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THORIUM-URANIUM SYSTEMS, A LITERATURE SURVEY

E. Fast and R. A. Peereboom

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I. INTRODUCTION

Two common isotopes, thorium and uranium-238, produce fissionable isotopes upon neutron irradiation. The latter undergoes the reaction

whereas with thorium it is

U-238 occurs in nature together with about 0.7 percent U-235, a fissionable isotope, so that critical systems are possible with proper geometry and moderators. Thorium in nature is a 100 percent isotope of atomic weight 232 and is three to four times as plentiful as uranium.

Both isotopes as well as mixtures of thorium and uranium in various proportions have been considered for breeding systems. U-238 has a smaller thermal cross section and larger resonance integral, and the irradiation product a shorter decay period than thorium. Whether the properties of one or the other is more desirable will depend upon the conditions under which each is to be used. It is conceivable, however, that a combination of the two in some optimum proportion would give better performance than either one alone.

Irradiations of thorium-natural uranium samples are proposed as part of the Budget Activity 04 40 01 01, "Reactor Physics Constants." The anticipated program is directed toward studying long-term reactivity effects. Reactivity changes can be measured with good precision on the ARMF. From such measurements effective cross sections, resonance integrals, effective η s, fuel content, and transient reactivity effects can be calculated.

The purpose of this report is to survey briefly the literature pertaining to thorium-natural uranium systems. The objectives are to determine: (a) feasibility of preparing samples containing thorium-uranium alloys or mixtures; (b) the problems associated with sample preparation--specifically with obtaining a metallurgical bond with the cladding; (c) what irradiation studies have been made; (d) what theoretical studies have been made. It appears most of the studies were made using partly or fully enriched U-235 in thorium. These

results are useful for points (a) and (b) above, but are not necessarily valid for (c) when natural uranium is substituted. In the following review a brief summary of the various applicable papers is followed by an evaluation in the light of the above objectives.

II. GENERAL SURVEY OF THORIUM-URANIUM PUBLISHED REPORTS

Early work on thorium-uranium systems is summarized in several publications. The literature before 1956 is essentially contained in the book, The Metal Thorium.¹ Three applicable portions are Chapter 13, "Mechanical Properties of Thorium and High-Thorium Alloys"; Chapter 15, "Fabrication and Cladding of Thorium Metal"; and Chapter 17, "Effects of Irradiation upon Thorium". A 1955 Geneva Conference Paper by Carlson, et al.,² is also a summary of thorium technology. Carroll³ describes work done at ORNL in 1955 in production of fuel plates containing a thorium-uranium alloy core. The plates made by the usual picture-frame technique were aluminum clad bonded by a 1.3 percent silicon-aluminum barrier material.

In 1958, Atomics International, Battelle Memorial Institute, and Nuclear Metals, Inc., initiated studies of thorium-uranium systems with the object of using these for reactor fuel. The uranium was partly or fully enriched U-235.

The early work of Atomics International with some contributions from other sources is summarized in two 1958 Geneva Conference Papers.^{4,5} Further work directed toward developing fuel for the SRE type reactor is given in subsequent reports.⁶⁻¹¹ They began with physical property measurements and metallography performed on thorium-uranium alloy samples containing up to 20 weight percent uranium.⁶ Microstructural changes on long time annealing were studied for alloys containing up to 10 weight percent uranium.⁷ Concentrations in excess of five weight percent uranium showed preferential agglomeration of uranium particles at grain boundaries.⁶ Irradiation studies were also undertaken. A number of thorium-11 weight percent uranium specimens were irradiated in the MTR with subsequent examination made at Battelle.¹¹ Burnup ranged from 0.5 to 1.5 total atomic percent and temperatures varied from 970 to 1250°F. Some swelling of the samples was observed. Swelling was described as a linear function of burnup at temperatures below 1100°F, and increased significantly above 1100°F. Irradiation did not appear to hasten the agglomeration of uranium particles in the thorium matrix. Thorium-five weight percent U-235 alloys were irradiated up to four percent burnup at 1000°F in the SRE and found to be dimensionally stable.⁸ Small changes in the density and appreciable increases in hardness were observed. Tensile strength and thermal conductivity also changed slightly. The fabrication of thorium-7.6 weight percent uranium fuel elements are described in a later report in great detail.⁹ A new and further study of vacuum induction melting and casting techniques have been undertaken and reported.¹⁰

