUM

Prepared by:

L.L. Marsh, Jr.

J.R. Keeler

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July 18, 1951

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Report No. BMI-76

METALLURGY AND CERAMICS

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Prepared by:

L. L. Marsh, Jr., and J. R. Keeler

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INTRODUCTION

Thorium is of considerable interest as a potential source of the fissionable isotope, U²³³, and for other applications. Its preparation and properties have been studied extensively since early in the history of the project. Recent proposals for the use of thorium in various reactors have increased the need for a critical survey of the information available on the physical, metallurgical, and engineering characteristics of the metal. Such a survey would serve not only to bring into clearer focus the present state of knowledge of the metal, but also to indicate the areas in which additional work is needed.

Most of the information in this report was obtained from the project literature and from unpublished data available to the authors. The data are believed to represent the best existing information to date. However, as additional high-purity iodide metal becomes available and experimental techniques are improved, the values shown for the various properties will undoubtedly be modified.

A more comprehensive and detailed survey of thorium is being prepared.

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PRODUCTION OF METAL

Raw Materials

Thorium is distributed widely over the earth's surface, but only small amounts are found in any one place. Deposits which contain significant amounts have been found in India, Brazil, Ceylon, Tasmania, Nigeria, the Ural Mountains, and the Scandanavian Peninsula.

In the United States, until recently, no large deposits were known. The largest were the beach sands of Oregon, and small alluvial deposits in the Piedmont Area in North and South Carolina, and in the complex mineral deposits in Florida. The gold-dredging operations in Idaho and California are substantial-potential sources because of the scale of dredging operations. Recently, a large discovery was reported in California.

In recent years, the principal source of monazite sand, which is the only significant ore, has been the deposits in India and Brazil. The sands consist essentially of the orthophosphates of the rare-earth metals together with smaller amounts of thorium and uranium. The sands are usually concentrated by ore-dressing methods until they contain from 5 to 7 per cent of thoria. A typical analysis of Brazilian concentrate is as follows:

ThO ₂	6.5%
U ₃ O ₈	0.17%
Rare-earth oxides (RE) ₂ O ₃	59.2%
P ₂ O ₅	26.0%
TiO ₂	1.75%
Fe ₂ O ₃	0.51%
SiO ₂	2.16%

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Several methods for the extraction of thorium compounds from monazite sand are available, although commercial operations are guarded with trade secrecy.⁽¹⁾ The usual commercial method probably is to digest the sand with excess concentrated sulphuric acid. A thick paste results which is gradually stirred into additional water and allowed to settle. The solution contains the bulk of the thorium and rare-earth oxides perhaps as phosphate complexes. The insoluble residue is largely siliceous material. This is followed by partial neutralization to effect fractional precipitation of thorium phosphate and resolution. In some cases, a carbonate separation, which is based on the fact that thorium carbonate is much more soluble in excess sodium carbonate than are the carbonates of the rare earths, is employed, or an oxalate separation based on the solubility of thorium oxalate in an ammonium oxalate solution.

Another method has been developed which depends on the digestion of the monazite sand with caustic soda and a solvent extraction of the thorium.⁽²⁾ This method has been operated on a pilot-plant scale but has not yet been applied to commercial production.

Iowa State College is currently working on the solvent extraction of thorium after digesting monazite sand with sulphuric acid.⁽³⁾⁽⁴⁾

Currently, commercial "mantle-grade" thorium nitrate is used as the starting material for the production of metal. At Ames, counter-current column extraction of the thorium with 20 per cent tributyl phosphate - 80 per cent dibutyl ether is used to purify this salt. The rare-earth elements, which, with uranium, are the principal contaminants in the commercial salt, are reduced to less than 1 ppm. Uranium is separated by precipitating the re-extracted thorium as the oxalate. The

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oxalate is converted to the oxide by heating to 650 C and is then hydrofluorinated with anhydrous HF at 550 C. The resulting thorium tetrafluoride is the basic material for the preparation of metal. (5)(6)

The mantle-grade nitrate can be used without purification. The resulting metal contains approximately 15 ppm of cerium, 5 ppm of lanthanum, 2 ppm of neodymium, and less than 1 ppm total of samarium, praseodymium, yttrium, gadolinium, and dysprosium.

Early Methods of Producing Metal

The production of metallic thorium in the pure state is particularly difficult because of the high melting point of the metal and its reactivity with hydrogen, oxygen, nitrogen, carbon, and other metals.

Prior to the MED project, thorium metal had been prepared in small quantities of varying degrees of purity by the reduction of its halides and oxide with alkali and alkaline-earth metals, by thermal decomposition of thorium compounds, and by the electrolysis of thorium compounds in fused salts. The production of thorium up to 1927 is fully summarized in Gmelin's "Handbuch der Anorganischen Chemie". (7)

At the beginning of the project, the Westinghouse Electric Company was making thorium on a small scale by the reduction of thorium with calcium. This method, as developed by Marden (8) and others at Westinghouse, (9) produced powdered metal which was pressed and sintered into solid bars. The metal thus produced was quite ductile and easily worked. The principal impurity was oxygen, which was present in amounts of 0.152 to 0.171 per cent. (10)(11)

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Bomb Reduction

The preparation of thorium by the method used for the production of uranium, that is, the reduction of the fluoride by calcium, was investigated by the Iowa State College group at Ames and brought by that group to its present state of development. All of the metal currently produced for the AEC is made by this method. [With the completion of new facilities at Ames, production of the metal is expected to reach 2-1/2 tons per month by July, 1951.]

The method now in use is essentially the reduction of the tetrafluoride with calcium metal using zinc chloride as a "booster" to obtain additional heat and to produce a low-melting thorium-zinc alloy. The reaction is carried out in a steel bomb lined with electrically fused dolomitic oxide. The size of the bomb has been gradually increased until a yield of approximately 56 pounds of 7-8 per cent zinc alloy is now obtained per charge.

