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EFFECTS OF IRRADIATION ON THORIUM AND
THORIUM-URANIUM ALLOYS

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Final Report - Metallurgy Programs 6.2.1 and 6.2.6

This report supersedes sections of the following
Metallurgy Division Progress Reports:

<u>Report No.</u>	<u>Reporting Period</u>	<u>Pages</u>
ANL-5097	April-June 1953	64, 66
ANL-5338	April-June 1954	80, 81
ANL-5643	July-Sept. 1956	13, 14
ANL-5975	1958	19, 20
ANL-6330	1960	108, 109
ANL-6516	1961	139-141

April 1963

Operated by The University of Chicago
under
Contract W-31-109-eng-38
with the
U.S. Atomic Energy Commission

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EFFECTS OF IRRADIATION ON THORIUM AND THORIUM-URANIUM ALLOYS

by

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ABSTRACT

Three separate irradiation experiments have been completed with thorium and thorium-uranium alloys. In the first experiment, three rolled plates of thorium and Th-5 w/o U alloy irradiated to total atom burnups up to 1.5 percent at 200°C showed no anisotropic growth and decreased in density at a rate of 1% per a/o burnup. In the second experiment, 15 swaged specimens of thorium and of the alloys Th-0.1 w/o U, Th-1.4 w/o U, and Th-5.5 w/o U were irradiated to burnups ranging from 0.3 to 3.6 percent of all atoms at temperatures in the range of 45 to 200°C. Again, no anisotropic growth was observed and densities decreased at rates near 1% per a/o burnup. A Th-1.4 w/o U alloy specimen with 2.0 a/o burnup was found to have retained significant room-temperature ductility. In the final experiment, a group of 44 chill-cast specimens of thorium alloys containing 10, 15, 20, 25, and 31 w/o uranium were irradiated to burnups ranging from 0.16 to 10.1 percent of all atoms. Maximum irradiation temperatures ranged from 260 to over 1000°C. Surface roughening occurred in the alloys containing 25 and 31 w/o uranium. Volume increases at any given temperature for all alloys were linear with increasing burnup. The rate of volume increase for all alloys rose from approximately 1% per a/o burnup at the lower temperatures to a value of 2.5 at 650°C. Thereafter the swelling rate increased somewhat, reaching a value of 6% volume increase per a/o burnup at 800°C. The rates of volume increase under irradiation of thorium-uranium alloys in the entire temperature range studied were significantly less than those reported for the best uranium-base alloys. It is suggested that the excellent resistance to high-temperature swelling of the cast thorium-uranium alloys resulted from the fact that a dispersion of very thin uranium particles was obtained. A high probability, therefore, existed for fission recoils to escape from the uranium particles into the isotropic and less densely packed thorium matrix.

INTRODUCTION

The use of thorium as a constituent in nuclear fuels is of interest because (1) in breeder reactors the conversion of thorium to U^{233} can greatly extend the world's reserve of nuclear energy sources, and (2) the isotropic nature and favorable high-temperature properties of thorium could make it a desirable element with which to alloy uranium for metallic fuels intended to operate at elevated temperatures. In 1950, when preparations were begun at Argonne National Laboratory to irradiate thorium fuels, item (2) above was largely conjecture based on the characteristics of the thorium-uranium phase diagram. Experimental work was needed to verify the expectation that thorium-rich uranium alloys were promising fuels.

Three separate series of irradiation experiments have been made during the ensuing 12 years with a variety of thorium and thorium-uranium alloys. The first group of specimens consisted of small plates of thorium and a thorium-5 w/o uranium alloy rolled to final size. These specimens were irradiated in the NRX reactor at Chalk River, Ontario, from March through December, 1952. The second irradiation experiment was made with a group of swaged rods of thorium and thorium-uranium alloys containing 0.1, 1.4, and 5.5 w/o uranium. The swaged specimens were irradiated in the MTR during the period from July 1953 to March 1956. The third group of specimens to be studied were cast rods of thorium-uranium alloys containing 10, 15, 20, 25, and 31 w/o uranium. These specimens were irradiated in the MTR during the period from December 1958 to January 1960. Preliminary results obtained on the first two groups of specimens were reported at a 1956 Conference on Thorium sponsored jointly by the U. S. Atomic Energy Commission and the American Society for Metals.⁽¹⁾