Battelle Memorial Institute approached the study of the thorium-uranium system from the standpoint of achieving improved irradiation

stability and corrosion resistance by control of processing techniques.¹²⁻²⁰ They observed that uranium particles are more uniformly dispersed in the arc-melted alloys than in the induction-melted alloys.¹³ Battelle undertook to outline the effects of thorium purity, casting methods and fabrication on uranium particle size and distribution. Recrystallization studies were made on alloys of thorium with 5, 10, 15, and 20 weight percent uranium. The results of these studies were published in a series of progress reports^{14,16-19} and a summary report.²⁰ Battelle showed that the casting techniques had the most effect on the micro-structure of the thorium-uranium alloy. Arc-melting was the best technique, with an upper concentration limit of 15 weight percent uranium, to produce uniform dispersion of uranium in the thorium matrix.

Studies by Nuclear Metals are found in a series of progress reports.²¹⁻²⁶ They show that thorium-uranium alloys have a higher corrosion rate than unalloyed thorium.²¹ They also attempted to produce, economically, good thorium-uranium slugs by casting to size. No definite conclusions were drawn except for the enumeration of pitfalls encountered with both the arc-melting and induction-melting techniques.

At this same time, Argonne National Laboratory instituted a program to investigate radiation effects on thorium-uranium alloys in the MTR. The results of these investigations showed that at up to 4.4% burnup the specimens, initially containing up to 5.53 percent U-235, showed excellent dimensional stability and good ductility.²⁷ Another series of samples was irradiated with compositions of 10, 15, 20, 25, and 28 weight percent uranium. Enrichments were adjusted so each sample contained 10 percent U-235 except for the last one which contained 26 percent U-235. The 10, 15, and 20 weight percent uranium specimens showed excellent irradiation stability at burnups of approximately three percent and temperatures of 680°C. The 25 weight percent uranium sample showed warpage and the 28 weight percent uranium sample was severely distorted.²⁸

Crowther, in several papers²⁹⁻³¹ has considered the advantages of thorium, uranium, and the combination of these two in all proportions as a breeding material. The maximum resonance capture occurs at a thorium fraction of 0.38, and the initial conversion ratio at a thorium fraction of 0.47. The calculations assumed the oxides of U-238 and thorium in a boiling water reactor.

III. SUMMARY OF LITERATURE

In view of the stated objectives information obtained in the literature may be summed as follows:

A. Feasibility of Thorium-Uranium Alloys

Thorium-uranium alloys have been studied containing up to 50 weight percent uranium. More than three weight percent uranium strengthens the thorium. Ductility decreases approximately linearly to not intolerable limits at 50 weight percent. Quenching and aging heat

treatments can affect the hardness of alloys. There are no intermetallic compounds formed in the system. Solubility of uranium in thorium is relatively low, i.e., about 2.5 weight percent uranium at 950°C up to 7.5 weight percent at 1250°C. The uranium-rich phase occurs as a fine precipitate evenly dispersed in the thorium matrix. The precipitate agglomerates as a function of time, temperature, uranium concentration, and perhaps irradiation. The agglomeration occurs preferentially at grain boundaries.

B. Cladding of Thorium-Rich Thorium-Uranium Alloys

It is assumed that in general cladding processes which are satisfactory for thorium also apply to thorium-rich alloys of thorium-uranium.

1. Aluminum

Cladding thorium with aluminum presents many obstacles. There are five intermetallic compounds which cause brittle compound layers to form readily at the bond interface. Warpage, weld-breakage, and separation is caused by large differences in the thermal expansion and conductivity properties of the two metals. Getting uniform cladding thickness in extrusion is difficult because flow characteristics of the metals under deformation are dissimilar.