After removing the charge from the bomb and mechanically cleaning, the zinc is removed by heating the biscuit in a graphite crucible in vacuum at 1200 C. The dezincd metal is then induction melted in a BeO crucible and bottom poured into graphite molds. Careful control of temperature is necessary during the casting operation in order to avoid excessive attack of the beryllia crucibles. A pouring temperature of approximately 1800 C, measured with a tungsten-columbium thermocouple, is usually used. (12)

The principal impurities in the final castings are aluminum and nitrogen, introduced primarily with the calcium metal; carbon, picked up

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from the crucible during dezincing and from the carbon heater during the final melt-down; silicon, from various sources; beryllium, picked up from the beryllia crucible; and oxygen, probably introduced by any water vapor present during the reduction and as a result of the reaction with the refractories.

Ames reported in 1947 ⁽⁶⁾ that the final casting contained from 1 to 6 per cent of combined thorium and that the average was 2 per cent. The usual contents of Be, N, and C were 0.06, 0.035, and 0.12 per cent, respectively. Table 1 shows the limits of the various elements reported in the metal. The results of analyses at other laboratories have generally fallen within these limits.

There have been some changes in technique and considerable improvement in handling facilities and equipment, but the basic process has not changed since 1948. Analyses obtained on 6 recent Ames billets are shown in Table 2. Tentative specifications for thorium for use in the Materials-Testing Reactor are shown in Table 3.

Iodide Method

Small quantities of metal have been produced recently by the DeBeer iodide process which, on the basis of hardness and microstructure appear to be of exceptional purity. ⁽¹²⁾ Thorium tetraiodide, produced by the reaction of iodine on machined chips of Ames metal, is thermally decomposed on a heated filament. The entire process is carried out inside a sealed Vycor tube and has been limited thus far to approximately 300 gram batches.

The product is a loosely knit crystalline deposit, which when arc melted in a helium atmosphere, has a hardness of 35 Vickers. This

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TABLE 1. LIMITS OF VARIOUS ELEMENTS FOUND IN THE FINAL CASTING (6)

Element	Lower Limit, ppm	Upper Limit, ppm	Usual, ppm
C	500	2000	1200
N	200	800	350
Al	100	700	300
Si	100	700	300
Zn	< 5	100	5
Fe	40	125	-
Ca	-	< 25	-
Mg	-	< 30	-
Ba	-	< 25	-
Na	5	15	-
Mn	1	7	3
Pb	-	< 5	-
K	5	10	-
Li	-	< 2	-
B	0.3	1.5	< 0.5
Cd	-	< 0.02	< 0.2
U	-	0.2	< 0.2
Be	600	2000	-
Free Th	94 per cent	99 per cent	97.8 per cent
Combined Th	1 per cent	6 per cent	2 per cent

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TABIE 2. ANALYSIS OF RECENT (1950-51) AMES BILLETS (PPM)*

Billet Number	O ₂ **	H ₂ **	N	C	Al	Si	Be	Mn	Fe	Cu	Ni	Cd	B	Mo	Pb	Mg	Cr	W
A-215	1700	89	60	1800	100 to 1000	43	217	2	200	10	108	<0.2	0.3	12	10	10 to 20	107	<100
A-217	1300	<20	80	1400	Ditto	38	225	3	200	10 to 20	121	<0.2	0.6	10	3	8	72	<100
A-233	1700	15	80	1100	"	80	225	3	250 to 350	4	78	<0.2	0.3	<5	<1	10 to 20	120	<100
A-240	1400	5	70	1200	"	30	270	3	217	10	104	<0.2	0.2	7.5	2	4	130	<100
A-245	1100	<5	290	1100	"	46	200	3	135	15 to 25	86	<0.2	0.4	<2	<2	6	111	<50
A-246	1400	<5	50	2100	"	24	280	5	132	5 to 15	45	<0.2	0.7	2	<2	8	90	<50

* Unpublished Battelle data, obtained on forged billets.

** Vacuum-fusion analysis.

TABLE 3. TENTATIVE SPECIFICATIONS ON THORIUM FOR
THE MATERIALS TESTING REACTOR (4)

Element	Maximum Parts Per Million
C	1000
O	500
N	100
Al	100
Fe	300
Be	1000
U ²³⁸	5
Ce	15
La	5
Nd	2
Dy	0.05
Pr	0.4
Sm	0.1
Y	0.05
Gd	0.2
Ca	Trace
Ni	Ditto
Si	"
Mg	"
Zn	"

hardness is roughly half that of as-cast Ames metal, and the micro-structure of the melted button is practically free of inclusions. Chemical analyses of the deposit have not been completed.

This method of producing the metal is not readily adaptable to large-scale operation and should only be regarded as a research method for the preparation of high-purity metal.

PHYSICAL PROPERTIES

The pertinent physical properties of metallic thorium are summarized in Table 4. These properties have been determined on thorium of varying impurity content over the past years. Many of the reported values have not been redetermined in the light of the purity of the present Ames thorium. Properties such as the electrical resistivity are adversely effected by impurity contents and such impurity-sensitive values will undoubtedly be revised in the future.

FABRICATION

Melting and Casting

Because of its high melting point and reactivity, thorium is a difficult metal to melt. It is desirable to melt in a vacuum or in inert atmosphere to avoid contamination with oxygen and nitrogen. Beryllia and zirconia are the only refractories which have been found to be satisfactory for crucible materials. The metal is usually heated by induction, but small melts have been made in arc furnaces.