EXPERIMENTAL MATERIALS AND PROCEDURE

A. Rolled Specimens

The specimens in the first group were rolled into the form of thin plates, 1.00 x 0.25 x 0.032 in. Three specimens were irradiated. One specimen was made of unalloyed thorium, one was made of thorium-5 w/o natural uranium alloy, and the remaining specimen was made of thorium-5.5 w/o uranium enriched approximately 93% in U^{235} .

The specimen materials were melted twice and then chill cast as 300-gm ingots. After machining to 1.75 x 0.287 x 0.132 in., they were annealed for 4 hr at 800°C in vacuum, rolled at room temperature from 0.132-in. to 0.032-in. thickness, and reannealed 30 min. at 700°C in vacuum.

A billet analysis furnished with the original thorium material showed the following impurities: 96 ppm Fe, 600 ppm N, 970 ppm C, 170 ppm Al, and 625 ppm Be. However, a spectrochemical analysis of the thorium showed no impurity greater than 50 ppm. A subsequent spectrochemical analysis of the Th-5.5 w/o U alloy casting showed 70 ppm Fe, 1000 ppm Si, and all other impurities less than 50 ppm.

The specimens were irradiated in the NRX reactor at Chalk River, Ontario, in AECL-type aluminum capsules and were wedged in aluminum blocks to provide for heat removal. Burnups and irradiation temperatures were calculated from the estimated flux values.

B. Swaged Specimens

A total of 15 specimens were in the swaged group. All specimens were in the form of cylinders, 0.190 in. in diameter and 1.500 in. long. Six of the specimens were made of unalloyed thorium. The remaining nine specimens included three different thorium-uranium alloys, with three specimens representing each composition. The alloys included thorium with 0.13, 1.39, and 5.53 w/o uranium. In each of the alloys the uranium was enriched approximately 93% in U^{235} .

The unalloyed thorium and the Th-0.13 and 1.39 w/o U alloys were vacuum melted twice in thoria crucibles and chill cast into $\frac{1}{2}$ -in.-diameter ingots. They were then swaged to a 0.224-in. diameter at room temperature. With the exception of three unalloyed thorium specimens, all were then annealed for 2 hr at 700°C. The specimens were then machined to final dimensions.

The Th-5.53 w/o U alloy could not be swaged at room temperature because of its high hardness. It was chill cast into a $\frac{1}{2}$ -in.-diameter ingot, machined to 0.340 in. in diameter, and jacketed in an ingot iron tube. It was then swaged at 600°C to a diameter of 0.250 in., after which it was annealed for 2 hr at 700°C and machined to final size.

Spectrochemical analyses of the Th-0.13 and 1.39 w/o U alloys showed an average iron content of 55 ppm and silicon content of 85 ppm. All other impurities were less than 50 ppm. Analyses of the unalloyed thorium and the Th-5.53 w/o U alloy are not available, but are not expected to differ significantly from those reported above.

The specimens were irradiated in the MTR in loosely fitting zirconium capsules containing NaK alloy for heat transfer. Each capsule contained an aluminum-0.5 w/o cobalt alloy wire for flux-monitoring purposes. The atom burnups in the specimens were determined by isotopic analysis of Cs^{137} . The U^{233} content was determined in some specimens by mass spectrographic analysis of the uranium.

C. Cast Specimens

A total of 44 induction-cast thorium-uranium specimens were in the third group. All specimens were 0.875 in. long and 0.144 in. in diameter. The compositions of the alloys included thorium with 10, 15, 20, 25, and 31 w/o uranium. In the first four alloys, the U^{235} enrichments were varied from approximately 93 to 40% to give a uniform U^{235} content in all specimens, regardless of alloy composition. The uranium in the Th-31 w/o U alloy was enriched approximately 93% in U^{235} .

