~~SECRET~~

UNCLASSIFIED

0079

NAA-SR-Memo-816

Page 1 of 15

Copy 28 of 40
Series A

Classification cancelled (or changed to UNCLASSIFIED)

by authority of Letter to Mr. DeLoach 11-6-58

by J. C. Ridenour T E, date 11-13-58

ISSUE DATE:

November 6, 1953

A DISCUSSION OF THE METALLURGICAL ASPECTS

OF THORIUM AS A FUEL MATERIAL

B. R. Hayward

This document is
PUBLICLY RELEASABLE

Hugh Kinser

Authorizing Official

Date

Hugh Kinser
9/28/06

In the more recent thinking on fuels for power reactors, thorium-uranium alloy has been considered as a prospective material. This memo attempts to compile recent data without complete detail and to mention the metallurgical advantages and problems involved with the use of thorium fuels for the type of power reactors now under design study at North American Aviation, Inc. It is first assumed that the general reactor configuration will follow the conventional SGR-SRE reactor design of a graphite moderated, sodium cooled, metallic fuel system. The discussion basically considers criteria important to this design.

Thorium has many attractive metallurgical features as a potential fuel material, principally in its dimensional stability and permissible operating temperatures. The thorium technology has been experimentally demonstrated in most phases of operation affecting reactor use; however, substantial effort will be required to put thorium in the same class as uranium. Thorium as metal is not presently available in large quantities. Present plant capacity could supply approximately 50-100 tons per year, if there is a demand. The preparation of thorium metal follows the general stages similar to uranium, ore, oxide, fluoride, metal, with a few variations due to different chemical properties. There are also many indirect factors which affect the metallurgical use of thorium as a fuel. Among these are: 1) availability of ore, and processing plants; 2) purity speci-

406 001

~~SECRET~~

SECURITY INFORMATION

UNCLASSIFIED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

~~SECRET~~

NAA-SR-Memo-816

Page 2

fications for the metal often depend on chemical phases of processing; 3) design and use of materials in the fuel element which may affect the chemical separations; 4) the economics, beside the technical feasibility, of any phase of thorium handling may affect the metallurgy of thorium.

These points are raised at this time as they affect the possible use of thorium for reactor fuel in the immediate future. Can thorium be considered as a reactor fuel only as a long term proposition?

Existing Facilities:

1. Thorium ore is concentrated, refined, and converted to purified nitrate by Lindsay Light and Chemical Company, production capacity unknown.
2. The nitrate was shipped to Iowa State College up to late spring of 1953 and converted to metal. This site is not processing thorium at this time but is capable of 4 to 5 tons of thorium metal per month. A similar plant is available at National Lead Company of Ohio, but has not been put into operation. It is assumed this plant has more capacity than ISC.
3. Thorium metal fabrication can be done at any of the uranium fabricating facilities including Simonds Saw and Steel and National Lead Company of Ohio.
4. Stockpile of thorium materials are not known to author. It is believed that about 100 tons of thorium as nitrate is available. The world supply of thorium ore is greater than uranium, but its availability to the U. S. may be uncertain.

General Metallurgical Properties of Thorium

Melting Point - $\sim 1680^{\circ}\text{C}$. This value is somewhat contradictory by information available in the literature. An English report¹ in 1949 indicated the melting point of "iodide" thorium to be $1140^{\circ}\text{C} \pm 20^{\circ}$. There has been no recent information that the iodide thorium produced in the USA has a lower melting point than indicated above (1680°C). All American fabrication procedures utilize the melting point of about 1700°C . It should be noted in the typical thorium metal analyses that the oxygen content of Ames

~~SECRET~~

406 002

~~SECURITY INFORMATION~~

~~SECRET~~

NAA-SR-Memo-816

Page 3

billet thorium is about 0.16 per cent. Oxides such as this tend to raise the melting point, as was the case with uranium 15 years ago.

Density - For reactor calculations the observed values of 11.55-11.63 g/cc are recommended. No density values are available on the Th-U alloys or thorium made by powder metallurgy.