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TABLE 4. PHYSICAL PROPERTIES

Atomic Weight	232.06
Atomic Number	90
Atomic Volume	0.415 cm ³ /g at
Period	7
Group	IV A
Crystal Structure	FCC
Lattice Constants	$a_0 = 5.077 \text{ \AA}$
Atomic Diameter,	3.59
Coordination No 12	
Valence Electrons	6d ² 7s ²
Chemical Valence	4
Pauling Valence	4
Isotopes	227, 228, 229, 230, 231, 232, 233, and 234. 232 only naturally occurring
Theoretical Density	11.7 g/cm ³
Density	11.6 g/cm ³ (Ames extruded)
Melting Point	1680 $\pm$ 25 C *
Specific Heat	0.02787 Btu/Lb/F * .117 Joules/g atom/C
Coefficient of Thermal Expansion	12.4 x 10 ⁻⁶ /C (25-1000 C), (No directional properties found) *

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TABLE 4. Continued

Electrical Resistivity	18.0 x 10 ⁻⁶ ohm-sec at 20 C
Magnetic Susceptibility	0.05 (-170 C)
Emissivity	No data found
Thermal Conductivity	Determined in an atmosphere of purified argon. Cross-sectional area corrected for oxidation. Material hot rolled 788 C and air cooled. *

Temperature C	100	200	300	400	500	600	650
Thermal Conductivity (cal sec ⁻¹ cm ⁻² cm ⁻¹ C ⁻¹)	.090	.093	.096	.100	.103	.106	.108

* Values determined on Ames Thorium.

References: 15, 16, 21, 45, 46, 47.

The melting point of thorium has been variously reported from as low as 1450 C⁽¹³⁾ to 1845 C.⁽¹⁴⁾ J. C. Thompson reported values of 1680 C and 1782 C⁽¹⁵⁾ and Hamby observed breaks in the cooling curves at 1625 C.⁽¹⁶⁾ A pouring temperature of 1800 C has been adopted at Ames on the basis of drip-melting tests. By melting charges of 10 to 50 pounds of metal in crucibles having 1-to 1-1/2-inch holes in the bottom, it was found that no appreciable flow was obtained until a temperature of 1775 to 1800 C was reached.⁽¹⁷⁾

Crucibles from a number of refractories have been investigated. MgO and CaO were reduced by thorium at temperatures of 1650 and 1750 C, respectively. Thoria showed but little attack at the melting point, but had reacted considerably at 1800 C. The reaction with beryllia at temperatures up to 1775 C is negligible and is only slight at 1800 C. There is a slight erosion of the crucible at 1800 C, but it is possible to make several melts in a single crucible before the crucible must be discarded. Zirconia is also satisfactory up to temperatures of 1800 C, but at 1900 C both BeO and ZrO₂ are severely attacked.

The pick-up of beryllium in the melt during the final casting operation at Ames is indicated in the previous analyses. Zirconium pick up during melts made in ZrO₂ crucibles at Oak Ridge was reported as negligible.

Melts can be made in graphite crucibles, but there is some pick-up of carbon. Complete carbonization occurs at 1800 C if the heating time is sufficiently long. Metal heated at 1600 C has been reported to contain 0.2 per cent carbon, and at 1650 C, the carbon content was 0.6 per cent.

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Tantalum crucibles have been tried but there was some pick-up of tantalum in the metal. The metal melted in tantalum was appreciably softer than after melting in BeO. (18)

Melts have also been made in crucibles prepared from TiN, ZrN, BN, and CeS, but none of these refractories appeared to be satisfactory. (19)

The castings at Ames are bottom poured into graphite molds. A beryllia stopper sealed in the bottom of the crucible with a slip of BeO is raised by raising the entire mold. The metal drops through a spout into the mold. Round castings up to 5 inches in diameter, containing approximately 100 pounds of metal, are usually made. However, 2-1/2 x 5 x 20-inch slabs have been cast.

Castings have also been made by top pouring from a tilting-type crucible and by the "self-pour" method. In the latter method, a plug of thorium is fitted into a hole in the bottom of the crucible, which is in a slightly cooler zone of the furnace than the main body of the crucible. The plug, therefore, melts out after the main portion of the charge has melted and the metal flows into the mold. Castings made by this method have had poor surface quality and a further disadvantage lies in the fact that crucibles can be used once only.

Thorium has also been melted in arc furnaces similar to those developed for melting titanium and zirconium. The metal is melted with a tungsten electrode on a water-cooled, dish-shaped, copper crucible under a partial pressure of inert gas. Vacuum-arc melts with a consumable electrode have also been made. (20)

These arc-melting methods offer a means of melting without contamination by a refractory but have been limited to relatively small melts of 100 to 300 grams of metal.

Mechanical Working

The mechanical-working characteristics of the currently produced Ames castings are generally good. The metal is soft and ductile when hot and can be worked by most of the standard metal-working procedures with only a few special precautions. An inert atmosphere or protective jacket is necessary when the metal is heated for hot working. There is no brittle-temperature range, although castings have a tendency to crack when cold worked. After the cast structure has been broken up, the metal can be fabricated at room temperature.

Extrusion

Thorium can be extruded at reasonable pressures at temperatures in the range 760 to 1000 C. The metal is generally jacketed with copper to protect the surface and to lubricate the die, but can also be extruded bare. Higher pressures are required to extrude unjacketed metal and some die erosion occurs. Good surface quality can be obtained in either case under proper conditions.

For thorium jacketed in 1/16-inch-thick copper, a pressure of 32 tons per square inch was required for a 16-to-1 reduction at 800 C. A 9-to-1 reduction under similar conditions required 25 tons per square inch. An extrusion pressure of 40 tons per square inch has been

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reported (21) for the extrusion of bare thorium at 950 C at an 8.93-to-1 reduction. The metal for this extrusion was heated in a salt bath and was extruded at 25 feet per minute.

Thorium and copper react to form a pyrophoric compound at temperatures of 900 C and above, and some reaction occurs at temperatures as low as 800 C. This reaction can be prevented by plating the interior of the copper can with chromium or by applying a BeO wash to the thorium prior to canning.