Two melts were made of each composition. Each melt was induction melted under a vacuum of 10^{-3} mm Hg or better. Crucibles and stopper rods were made of thoria, and thoria-coated graphite molds were used. The molds were fitted in a water-cooled copper base to promote directional solidification of the castings. The molds were also positioned so that the hot top and distributor were heated by the induction coil. The alloys were poured at temperatures ranging from 1775 to 1880°C, with the alloys containing the lowest uranium contents being poured at the higher temperatures. These specimens were cast directly to size, with machining done only to face the ends of the specimens. Chemical analyses of each melt are shown in Table I.

Table I

COMPOSITION OF ALLOYS USED FOR CAST SPECIMENS

Melt No.	Total U, w/o	U^{235} Enrichment, %	C, ppm	Fe, ppm	Si, ppm
C-16F-221	9.43	93.26	188	60	70
C-16F-225	10.7	93.25	281	60	150
C-16F-218	15.1	67.2	272	150	200
C-16F-224	15.2	65.7	349	100	200
C-16F-219	20.4	50.4	299	150	200
C-16F-229	20.6	50.0	362	200	500
C-16F-220	25.3	40.2	195	300	300
C-16F-223	25.2	40.4	208	60	80
Y-16F-189	31.4	93.26	425	70	100
Y-16F-190	31.6	93.29	338	150	100

The solubility limits of uranium in alpha thorium have not been well established. A published equilibrium diagram⁽²⁾ shows a maximum solubility of approximately 8 w/o uranium near 1280°C. Most of the equilibrium

studies⁽³⁻⁵⁾ indicate that the solubility of uranium in thorium at 1000°C is near 2 or 3 w/o. All of the cast alloys, therefore, contained uranium in amounts beyond the solid solubility limits of uranium in thorium. Because of this, and because of the higher melting point of thorium (1750°C) compared with that of uranium (1132°C), segregation of uranium into the thorium grain boundaries was expected. This did occur, as is shown in Figures 1 through 5. The figures show microstructures of typical specimens from each melt. Not only is grain-boundary segregation evident, but a much finer precipitate within the thorium grains was resolved in some of the structures. It is believed that these finely divided particles resulted from uranium, originally in solid solution, which was rejected from the thorium as it cooled. In the alloys with the higher uranium contents, the uranium phase in the grain boundaries approached a continuous network. The thickness of the uranium phase in the grain boundaries in most of the castings was less than one micron. The remaining castings contained uranium particles averaging 2 or 3 μ in thickness.

Most of the cast specimens were irradiated in uninstrumented NaK capsules in the MTR. Other specimens were irradiated in instrumented temperature-controlled capsules in the CP-5 reactor. Aluminum-0.5 w/o cobalt alloy flux-monitor wires were placed in all capsules for measurement of flux and preliminary determination of atom burnups. At least one specimen in each capsule was subjected to a uranium isotopic analysis. The final burnup values for these specimens were calculated from the relation⁽⁶⁾

$$\text{Total a/o burnup} = C \left[\frac{(a_0 + b_0) - (a + b)}{(1 + \alpha) - (a + b)} \right],$$

where

C = a/o U in specimen

a_0 = fraction of uranium that is U^{234} before irradiation

a = fraction of uranium that is U^{234} after irradiation

b_0 = fraction of uranium that is U^{235} before irradiation

b = fraction of uranium that is U^{235} after irradiation

α = σ_c / σ_f

σ_c = capture cross section of U^{235} (112×10^{-24} cm²)

σ_f = fission cross section of U^{235} (582×10^{-24} cm²).

The fission contribution of U^{233} formed from thorium was calculated from equations given in ANL-5335.⁽⁷⁾ This increment of burnup did not exceed approximately 3% of that resulting from U^{235} fission.

The maximum irradiation temperatures of the specimens in the uninstrumented capsules were calculated from the fuel power density resulting from the fission rate required to produce the observed changes in uranium isotopic ratios, and by means of an electrical geometrical analogue technique⁽⁸⁾ to determine the internal temperature gradients existing in the capsules during irradiation.

26203

500 X

a. Melt C-16F-221

26204

500 X

b. Melt C-16F-225

Figure 1. Microstructures of Cast Thorium-10 w/o Uranium Alloys.