Chemical Purity - This particular factor is difficult to appraise at this time. Thorium has been studied mainly on a large scale experimental development basis. The metal obtained, although quite pure, has been taken as it was produced without the rigid specifications as are imposed on uranium. From the typical analyses shown in Table I, it is clear that the purity is good but there are none the less considerable impurities in ppm compared to uranium. The thorium made from the iodide process is very good but too expensive for present reactor use. Since no specifications have been maintained, it is important to know the reproducibility of the material on a production scale to give a uniform product. Accurate and consistent analytical procedures are required in addition. Certain elements (O_2 , C, and others) have definite effects on the physical properties of thorium and need to be controlled within limits for satisfactory fabrication and reactor performance. The above discussion on chemical purity is based on information about one year old, and there have been some improvements in the situation since that time.

Thermal Conductivity - The thermal conductivity of thorium is about 25 to 50 per cent greater than uranium depending on temperature; at 100° C, 0.090 vs. 0.063 cal/sec cm °C. At elevated temperatures, thorium is reported 0.108 cal/sec cm °C at 650° C vs. 0.084 cal/sec cm °C² for uranium at 650° C.

~~SECRET~~

406 003

~~SECURITY INFORMATION~~

~~SECRET~~

NAA-SR-Memo-816

Page 4

Thermal Expansion

The increase in the mean linear expansion coefficient of thorium with temperature is shown in the following data.

<u>Temperature Range °C</u>	<u>Mean Linear Expansion Coefficient per °C x 10⁻⁶</u>
30 - 100	11.5
30 - 200	11.5
30 - 400	11.7
30 - 600	12.0
30 - 800	12.2
30 - 1000	12.4

Since thorium has a cubic structure, these values are quite reliable in contrast to uranium values which vary considerably due to its non-cubic crystal structure in the low temperature phases. A rough estimate indicates that uranium has a volume coefficient of expansion somewhat greater than thorium; for U in temperature range 25 to 125° C = ~45, in temperature range of 25 to 625° C = ~60.³

Phase Transformations - Thorium has a face centered cubic structure and undergoes no phase changes below 1400° C. The indication of a phase change from face centered cubic to body centered cubic at 1425° C was reported very recently by Iowa State College⁴ during the preparation of a thorium alloy. The effects of this phase change appear to be minor since both are cubic structure. It is due to the cubic structure, which is dimensionally stable, and the lack of phase transitions that permit higher operating temperatures in thorium than in uranium providing there is sufficient strength and compatibility with contacting materials.

Corrosion in Liquid Metals - Although in general thorium is more corrosion resistant than uranium to water and liquid metals, it would not be advisable to consider this as sufficient criterion for using unclad unalloyed thorium fuel unless the concept of fission products and mass transfer in the coolants is revised.

~~SECRET~~

406 004

~~SECURITY INFORMATION~~

~~SECRET~~

NAA-SR-Memo-816

Page 5

Examples of thorium corrosion³ are as follows: 1) The corrosion resistance of thorium in NaK is very good. Rates of 0.006 mg/cm² hr from a 6-day static test at 1100° F were reported; 2) Thorium is relatively resistant to Li at 1100° F, Pb-Bi at 930° F, and Pb at 1650° F, but is poor in Ga at 1100° F, Pb-Bi at 1650° F and Pb at 1830° F. Other data from MIT⁵ indicates that liquid Sb, Pb, In and Tl dissolve thorium to a very limited extent. Bismuth and tin dissolve small amounts of thorium with aluminum being the best solvent for thorium. Note that Mg was not included in this series of tests.