Either shear-type or 60°-angle dies can be used and good extrusions have been obtained with both types. (22)

Forging (23)(24)(25)

Thorium forges readily at temperatures of 750 to 800 C. There is some tendency for the 4-to 4-3/4-inch-diameter Ames casting to crack at the top end of the casting, but the metal loss resulting from such cracks is not excessive. These billets are heated to 750 to 800 C in an electric muffle-type furnace in an inert atmosphere. Reheating one or two times is usually necessary, because the metal becomes too stiff to flow properly under the hammer. The full capacity of a 4900-foot-pound air hammer is required to forge a 4-3/4-inch-diameter billet. Flat dies are usually used to draw down the billets to smaller bars or plates suitable for rolling.

Rolling

After the cast structure has been broken up, thorium can be rolled over a wide range of temperatures. The cast billets are usually

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forged or extruded prior to rolling, but castings can also be hot rolled directly. The metal is usually rolled in the range 750 to 900 C, where reductions of 25 to 30 per cent per pass are feasible. Standard closed-pass rolls, designed for rolling steel rods produce satisfactory thorium rods.

Aluminum in the metal makes it hot short, but nitrogen in amounts up to approximately 1000 ppm does not affect the hot-working characteristics. A billet containing 3500 ppm of Al could not be rolled, but a heat containing 235 ppm of Al and 885 ppm of N rolled at 850 C (1560 F) without difficulty. A hot-rolled 3/4-inch-diameter rod of this heat was subsequently cold rolled to 0.47-inch diameter in hand-rounding rolls without cracking. (26)

The "as-cast" metal can be cold rolled but develops edge cracks after reductions of approximately 10 per cent. Hot working greatly improves the cold-rolling properties of the metal. Reductions of 50 to 60 per cent can be made on previously hot-rolled sheet without serious edge cracking, and one-mil foil has been rolled from .020-inch-thick hot-rolled sheet without intermediate anneals. Hot-rolled bar stock has been rolled from 0.875-inch diameter to 0.427-inch diameter in hand-rounding rolls without evidence of cracking.

An indication of the hot and cold-working characteristics of a large number of alloys has been obtained by forging and rolling small (approximately 38 g) arc-melted buttons of various alloys. Alloys containing 1 and 5 atomic per cent of Zr, Sn, Pb, Cb, Bi, Tl, Ce, Te, V, Ta, Ti, W, Mo, Cr, Mn, Fe, Ni, Co have been made. Of these, only the 5 per cent alloys of Bi, Pb, Sn, Tl, Fe, and Co could not be forged at

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700 C and rolled at that temperature to 0.080-inch sheet. All of the alloys which could be hot rolled could also be cold rolled to 50 per cent reduction.

Induction-melted alloys containing up to 6 weight per cent of Ti, Zr, and Cb have been found to be ductile and the castings could be cold rolled to 75 per cent reduction without cracking. All of these elements reduced the as-cast hardness markedly.

The effects of oxygen and carbon on the general fabricating characteristics have not been specifically investigated. However, Westinghouse metal which contained 0.152 to 0.172 per cent oxygen was readily fabricated both hot and cold, and Ames metal, containing 0.21 per cent carbon, has been forged and rolled without difficulty.

Other Fabrication Methods

Thorium can be swaged to wire in properly designed dies. In dies designed for steel with a relief angle of approximately 30°, the soft metal tends to form and rough surfaces result. Wire drawing is feasible if a copper jacket is used to lubricate the dies, and 0.004-inch diameter wire has been made by this method. The bare metal seizes to Carboloy and steel dies. A proprietary lubricant developed by the Superior Tube Company for drawing titanium prevented seizure during the drawing of bare-thorium tubes, but no other satisfactory lubricant has been found.

Small-diameter, thin-walled tubing can be drawn on mandrels from drilled bar stock or from extruded tubes. Preliminary efforts to produce large-diameter tubing (3-inch O. D.) by piercing forged billets

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in a Mannsman mill indicated that this method may be feasible, but additional development work will be required to produce high-quality tubing.

Welding

Single-pass welds can be made in 1/8-inch-thick hot-rolled sheet, with a shielded-tungsten arc, but the welds have a tendency to crack. A second pass over the weld with the arc invariably results in cracking.

Satisfactory welds have been reported in thorium and also between thorium and zirconium, titanium, and tantalum. The welds were made by the Heliarc process with a-c current. No cracking was observed in these samples. Spot welds were also made between thorium and thorium, and between thorium and tantalum. (18)

Resistance-butt welds and flash welds have been made, but no data on the properties of these welds have been obtained.

Silver-soldered joints in thorium are brittle. (27) Efforts to furnace-braze thorium with various commercial brazing alloys have been unsuccessful, because the alloys fail to wet the thorium surfaces.

Machining

The machining characteristics of thorium are comparable to those of mild steel. The metal can be turned with high-speed tools at lathe speeds of 150 to 175 feet per minute. Coolants are desirable, but dry turning is practical.

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The scale resulting from hot working is hard and dulls the cutting edge of tools much more rapidly than the clean metal. The surface of castings may be pyrophoric and must be machined slowly to avoid combustion of the chips.

Surface grinding produces a smooth, highly reflecting surface, which darkens on standing in air. The grinding wheels, however, tend to become loaded with metal. Shaping and milling operations are also practical.

Electroplating

Electroplating techniques have been developed for plating Al, Zn, Cr, Fe, Ni, Cu, Sn, Pb, Ag, In, Au, and Rh on thorium. (28) A chemical pretreatment is necessary in order to obtain good adherence and uniform deposition. This treatment consists of a 3-to-5 minute anodic pickle of the abraded or vapor-blasted surface in 10 per cent by volume of HCl with a current density of 125 to 250 amperes per square foot at room temperature. This is followed by a 3-to 5-minute chemical pickle in 10 per cent sulphuric acid, also at room temperature. The sample is then rinsed in tap water and immersed in the desired plating bath. With the above pretreatment, good adherence was obtained with each of the metals previously indicated.