26201

500X

a. Melt C-16F-218

26202

500X

b. Melt C-16F-224

Figure 2. Microstructures of Cast Thorium-15 w/o Uranium Alloys.

26205

500X

a. Melt C-16F-219

26206

500X

b. Melt C-16F-229

Figure 3. Microstructures of Cast Thorium-20 w/o Uranium Alloys.

26207

500X

a. Melt C-16F-220

26208

500X

b. Melt C-16F-223

Figure 4. Microstructures of Cast Thorium-25 w/o Uranium Alloys.

35439

500X

a. Melt Y-16F-189

35441

500X

b. Melt Y-16F-190

Figure 5. Microstructures of Cast Thorium-31 w/o Uranium Alloys.

RESULTS AND DISCUSSION

A. Rolled Specimens

A summary of the changes produced by irradiation of the three rolled plate specimens is shown in Table II. Irradiation temperatures are estimated not to have exceeded 200°C. Figure 6 shows the appearance of the specimens after irradiation.

Table II
EFFECTS OF IRRADIATION ON ROLLED SPECIMENS

Spec. No.	Composition	Burnup, a/o	Length Change, %	Width Change, %	Thickness Change, %	Weight Change, mg	Density Change, %	Hardness Change, Rockwell 30T
3	Thorium (unalloyed)	0.12	-0.01	-0.28	-0.03	-0.4	0.08	26.5
1	Th-5 w/o U (natural U)	0.13	-0.02	-0.12	0	-0.1	0.08	15.5
2	Th-5.5 w/o U (93% enriched U)	1.4	0.11	0.40	0.06	0.3	-1.44	13.0

Negative No.

14459

14458

14461

Specimen No.
Composition, w/o
Burnup, a/o

3
Thorium
0.12

1
Th-5 U
0.13

2
Th-5.5 U
1.4

Figure 6. Appearance of Rolled Specimens after Irradiation at a Temperature Estimated to Have Been Less than 200°C. Magnification 4X.

The thorium and the Th-5 w/o U alloy specimens were removed from their aluminum containers with no difficulty after irradiation. The Th-5.5 w/o U alloy specimen, which, because of U^{235} enrichment, achieved a much higher burnup, was tightly adhered to the aluminum. It was freed by dissolving away the aluminum in a concentrated solution of NaOH.

As shown in Table II, dimensional and density changes were small in the thorium and in the Th-5 w/o U alloy specimens. The low burnups which these specimens attained were sufficient to cause a marked increase in hardness, particularly in the unalloyed thorium. The Th-5.5 w/o U specimen, which received a burnup of 1.4 a/o, showed more significant changes in dimensions and density as well as hardness. The dimensional changes were primarily in length and width, the directions in which restraint was least. The rate of density decrease was approximately 1% per a/o burnup. None of the three specimens changed significantly in surface appearance as a result of irradiation.

B. Swaged Specimens

Table III summarizes results from the 15 swaged specimens irradiated in the MTR. Typical irradiated specimens are shown in Figure 7.