Tensile, Yield and Creep Strength - There are many values for the strength of thorium. The main reasons for the discrepancies are the purity of the test material, effect of cold working, and the time for the test. As shown in the typical metal analyses, there is a large difference in the purity of arc-melted iodide thorium and regular wrought thorium. The impurities increase the strength considerably. Since oxygen, nitrogen and carbon are a large percentage of the total impurities and tend to increase the tensile strength of thorium, the assay of these elements is particularly important when strength data are used for calculations. The annealed values would more nearly represent conditions of SRE-SGR fuel operation. Typical annealed strength data for Ames thorium include values of 25,000 to 28,000 psi yield strength (0.2 per cent offset) and 30,000 to 35,000 psi ultimate strength at room temperature;³ at elevated temperatures the ultimate tensile strength decreases appreciably to values of 2100 psi at 1500° F for a short time test⁶ with the yield strength decreasing at a greater rate. The following table indicates the yield strength of typical thorium metal vs. temperature.

<u>Temperature, °F</u>	<u>As-Cast Ames Th, psi³</u>	<u>Hot Rolled & Annealed</u>	
		<u>Ames Th, psi³</u>	<u>Th-U (3% U) psi</u>
80	25,000	27,000	27,000
200	17,000	19,000	---
400	12,000	13,000	---
600	9,500	11,000	---
800	7,600	9,700	---
1000	6,000	9,300	---

~~SECRET~~

406 005

~~SECURITY INFORMATION~~

~~SECRET~~

NAA-SR-Memo-816

Page 6

The creep strength of thorium has not been extensively studied. Reported values at relatively low temperatures indicate a reasonable creep rate (negligible at 300° C up to 12,000 psi stress). These creep values appear questionable upon consideration of the relatively low yield and tensile strength at elevated temperatures. More recent data⁷ describes thorium as having a lower creep rate at 400° F than at 200° F with the same stress. This appears to be due to aging.

There is no known available data on the strength properties vs. temperature of Th-U alloys other than the fact that increasing uranium content increases the strength. Some room temperature strength values are known for the Th-U alloys¹ as shown above. The data in the above table appears misleading for comparing strength values; however, the standard Th specimen tested in series with the Th-U alloys showed a room temperature yield strength of 20,000 psi.

Metal Fabrication - Thorium is soft and ductile, can be quite easily fabricated in most all forms. It lends itself to extrusion, forging, and hot rolling, wire drawing, etc. The welding of thorium has not been extensively examined and results were rather poor in tests conducted to date.

Sylvania and Westinghouse have made some thorium shapes by powder metallurgy although this method has not been thoroughly evaluated due to a lack of demand. Thorium powder metallurgy uses a hydriding method that is very similar to that for uranium. There are current programs at Ames and Sylvania aimed toward reducing processing costs by converting the oxides of uranium and thorium to powder metal.

Thorium Alloys - The primary objective of the use of alloying elements in the thorium fuels is to improve the physical properties. In their selection, attention must be given to the maintenance of a critical mass in the main reactor core without decreasing the nuclear efficiency. At this time the only thorium alloy considered for the core is thorium-uranium, although Th-Pu may be a future possibility. The alloying elements that increase the strength of thorium are indium, carbon, and uranium. Of these, carbon and uranium are quite fortunate, in that carbon is usually present as a low

~~SECRET~~

406 006

~~SECURITY INFORMATION~~

~~SECRET~~

cross section impurity and uranium is the alloy of immediate interest. The carbon present usually results from mold contamination. The cross section of indium is too high for use as an alloying element in the fuel.

There are three methods of making the Th rich Th-U alloys: 1) by co-reduction of the respective fluorides, 2) direct addition in the remelt and casting operation, 3) powder metallurgy. Since the uranium will be highly enriched, the method of alloying would probably be by (2) or (3). It should be considered with respect to economics (dollars per gram of U^{235}) that a higher per cent uranium alloy containing the same quantity of U^{235} but of a lower concentration may be advisable; i.e., Th-U (2% U) may be more expensive than Th-U (6% U) for the same total U^{235} content.