Cladding

Protective-metal coatings can also be applied to thorium by dipping in molten-metal baths and by roll-cladding techniques. Aluminum, zinc, and tin coatings can be applied by dipping in molten

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baths of the respective metals. Intermetallic compounds are formed at the interface between the coating and thorium, and interdiffusion is rapid at the bath temperatures. Thorium dipped in copper became coated with a copper-thorium compound which the bath would not wet. Similar results were obtained in an aluminum-silicon eutectic alloy. Only spotty wetting was observed in a lead bath.

Thorium, dip clad with 2S aluminum at 800 C, could be cold rolled from 0.965 to 0.007 inch thick without breaking the bond. Efforts to roll-clad thorium with aluminum by the picture-frame technique have been unsuccessful, but thorium can be clad with zirconium by this technique. A thorium core is fit into a zirconium picture frame and zirconium covers are placed on each side of the core and frame. This entire assembly is then canned in a steel can by the same procedure. The steel can is welded shut to protect the zirconium and thorium from oxidation and the pack hot rolled at 900 C (1650 F) to a total reduction of 50 per cent or more. Good bonding is obtained on the flat surfaces but bonding at the edges is variable and is dependent on the sample geometry and on the rolling conditions.

The roll cladding of thorium with zirconium, titanium, and stainless steel is being investigated at Battelle and at Oak Ridge.

Powder Metallurgy

No data are available in the classified literature on the powder metallurgy of thorium other than a reference to the Westinghouse process for the production of massive-metal bars from powder obtained in this reduction process.

The powdered metal, after washing and drying, is compressed at 10 to 20 tons per square inch and sintered in vacuum at approximately 1400 C. The resulting metal has good ductility and the properties are, in general, similar to those of Ames metal.

Thorium powder can be obtained from massive metal by forming the hydride and reducing this hydride to metal by heating in a vacuum. (29)

CHEMICAL PROPERTIES

The chemical properties of thorium and its compounds are admirably summarized in a report by G. K. Rollefson and French Hagemann, (1) with an appended bibliography of 188 references. No attempt will be made to abstract this report, although some of the general chemical characteristics of thorium are shown below.

Metallic thorium is a reducing agent which falls between aluminum and magnesium in the potential series. It resembles most closely quadrivalent cerium and zirconium, but is somewhat more electro-positive than either of these elements. Thorium forms only one series of compounds, in all of which it has a valence of +4. It is more basic than the lighter elements in the same group of the periodic system and has about the same basicity as quadrivalent cerium. Acidic properties are almost entirely absent. Unless the anion is colored, all of the salts of thorium form colorless solutions.

Thorium forms double salts with almost every negative ion, for example, $K_4Th(SO_4)_2 \cdot 2H_2O$, $K_2ThF_6 \cdot 4H_2O$, etc. There is also a pronounced tendency to form basic salts, such as $ThOCO_3 \cdot 8H_2O$ and $Th(OH)_2Cl_2 \cdot 4H_2O$.

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Aqua regia dissolves thorium metal rapidly as does concentrated hydrochloric acid. Concentrated nitric acid soon renders the metal passive and the reaction stops. The addition of a small amount of fluoride or fluosilicate ion (e.g., 0.05 M) destroys this passivity and solution proceeds rapidly. Dilute hydrochloric, hydrofluoric, nitric, sulfuric, concentrated perchloric, and phosphoric acids attack the metal slowly. The alkali hydroxides do not react with the metal.

The metal reacts vigorously with fluorine, chlorine, bromine, iodine, and sulfur at temperatures up to 450 C and with nitrogen at 650 C. Hydrogen reacts with the powder at room temperature and with the massive metal at 300 to 400 C with the evolution of much heat. Thorium carbides are formed when the metal is heated with carbon, the phosphide when heated with phosphorus, the nitride with nitrogen, and the boride with boron.

The nitrate, perchlorate, acetate, sulfate, chloride, bromide, and iodide are common water-soluble salts.

Analytical Techniques

The determination of thorium in alloys and minerals requires a separation of thorium from the associated anions and the gravimetric or titrametric measurement of the separated element.

The method of separation depends to some extent on the type of material being analyzed, but usually consists of a precipitation of thorium with oxalic acid from slightly acidic solutions.

Zirconium and hafnium, as well as the rare-earth elements, and scandium interfere with the separation, and when present require special

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techniques. The analytical aspects of thorium chemistry are summarized in a review by Mueller, Schwertzer, and Starr.(30)

The analysis of relatively pure thorium metal is a special problem and, as such, requires special techniques. The metallic elements are usually determined spectrographically, using silver chloride as a carrier. If the amount of impurities present is very small, a preliminary separation may be required. Nitrogen is determined by the Kjeldahl method and carbon by combustion. Vacuum-fusion methods may be used to determine oxygen and hydrogen.

The latter method consists of dissolving a thorium sample (0.2 to 0.5 gram) in an outgassed tin bath (5 to 20 grams) contained in a graphite crucible. Using an operating temperature of 3200 F (1760 C), the oxygen content of the specimen is extracted as carbon monoxide. One hour is usually required to complete the extraction. Oxygen results are repeatable on duplicate specimens to ± 5 to 10 per cent of the obtained value. The evolved gas contains free nitrogen and free hydrogen, in addition to carbon monoxide. The amount of nitrogen usually obtained is quite small compared with the amount of carbon monoxide. Consequently, the vacuum-fusion nitrogen analysis is not very precise and the Kjeldahl method for nitrogen is to be preferred.