Table III
EFFECT OF IRRADIATION ON SWAGED SPECIMENS

Spec. No.	U, w/o	Method of Preparation	Burnup, a/o	Irradiation Temp, °C		Length Change, %	Diameter Change, %	Hardness Change, RA	Weight Change, mg	Density Decrease, %	% Δ Vol(a) a/o Burnup	Remarks
				Surface	Center							
H-10	0	Swaged at 25°C	1.2	76	88	-0.087	1.42	16.9	1.5	0.61	0.51	
H-14	0	"	1.5	82	96	0.18	0.68	16.3	1.4	1.09	0.77	
H-15	0	"	1.8	86	100	0.15	0.63	16.0	-0.1	1.45	0.97	
H-11	0	Swaged at 25°C, annealed at 700°C	0.26	75	87	0.24	-0.37	26.2	(b)	0.064	0.25	
H-12	0	"	0.34	81	95	0.14	0.47	34.3	(b)	0.85	2.5	
H-13	0	"	0.35	82	96	0.25	0.32	24.2	(b)	0.66	1.9	
H-6	0.13	Swaged at 25°C, annealed at 700°C	0.37	45	49	0.14	0.11	21.2	(b)	0.11	0.30	
H-5	0.13	"	1.6	45	49	0.47	0.63	26.2	2.1	1.07	0.69	
H-4	0.13	"	1.9	55	63	0.53	0.84	27.2	1.6	1.40	0.76	
H-3	1.39	Swaged at 25°C, annealed at 700°C	0.45	83	95	0.15	0.37	9.2	(b)	0.48	1.1	
H-2	1.39	"	0.69	98	115	0.21	0.84	16.5	(b)	0.70	1.0	
H-1	1.39	"	2.0	90	105	(c)	1.11	7.9	2.1	1.45	0.85	Bent during opening of capsule
H-9	5.53	Swaged at 600°C, annealed at 700°C	1.3	125	150	0.43	1.11	26.8	(b)	2.33	2.2	
H-8	5.53	"	2.8	110	130	0.17	1.74	15.9	1.0	3.56	1.3	
H-7	5.53	"	3.6	160	200	(c)	2.58	15.0	(b)	4.79	1.4	Fractured during opening of capsule

(a) Calculated from the expression $\% \Delta \text{Vol} = 100 \left(\frac{\rho_i}{\rho_f} - 1 \right)$, where ρ_i and ρ_f are the initial and final densities, respectively.

(b) Measurement not taken.

(c) Condition of specimen did not permit measurement.

Dimensional and surface stability of all of the swaged specimens was excellent. No marked tendency for anisotropic growth was evident in any of the specimens, including those made from cold-worked thorium. However, some of the specimens, particularly those with higher uranium contents and burnups, increased in diameter at rates somewhat higher than their rates of length increase.

Figure 7. Appearance of Typical Swaged Specimens after Irradiation at Temperatures Not Exceeding 130°C. Magnification 2X.

The addition of uranium had no significant effect on the irradiation behavior of the thorium. Density decreases were much less than are observed with alpha uranium. At about 1.5 a/o burnup, for example, the density decreases observed in this group of specimens were approximately 1%, compared with approximately 4% in beta-quenched uranium.⁽⁹⁾

During the opening of the zirconium irradiation capsules which contained specimens H-1 and H-7, it was noted that the capsules had become embrittled. This resulted in fracturing of the capsules during the opening operation. In both instances the specimens contained in the capsules were inadvertently damaged by the capsule fragments. In the case of specimen H-1, which contained 1.39 w/o uranium and achieved a burnup of 2.0 a/o, an unexpected degree of ductility was shown. When the irradiation capsule fractured, the specimen was permanently bent to an angle of 28° without fracture. A photograph of this specimen is shown in Figure 8. It is estimated from measurements made from the photograph that the outer fibers of the specimen were elongated about 4%. Quantitative confirmation of the retention of significant ductility in highly irradiated thorium has since been reported.⁽¹⁰⁾

19808

2X

Figure 8. Swaged Specimen H-1, Th-1.39 w/o U, with 2.0 a/o Burnup, Showing Manner in Which Specimen was Bent during Capsule-opening Operations.

The other specimen, No. H-7, failed with a brittle fracture and is shown in Figure 9. This specimen contained 5.53 w/o uranium and had achieved 3.6 a/o burnup.

19814

2X

Figure 9. Swaged Specimen H-7, Th-5.53 w/o U, with 3.6 a/o Burnup, Showing Manner in Which the Specimen Broke with a Brittle Fracture during Capsule-opening Operations.

C. Cast Specimens

Table IV lists the irradiation conditions for the cast specimens and summarizes the changes that were observed. As can be seen, the irradiation conditions were more severe for the cast specimens than for the two preceding groups of specimens. Central irradiation temperatures exceeded 1000°C in some of the specimens, and burnups as high as 10.1 a/o (expressed as percent burnup of all atoms) were achieved.