The alloying characteristics of thorium directly determine the compatibility of thorium and other materials. In reactor operations the compatibility criteria involve eutectic formation, rapid corrosion, welding in presence of radiation, solid state diffusion, etc. Low melting thorium alloys are listed in Table II. Thorium and uranium form eutectics with many of the same elements such as Fe, Cr, Ni, with the Th alloys melting at slightly higher temperatures. There are two notable exceptions to this similarity in the eutectic alloys of thorium and those of uranium. These are magnesium and silver and are mentioned under the paragraph on Chemical Processing. The corrosion of Th in liquid metals was mentioned in a previous section. There is very little information on the irradiation welding of thorium. The solid state diffusion as far as directly concerns our present interests is covered under the paragraph on cladding. The thorium-uranium alloy phase diagram is shown in Fig. A, together with the latest information on the solubility of uranium in thorium.

Dimensional Stability - The thermal cycling results on thorium rods after 1000 cycles between 100° C and 500° C indicated very minor distortion.⁸ From the samples tested, the distortion which occurred was due to the residual stresses from fabrication and these can be minimized by proper annealing heat treatment. As would be expected from its cubic structure, the thermal cycling of thorium does not appear to be a problem. It should be noted, however, that reactor conditions or SRE operating temperatures were not simulated nor were the thorium-uranium alloys tested.

~~SECRET~~

406 007

~~SECURITY INFORMATION~~

~~SECRET~~

NAA-SR-Memo-816

Page 8

There are currently in various reactors specimens of thorium and thorium-uranium alloys being irradiated for the study of radiation damage to these materials. Recent information from ANL indicated that two per cent burnup of the thorium-uranium alloys showed no marked change. Thorium-uranium alloy fuel plates are now being tested at MTR (3800 MWD exposure in July, 1953, and specimens are satisfactory).⁹ It has been estimated that thorium rich thorium-uranium alloys should be able to be used to 15,000 MWD or even greater.

Cladding Materials - Thorium may be successfully clad in zirconium by roll cladding and extrusion cladding. Attempts at cladding with steel and aluminum have met with only limited success to date. Other methods such as dipping in molten metal baths, electroplating, etc., have been successful in some instances, but large scale effort has not been expended on these methods. Generally, it may be said that thorium and probably thorium-uranium alloys can be as easily or more easily clad than uranium.

On the basis of present knowledge, thorium or thorium alloy SRE fuel elements could be produced by one of two methods: 1) same as present, substituting thorium for uranium, 2) co-extrusion of thorium and zirconium into clad solid or hollow rods.

Chemical Processing - The present chemical separations process for irradiated thorium (Thorex) is similar in some respects to the solvent extraction for uranium. This Thorex process consists of separating the thorium, U²³³, and fission products, into individual product streams. As far as is known, this process is on a pilot plant scale only. There are no large scale chemical processes or plants for processing large quantities of highly irradiated thorium-uranium alloy. Many important chemical processing questions remain unanswered with respect to the use of thorium as a reactor fuel.

Future prospects for improving thorium-uranium fuel processing are being studied with laboratory scale experiments at NAA. One process which is a liquid metal extraction method utilizes the immiscibility of uranium in molten magnesium and the miscibility of thorium in molten magnesium with the Th-Mg eutectic melting at 605° C. An analogous situation exists with molten

~~SECRET~~

406 008

~~SECURITY INFORMATION~~

~~SECRET~~

silver as the extraction medium. Another phase of reprocessing utilizes the hydriding of the Th-U alloy as either: 1) a method to increase the surface area available for other chemical reactions, or 2) as a step in the re-assembly of processed materials into new fuel elements.

Advantages in the Use of Thorium as a Fuel

The most important factors in the use of thorium are:

1. Higher peak fuel temperatures are permitted; that is, greater than the 1200° F now used with uranium.
2. It is dimensionally stable and thus may be used for potentially longer burnups, perhaps to 15,000 MWD or greater.
3. At present costs, thorium is cheaper than uranium. In addition, longer fuel burnup would require a lower fuel inventory.
4. Since thorium does not at present belong in a potential weapons category, its use could be solely for the support of a reactor industry.
5. Higher thermal conductivity than uranium.
6. Better corrosion resistance to liquid metals and water than uranium.
7. High potential breeding gain for a thermal reactor.