Vacuum-fusion hydrogen values tend to be erratic and high. This is believed to be caused by hydrogens being evolved from the furnace assembly through the vaporization of the tin bath. Lower hydrogen values are obtained with a small tin bath than with a larger tin bath.

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The tin-fusion method for hydrogen in thorium appears to give better results than does the vacuum-fusion method. This method consists of dissolving the sample in a large tin bath (100 grams) contained in a carbon-free furnace assembly. The operating temperature is 1000 C. The gas extraction is usually complete within 15 minutes. Practically all the gas evolved appears to be hydrogen.

Corrosion in Air

Thorium has been shown to oxidize in air by the parabolic law at low temperatures and linearly at higher temperatures.⁽⁵⁵⁾ Scaling tests in air, nitrogen, argon, and carbon dioxide indicate that in air a marked increase in the rate of scaling occurs between 800 and 900 C. There was also a marked increase in the rate of scaling after one hour at 800 C. The weight gain after 1/2 hour at 800 C in the various gasses is shown below:⁽³¹⁾

<u>Atmosphere</u>	<u>Weight Gain</u> <u>g/cm²</u>
Air	6.0
Tank N	4.4
Purified N	2.0
Tank A	1.0
Purified A	0.75

The weight gain in 4 hours in air at various temperatures is shown below:⁽³²⁾

<u>Temperature,</u> <u>C</u>	<u>Weight Gain in 4 Hours</u> <u>g/cm²</u>
200	Negligible
300	0.12

<u>Temperature</u> <u>C</u>	<u>Weight Gain in 4 Hours</u> <u>g/cm²</u>
400	1.72
450	21.4
500	34.75

A thorium - 2 per cent beryllium alloy showed somewhat higher weight gains under similar conditions.

Corrosion in Water

Thorium becomes covered with scale and gains weight when exposed to boiling distilled water. Weight gains of 0.03 mg per cm² per hour to losses of 0.0006 mg/cm² have been reported. (24)(33)(34) An anodic pretreatment is reported to reduce the rate of attack in water. (35)

Coupling aluminum and thorium had no effect on the thorium, but the corrosion rate of the aluminum was increased. Thorium alloys containing 1 to 4 per cent silicon were similar to pure thorium, as were alloys containing 2.75 to 5.53 per cent iron. The addition of 0.4, 2, and 4 per cent beryllium adversely affected the corrosion characteristics. Alloys with 2 and 4 per cent of columbium and 0.3 to 1.24 per cent carbon were also less resistant than pure thorium. (36)

The addition of thorium nitrate (0.3 M) or nitric acid (0.5 M and 15.4 M) caused partial disintegration of pure-thorium samples.

In water at 300 F, a sample of rolled thorium was severely attacked and partially disintegrated after an exposure of 144 hours. At 600 F in water, the attack was extremely rapid and the safety diaphragm on the bomb was ruptured after only 2 hours' exposure.

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A qualitative test on thorium wire in 65 per cent (volume) hydrofluoric acid at 140 F indicated that only slight attack occurs in this medium. The sample became covered with a gray scale and gained slightly in weight.

Corrosion in Liquid Metals (22)(37)(38)(39)(40)(41)(42)(43)

The corrosion resistance of thorium in sodium-potassium is excellent. At 600 C, the corrosion rate during a static six-day test in sodium-potassium, which had been cleaned with uranium chips, was ± 0.006 mg per square centimeter per hour. The corrosion rate increased as the oxygen content of the sodium-potassium increased. The effect of stress on the corrosion resistance of thorium in sodium-potassium was negligible.

Thorium was not significantly attacked by lithium in six days at 600 C, but was completely disintegrated by gallium at 600 C. In a eutectic alloy of bismuth and lead, thorium was wet by the alloy but was only slightly attacked in one hour at 300 and 500 C. At 900 and 1000 C, the samples were badly eroded. Severe attack occurred in pure bismuth in one hour at 900 C, but only slight oxidation was observed on samples immersed for one hour in pure lead at 900 C.

Pickling(31)(35)

The removal of the scale resulting from heat treatment or hot working is difficult. Sandblasting is the most satisfactory method because no satisfactory pickle has been found. Dilute (1:1) nitric acid to which has been added approximately 0.05 N of HF, or fluosilicic

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acid can be used if only a light scale is present, or if the metal has been previously sandblasted. This pickle attacks the metal under the scale and thus loosens the particles of oxide. Severe pitting results if heavy scale is present. Fused potassium acid fluoride removed heat-treating scale but the bath deteriorated. Other fused salts investigated were ineffective.

MECHANICAL PROPERTIES

A considerable amount of data on the mechanical properties of thorium is available in the classified literature. Thorium, like other metals, is influenced by impurity content, prior history, and the strain rate. Thorium has definitely been found to be strain-rate sensitive and highly susceptible to oxidation at elevated temperatures. Consequently, data in the literature that do not give the chemical analysis of the specimens and the atmosphere in which tests at elevated temperatures were made are not mentioned in this survey. The properties selected on the basis of these criteria are summarized below.

Tensile Properties

The tensile values tabulated below were determined at Battelle Memorial Institute on Ames thorium, hot rolled at 1450 F and annealed one hour at 1450 in a helium atmosphere. Tests were made on standard 0.505-inch-diameter specimens at room temperature. The analysis of the thorium is contained in Table II, Billet A-233.