Table IV
EFFECT OF IRRADIATION ON CAST SPECIMENS

Spec. No.	U, w/o	Melt No.	Burnup, a/o	Midlength Irradiation Temp, °C		Length Change, %	Diameter Change, %	Weight Change, mg	Density Decrease, %	% ΔV_0 (a) a/o Burnup	Remarks
				Surface	Center						
ANL-42-8-1	10.7	C16F-225	0.90	280	290	0.57	1.18	-1.7	1.24	1.4	Upper end swelled.
-4-1	9.43	-221	1.2	330	340	0.89	1.18	-0.6	2.31	2.0	
-6-1	9.43	-221	1.6	450	470	2.90	1.33	41.7	15.65(b)	12	
-2-1	9.43	-221	2.2	650	680	3.25	4.59	-3.5	8.78	4.3	
-3-1	9.43	-221	2.9	370	380	1.87	1.18	-1.0	5.26	1.9	
-1-1	9.43	-221	3.9	510	530	2.24	1.33	-1.3	6.71	1.8	
-7-1	10.7	-225	4.0	420	440	1.97	1.46	-1.1	5.63	1.5	
-5-1	9.43	-221	4.0	540	560	2.27	0.91	-1.4	7.28	2.0	
CP-12-1	15.1	-218	0.16	605	650	0.03	0.20	1.4	0.34	2.1	
-11-2	15.1	-218	0.47	625	665	0.60	1.20	-0.2	1.80	3.9	
ANL-42-8-2	15.2	-224	1.0	290	300	0.52	1.75	-1.7	1.94	2.0	Upper end swelled. Upper end swelled and broken off.
-4-2	15.1	-218	1.4	390	410	0.82	1.45	-3.0	2.95	2.2	
-6-2	15.2	-224	1.8	520	540	3.81	2.87	56.3	3.56(b)	2.1	
-2-2	15.1	-218	2.6	720	750	(c)	5.37	-550.8	11.12(b)	4.8	
-3-2	15.1	-218	3.3	430	450	2.27	1.81	-1.6	5.74	1.8	
-7-2	15.2	-224	3.4	440	460	2.42	1.96	-1.2	7.93	2.5	
-1-2	15.1	-218	4.5	600	630	3.27	2.79	-1.9	9.45	2.3	
-5-2	15.1	-218	4.5	610	640	3.44	2.49	-1.5	10.32	2.5	
CP-12-4	20.4	-219	0.17	605	650	0.23	0.20	-1.0	0.28	1.7	
-11-5	20.6	-229	0.46	500	540	0.59	0.76	1.4	1.80	4.0	
ANL-42-8-3	20.6	-229	1.1	290	300	0.72	1.88	-0.8	1.85	1.7	Upper end swelled. Upper end swelled.
-4-3	20.4	-219	1.5	400	420	0.78	2.29	-3.9	2.48	1.7	
-6-3	20.6	-229	1.9	540	560	3.87	2.08	11.7	4.00(b)	2.2	
-2-3	20.4	-219	2.7	740	770	3.76	7.82	-7.3	12.27(b)	5.2	
-3-3	20.4	-219	3.5	440	460	2.99	2.16	-0.7	7.08	2.2	
-7-3	20.6	-229	3.5	450	470	2.87	1.43	-1.5	7.53	2.3	
-1-3	20.4	-219	4.5	610	640	2.91	3.35	-0.8	10.67	2.6	
-5-3	20.6	-229	4.7	620	650	5.69	2.98	-0.7	12.09	2.9	
ANL-42-8-4	25.2	-223	0.85	250	260	0.91	4.59	-1.4	1.78	2.2	
-6-4	25.2	-223	1.8	510	530	-0.15	3.20	-0.6	3.45	2.0	
-4-4	25.3	-220	2.0	430	450	-0.51	2.22	-2.4	2.35	1.2	Warped, slightly roughened surface. " " " " " "
-2-4	25.3	-220	2.5	620	650	2.49	14.98	21.3	12.30	5.6	
-3-4	25.3	-220	3.0	390	410	-2.25	4.67	-1.0	6.24	1.2	
-7-4	25.2	-223	3.4	430	450	2.22	4.32	-0.5	8.69	2.8	
-5-4	25.2	-223	4.2	580	600	4.72	3.74	-0.5	6.73	1.7	
-1-4	25.3	-220	4.7	640	670	6.63	5.68	1.3	15.25	3.9	
ANL-42-8-5	31.6	Y16F-190	1.7	490	510	-0.68	1.38	-2.0	4.11	2.5	
-4-5	31.4	-189	3.4	690	720	5.05	5.64	-2.8	3.52	1.1	
-6-5	31.6	-190	4.1	860	900	17.2	12.0	45.9	24.81	8.0	
-2-5	31.4	-189	4.8	>1000	>1000	45.0	46.8	(c)	(c)	-	
-3-5	31.4	-189	6.5	690	720	18.1	11.5	4.2	26.86	5.6	Severely distorted.
-7-5	31.6	-190	7.6	830	860	5.09	1.68	-0.1	22.22	3.7	Roughened surface.
-5-5	31.4	-189	9.5	>1000	>1000	25.5	47.0	71.2	45.81	8.5	Severely distorted.
-1-5	31.4	-189	10.1	>1000	>1000	27.5	33.3	60.1	46.36	8.4	Severely distorted.