Disadvantages and/or Problems Associated with the Use of Thorium as a Fuel

1. The U²³⁵ added to the thorium-uranium alloy may be highly enriched. This is an end product of the U²³⁵ diffusion plant, for the first reactor loading, and is expensive.
2. There are no metallurgical plants in operation to supply large quantities of thorium metal.
3. There are no chemical plants to handle large quantities of irradiated thorium. Similarly, would existing processes for chemical separations on thorium be satisfactory for longer burnup fuel?

~~SECRET~~

406 009

~~SECURITY INFORMATION~~

~~SECRET~~

NAA-SR-Memo-816

Page 10

Recommendations

The following general recommendations are made for the consideration of thorium or thorium alloys for fuel in the SGR-SRE type reactor. Some of the factors are short term and others based on a long term reactor outlook. Also, it will be noted that some of the points mentioned have indirect bearing on the metallurgy of these materials. These items to be studied or evaluated are in no particular order.

1. To develop specimens of thorium-uranium alloys prepared by various methods (cast, rolled, extruded, coextruded, powder compacted) and of shapes of interest (thin rods, rods, hollow rods) followed by testing these specimens under SRE temperature conditions with promising specimens to be further tested under radiation. Samples from this development work could be used for chemical separations work. The completion of the Th-U phase diagram should be included.
2. To study maximum operating temperatures for thorium alloy fuel elements.
3. To study high temperature properties of thorium and thorium-uranium alloys, including thermal conductivity and strength as the most important.
4. To study compatibility with cladding and bonding materials at SRE temperatures.
5. To economically evaluate thorium with respect to availability of ore, plant processing capacity, chemical separations methods and capacity, plus new chemical separations methods.
6. To study the chemical separations for long burnup thorium-uranium fuels; problems include: a) holdup for Pa, b) effect of high concentration of fission products, c) undesirable uranium isotope buildup.
7. To have reactivity tests made on production grade thorium to compare these with chemical and spectrographic analyses.
8. To consider remote metallurgical refabrication of irradiated thorium-uranium fuel materials.

~~SECRET~~

406 010

~~SECURITY INFORMATION~~

~~SECRET~~

NAA-SR-Memo-816

Page 11

9. To continue radiation damage studies (particularly long term) under conditions for use in reactors of NAA design; study physical property change versus burnup.

10. To study danger coefficients of thorium and thorium-uranium alloys. (This may already have been started at NAA.)

REFERENCES

1. AERE-C/R-425, "Preparation of Pure Thorium".
2. Private Communication - B. R. Hayward and J. Droher.
3. Reactor Handbook, Vol. 3, Materials.
4. ISC-340, "Th-U System".
5. TID-65, "Solubility of Uranium and Thorium in Liquid Metals".
6. ISC-36, Progress Report, Metallurgy, April, 1948.
7. BMI-866, "The Creep Properties of Thorium".
8. ORNL-1090, "Metallurgy of Thorium and Thorium Alloys".
9. IDO-16111, "Status of MTR Irradiations".
10. BMI-89, "The Properties of Thorium Alloys".

Additional General References on Thorium

ORNL-910	Quarterly Progress Report, Metallurgy, October, 1950
BMI-76	The Technology of Thorium
WASH-90	"Minutes of Thorium Research Meeting, May, 1952"
ISC-251	"Properties of Unalloyed Thorium"
FMPC-173	"Review of Thorium Production"
NYO-3727	"Investigation for the Production of Thorium Metal"
BMI-720	"A Study of Thorium Base Alloys"