Strain Rate, in./in./ min	Yield Strength 0.2% Off- set, psi	Tensile Strength, psi	Prop. Limit, psi	Modulus Elasticity, psi	Elongation in 2 in.,%	Reduction Area, %
0.003	27,000	37,000	22,000	$10 \pm 0.2 \times 10^6$	47	64.0
0.16	32,300	37,300	22,500	$10 \pm 0.2 \times 10^6$	48	60.7

The error in strain readings was $\pm 2 \times 10^{-6}$

Tensile data reported (20) on thorium having the following analysis: 0.07% C, 0.15% O₂, 0.07% N₂, and traces of Cu, Fe, Si, and Mg are as follows:

Yield Strength, psi	Tensile Strength, psi	Prop. Limit, psi	Elastic Modulus, psi	Elongation in 2 in %	Reduction Area, %
24,300	32,500	20,100	9×10^6	63	69.4

These values are the averages for five specimens tested at a constant crosshead speed of 0.1 in/min. Values over a higher strain rate fail to exhibit the sensitivity of thorium to strain rate. If the yield strength is assumed to be the 0.2% offset value, the lower yield strength may be attributed to a difference in impurity content.

The tensile properties of thorium at elevated temperatures are to be approached with caution. In the process of obtaining data concerning tensile properties, heat treatment, and the dynamic studies, it has become increasingly apparent that at elevated temperatures thorium has to be tested in a vacuum unit or an excellent protective atmosphere. It has been found that the dynamic modulus was significantly

increased when testing at room temperature after determinations up to 1550 F in argon. Tensile tests conducted at Battelle Memorial Institute at 572 F in an argon atmosphere and in a vacuum unit indicated a substantial difference in results which can well be expected to have more significance at higher temperatures. In argon, at 572 F, the only indication of oxidation was a slight darkening of the metal. The specimens used were from the same ingot with identical histories. A tensile test at 932 F in an argon atmosphere had a white-oxide layer 1/16-inch deep at the end of the test.

The elevated-temperature tensile properties determined at Battelle Memorial Institute to date on Ames thorium with the same composition as reported above are as follows:

Type of Atm.	Temp, C	Strain Rate, in./in./ min	Yield Strength, 0.2% Off- set, psi	Tensile Strength, psi	Prop. Limit, psi	Modulus of Elasticity, psi	Elong. in 2 in, %	Reduction Area %
Argon	300	.006	12,700	25,800	8,500	8×10^6	37.5	62.0
Vacuum	300	.006	11,350	22,400	7,300	8×10^6	32.5	65.5
Vacuum	200	.006	12,300	24,500	8,100	9×10^6	34	43

Compression Properties

The compression data reported by the various investigators are in general agreement. The 0.2 per cent offset yield strength and the proportional limit at various strain rates further confirm the necessity for including the strain rate when reporting strength data. The compressive properties are listed below for room temperature.

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Strain Rate in./in./min	Yield Strength 0.2% Offset, psi	Prop. Limit, psi	Elastic Modulus, psi	Poisson's Ratio
.005	23,900	13,500	$9.7 \pm 0.2 \times 10^6$	$.28 \pm .02$
.025	26,000	15,000	$10.0 \pm 0.2 \times 10^6$	$.27 \pm .02$
.05	25,000	-	-	-
.1	27,500	-	-	-

Compression properties at elevated temperatures have been reported⁽²²⁾⁽⁴⁾ on samples 1.0-inch long and 0.50-inch diameter.

The samples were apparently annealed in an argon atmosphere and tested in a vacuum.⁽²⁰⁾

Temperature, C	Prop. Limit, psi	Load at 10% Reduction, psi	Load at 20% Reduction, psi	Time in Furnace, Hours
60	22,000	35,000	44,000	-
250	19,000	30,000	39,500	1.10
400	17,000	26,500	33,000	1.10
500	13,000	21,000	26,000	1.10
595	8,000	14,500	18,300	1.00
675	7,500	11,400	14,000	1.00
775	4,700	7,200	8,000	1.00
835	5,500	7,100	8,000	1.00
905	4,700	5,800	6,300	1.00
965	3,000	4,500	5,000	1.00

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Torsion Properties

ORNL(21) has reported static shear modulus values of 4.08×10^6 , 3.91×10^6 , and 3.89×10^6 psi. The values obtained at Battelle Memorial Institute were:

Strain Rate in./in./min	Yield Strength 0.2% Offset, psi	Proportional Limit, psi	Static Shear Modulus, psi
0.003	22,400	19,000	4.5×10^6
0.006	19,000	17,000	4.4×10^6

The composition was the same as mentioned above in the section on tensile properties. Using the relationship

$$G = \frac{E}{2(1 + \mu)}$$

and taking the values of $E = 10 \times 10^6$ psi and $\mu = 0.28$, the value of the shear modulus is 3.9×10^6 psi. Considering the above data, a value for the shear modulus of $4.1 \pm 0.2 \times 10^6$ would appear to be in order.

Moduli

The static Young's modulus appears to be $10 \pm 0.2 \times 10^6$ psi to a very close approximation. The dynamic-tensile modulus determined at Battelle Memorial Institute was 11.6×10^6 psi

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at room temperature and decreased by 2760 psi/F. This linearity held up to approximately 950 F. The dynamic shear modulus was found to be 4.7×10^6 psi at room temperature.

Creep Strength

There are no creep data available in the literature. Preliminary vacuum creep tests on Ames thorium hot rolled at 1450 F, annealed one hour at 1450 F in a helium atmosphere, and machined to 0.505-inch-diameter standard tensile specimens, indicate that at 300 C negligible creep results from stress levels up to 12,000 psi.

Impact Properties

Notched-bar impact tests were made on the V-notched Charpy-type specimens at Battelle Memorial Institute over a temperature range of from -75 C to 250 C. A gradual transition was found to exist between 75 C to 150 C during which the type of fracture progressed from a semi-brittle to the ductile type. Hardness surveys across each sample indicated no aging as a result of the reheat. The specimens were held at temperature for five minutes prior to testing. The temperature region of transition agrees very well with results obtained at Oak Ridge National Laboratory. (56)

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METALLURGICAL CHARACTERISTICS

Any analysis of the metallurgical characteristics must be governed by the same stipulations with regard to impurity content and prior history as were employed in the consideration of the mechanical properties.