High-quality bonding has been obtained by rolling between 260-400°C without the aid of evacuation (no compound layers at interface). Using low-strength grade thorium and a high-strength aluminum alloy for the cladding helps to obtain a uniform clad thickness. A method is available to obtain composite tubes by co-extrusion. The thorium-aluminum bond is thermally unstable so that such samples cannot be used at temperatures over 150°C except on an extremely short-term basis.

2. Zirconium

Thorium and thorium-aluminum alloys can be clad directly with zirconium by extrusion and roll cladding techniques. The resultant bond is ideal since composites can be further processed by drawing, bending, heat treating, quenching, or other methods of forming and deforming without ill effect. The only distinct disadvantage is the tendency of thorium and zirconium to absorb gas. Since surface films can act as effective barriers and prevent bonding it is necessary to minimize gas pickup by the metals during processing. Two different methods of accomplishing this are available. One is described in ORNL-1366.³²

3. Intermediate Bonding Materials

Intermediate materials which bond to both the thorium-uranium alloy and to the cladding material have been successfully employed. An early ORNL experiment used a 1.3% silicon-aluminum barrier material to clad thorium-uranium plates with 52S aluminum by rolling at 500°C. A thin layer of nickel and other elements have been used. The samples irradiated

in the MTR by Atomics International and others have been encapsuled in stainless with a liquid metal NaK bond.

4. Miscellaneous

Because of their properties titanium, molybdenum, and tantalum should be usable as direct cladding material.¹ However, no extensive testing has been done with these.

C. Irradiations

Irradiation experience is confined to thorium containing partially or fully enriched U-235 for use as reactor fuel. Significant damage is observed above a few percent burnup.

D. Theoretical

The only applicable theoretical calculations were made by Crowther, who considered mixtures of U-238 and thorium.³¹ The results are interesting in that mixture with uranium is in all cases an improvement over the use of thorium alone (based on resonance neutron absorption efficiency) and better than uranium alone for most of the range. Optimum concentrations may be a uranium-rich mixture if nuclear properties alone are considered, but if economics are included the shift would be toward thorium.

IV. DISCUSSION

Preparation of thorium-rich thorium-uranium alloys present no great problem. However, a fine dispersion rather than a true alloy is obtained at uranium concentrations above a few percent. This should not hinder appreciably the use of these samples in the study of thorium-uranium systems.

Radiation damage is not expected to be serious. The damage reported in the literature was on samples containing enriched uranium, where damage was primarily that caused by fission fragments. After a corresponding number of fissions have occurred in the systems under consideration, it is probable that damage would be comparable.

Zirconium appears to be the best cladding material and will probably be recommended for any samples used here. Aluminum can be used with some difficulty and limitations. The NaK bond introduces additional complications in the interpretation of results and is not seriously being considered.

The calculations of Crowther have some interesting implications as to the possible importance of thorium-uranium mixtures. Results indicate that the optimum concentrations may be more nearly equal parts of thorium and uranium or uranium-rich rather than thorium-rich alloys. Apparently no experimental work has been done to confirm these values. Because of this it would appear profitable to plan a comprehensive

long-term irradiation program, with interim ARMF measurements, to study the reactivity changes in thorium-natural uranium systems.

A minimum experimental program should include three different proportions of uranium and thorium, and two irradiation flux spectra. Duplicates of each concentration would be retained as comparison standards. Additional standards would be needed to cover the range of fissionable and poison isotopes resulting from irradiation. The standards are necessary for interpreting the reactivity measurements made in the ARMF. Irradiation of several proportions should allow a reasonable comparison with calculated values and, hence, extrapolation to the probable optimum mixture. The evident importance of the resonance flux component³⁰ makes it desirable to irradiate in different flux spectra.

Other references not specifically quoted above and some recent bibliographies on thorium are also recorded below.

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