~~SECRET~~

406 011

~~SECURITY INFORMATION~~

~~SECRET~~

NAA-SR-Memo-816

Page 12

TABLE ICHEMICAL AND SPECTROGRAPHIC ANALYSES OF THORIUM, ppm

<u>Element</u>	<u>Thorium (Ames Billet)</u>	<u>Thorium (Iodide)</u>	<u>Thorium MTR (Spec.)</u>	<u>Alpha Rolled Uranium</u>	<u>Powder Compacted Uranium</u>
O ₂	1600	27	500	—	—
H ₂	2	8-10	—	6	8
N ₂	200	<20	100	40	140
C	593	200	1000	300-600	375
Al	49	30	100	<20	—
Mn	<20	<2	—	2-10	—
Si	52	91	Tr	45	35
Fe	78	135	300	70	140
Be	144	10	1000	<0.1	<0.1
Cu	—	5	—	2-5	2-5
Ni	—	3	Tr	<10	10-50
Cd	<0.2	<0.2	—	<1	<1
B	<0.2	0.9	—	<0.02	<0.02
Mo	—	<5	—	<2	<2
Cr	—	33	—	<1	<1-1
Ba	—	40-80	—	<10	—
Mg	<20	18	—	15	2
Ce	—	—	15	1-10	2
La	—	—	5	<15	—
Nd	—	—	2	—	—
Dy	—	—	0.05	—	—
Pr	—	—	0.4	—	—
Sm	—	—	0.1	—	—
Y	—	—	0.05	—	—
Gd	—	—	0.2	—	—
Ca	48	—	Tr	<5	—
Zr	21	<20	Tr	<100	<100
W	—	85	—	—	—

~~SECRET~~

406 012

~~SECURITY INFORMATION~~

~~SECRET~~

NAA-SR-Memo-816

Page 13

TABLE II

LOW MELTING THORIUM ALLOYS

<u>Alloy</u>	<u>Thorium a/o</u>	<u>Thorium w/o</u>	<u>mp °C</u>
Th-Mg	6	37	605
Th-Al	4	26	630
Th-Cr	40	75	1230
Th-Cu	10-90	20-90	940
Th-Au	10	11	814
Th-Ni	22	92	1000
Th-Ag	55-10	70-15	894
Th-U	4	4	1100
Th-Zr	60	80	1300
Th-Ti	-	88	1175
Th-Mn	>80	-	911
Th-Fe	54	-	860
Th-Cb	-	Th rich	1315
Th-Si	-	87	>1300
Th-Zn	-	93	1200
Th-Na	3	23	93*

* Numerous attempts to duplicate this result have had no success.

~~SECRET~~

406 013

~~SECURITY INFORMATION~~

Figure A

NOTE: The dotted areas on the Th-rich side of the diagram indicate the solubility of U and Th is in doubt. Information from Battelle¹⁰ indicates that as-cast alloys contained 5 w/o or more of U in solution. At 315°C the solubility is 3 or 4 w/o while at 705°C it appears to be about 5 w/o.

✱ ✱ ✱ ✱ ✱ ✱ ✱ ✱ ✱ ✱ ✱

During a recent discussion with Dr. Hausner, from Sylvania, the solubility of uranium in thorium was observed in powder compacted samples containing one to two per cent uranium. Near the melting point of uranium, 1130°C , little interaction was observed after a reasonable time at temperature. At 1250°C the uranium phase completely disappeared indicating complete solubility in the solid thorium. This predicts that the apparent limiting temperature of approximately 1100°C (2000°F) as shown on the phase diagram due to the presence of a liquid phase, may possibly be extended to 1400° to 1600°C .

There are a few thorium-uranium alloy samples on hand at North American Aviation, Inc., which were prepared by the melting method. Specimens will be examined by the x-ray laboratory for lattice spacing. This may further indicate the solubility or insolubility of uranium in thorium.

~~SECRET~~

406 014

~~SECURITY INFORMATION~~

~~SECRET~~

NAA-SR-MEMO-816

Page 15

Distribution

SGR Distribution

Beeley

Cubicciotti

Bareis

Weisner

Reed

Droher

Cockrell

Henrie

DO NOT PHOTOSTAT

~~SECRET~~

~~SECURITY INFORMATION~~