Metallography

There are many techniques available to study on the metallography of thorium. The chief difficulty arises when the inclusions are to be retained in an etched matrix. Of necessity, a compromise has to be reached between the retention of inclusions and an etched structure. Two polishing techniques will be mentioned that yield consistent results. ORNL suggests paper polishing, followed by polishing on a silk cloth with medium-fine alumina powder as the abrasive. Final polishing is done electrolytically in a solution of one part of perchloric acid and ten parts glacial acetic acid. Voltage was 50 at a current density of 4 amp/in². Final dipping in fresh electrolyte removed the slight polishing film.

The method used at Battelle Memorial Institute at present consists of paper polishing, followed by etch-polishing on Forstmann cloth with Linde B as the abrasive and a solution of 50 cc HNO₃ - 50 cc H₂O plus 4 drops of hydrofluorosilicic acid. Grain boundaries are obtained electrolytically using a 10 per cent solution of AgNO₃ or Cn(NO₃)₂ with 10 volts on open circuit. The black deposit is removed in the final wheel by further polishing the surface slightly.

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Work Hardening

The variation of hardness with the severity of cold deformation indicates that the hardness increases rapidly during the first ten per cent reduction in area and then levels off. ORNL⁽²¹⁾ gives data on Ames thorium and also on iodide thorium from Battelle Memorial Institute which illustrate this ability to work harden very nicely.

<u>Ames Thorium</u>						
% Deformation	0%	10%	20%	40%	60%	80%
VHN	78	114	118	119	120	123

<u>Iodide Thorium</u>						
% Deformation	0%	10%	20%	40%	60%	80%
VHN	37	50	55	60	52	70

The pronounced difference between the as-received hardnesses of the two types of thorium further emphasizes the necessity for reporting the chemical analysis in conjunction with property determinations.

Heat Treatment

To date, no confirmed evidence has been reported as to the possibility of a phase modification in thorium. Cooling curves tend to indicate a solubility effect rather than an allotropic modification. Considerable data exist in the classified literature concerning annealing in the region of recrystallization for thorium.

The recrystallization kinetics of thorium have been studied,⁽⁵⁴⁾ but the process was complicated by a precipitation process. The lowest temperature for recrystallization is approximately 500 C. The recrystallization temperature varies with impurity content and ORNL reports that iodide thorium recrystallizes at a higher temperature than Ames thorium. Very little has been done concerning the temperature for extensive grain growth, reported to be approximately 750 C.⁽⁴⁷⁾ The previous work on the recrystallization of thorium indicated that the activation energy for the process was of the order of 15,000 cal/mol. The activation energy associated with the accompanying precipitation process was on the order of 5,000 cal/mol.

At Battelle Memorial Institute, thorium rod hot rolled at 1450 F and annealed one hour at 1450 F in a helium atmosphere has been cycled between 100 C and 500 C. Another rod further annealed for twelve hours at 800 C has been similarly cycled. No indications of instability have been obtained after 1450 cycles.

Diffusion Characteristics

No quantitative investigations concerning the diffusion rates involving thorium have been reported.

Alloys

Considerable information is available in the classified literature concerning the alloy systems of thorium. These data are condensed below. A more comprehensive survey will be issued in the future concerning diagrams of the various systems and the properties of the alloys.

Thorium alloys readily with Fe, Si, Mo, Co, Ni, Cu, Au, Ag, W, Ta, Zn, Bi, Pb, Hg, Na, Be, Ce, Cr, Zr, and U. Aluminum additions to thorium result in the formation of a eutectic compound which when precipitated at the grain boundaries produces hot shortness. Ce is completely soluble in the liquid and solid phases producing an extremely cored structure. These alloys are easily made under an argon atmosphere. There is also a possibility that Mg and In have appreciable solid solubility. Columbium improves the workability of thorium by tying up the carbon. Zirconium and titanium act as grain refiners. Intermetallic compounds are formed with the following elements: Si, Be, Bi, (Th₂Bi), Ni (ThNi, ThNi₂, ThNi₃, ThNi₄, ThNi₅, ThNi₁₂), and Mn (ThMn₂, ThMn₄). (1)(5)(18)(29)(48)(50)(51)(52)(53)

The mechanical properties of several thorium-rich binaries made with Ames metal have been determined at Battelle Memorial Institute and are summarized in Table 5.

TABLE 5. MECHANICAL PROPERTIES OF THORIUM ALLOYS.

Alloying Addition, Atomic, %	0.2% Offset Yield Strength, psi	Ultimate Strength, psi	Elongation, % in./in.	Reduction Area, %	B*	N*	As-Cast VHN
0	29,000	39,000	32	46	66,000	.18	106
1.0 Bi	32,000	48,000	23	24	80,000	.18	120
5.0 Bi	Could not be fabricated						
1.0 Sb	32,000	46,000	32	42	78,000	.19	109
5.0 Pb	Could not be fabricated						
1.0 Zr	45,000	56,000	12	25	76,000	.09	93
5.0 Zr	18,000	34,000	23	43	62,000	.24	71
1.0 Sn	30,000	47,000	28	43	81,000	.19	116
5.0 Sn	Could not be fabricated						
1.0 Cb	30,000	45,000	36	54	82,000	.21	103
5.0 Cb	-	-	-	-	-	-	-
1.0 Tl	32,000	45,000	32	31	80,000	.20	111
5.0 Tl	Could not be fabricated						
1.0 Ce	33,000	47,000	26	32	80,000	.17	115
5.0 Ce	31,000	46,000	36	41	78,000	.18	112
10.0 U (wt %)	36,000	52,000	17	23	88,000	.17	-

* $\sigma = \beta \delta^n$, where σ is true stress and δ is true strain.

β is a constant.

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