(a) Calculated from the expression $\% \Delta V_0 = 100 \left(\frac{\rho_i}{\rho_f} - 1 \right)$, where ρ_i and ρ_f are the initial and final densities, respectively.

(b) Measurement taken after swelled end was removed.

(c) Condition of specimen did not permit measurement.

The extra U^{235} content in the 31 w/o uranium alloy specimens resulted in sufficiently high fission rates that it was calculated that the surfaces of three of these specimens exceeded the boiling point of the NaK in which the specimens were submerged. Since the electrical analogue used for temperature calculations was based on conductive heat transfer, it is evident that convective effects arising from boiling would introduce errors of unknown magnitude into the procedure. Because of this, only the minimum possible temperatures are indicated for the three specimens, assuming that all uncertainties are grouped so as to give the lowest temperature. This temperature was taken as 1000°C.

Table V lists the changes in uranium isotopic ratios for the cast specimens which were subjected to mass-spectrographic analysis after irradiation. The buildup of residual U^{233} in the analyzed specimens was as

high as 6.88 percent of the uranium present. The ratios of U^{233} to thorium were approximately double those which would be expected through use of the equations in ANL-5335.⁽⁷⁾ On this basis it is likely that the U^{233} contribution to the burnup in each specimen was also larger than calculated, and hence the total burnup for all specimens is also somewhat higher than that shown in Table IV.

Table V

CHANGES IN URANIUM ISOTOPIC RATIOS RESULTING FROM
IRRADIATION OF THE CAST SPECIMENS

Spec. No.	Preirradiation Analysis or Postirradiation	U^{233} , w/o	U^{234} , w/o	U^{235} , w/o	U^{236} , w/o	U^{238} , w/o
ANL-42-1-3	Preirradiation	-	0.56	50.4	0.25	48.8
	Postirradiation	2.94	0.67	30.4	4.52	61.5
ANL-42-2-1	Preirradiation	-	1.04	93.3	0.46	5.25
	Postirradiation	5.18	1.32	80.7	6.07	6.72
ANL-42-3-1	Preirradiation	-	1.04	93.3	0.46	5.25
	Postirradiation	6.88	1.43	76.3	8.27	7.13
ANL-42-4-3	Preirradiation	-	0.56	50.4	0.25	48.8
	Postirradiation	0.90	0.59	44.7	1.55	52.3
ANL-42-5-4	Preirradiation	-	0.45	40.4	0.20	58.9
	Postirradiation	2.35	0.53	24.11	3.57	69.4
ANL-42-5-5	Preirradiation	-	0.96	93.3	0.40	5.41
	Postirradiation	1.83	1.26	80.86	8.41	7.63
ANL-42-6-4	Preirradiation	-	0.45	40.4	0.20	58.9
	Postirradiation	0.86	0.46	33.9	1.48	63.3
ANL-42-7-2	Preirradiation	-	0.74	65.7	0.33	33.2
	Postirradiation	3.77	0.93	48.5	5.17	41.6
ANL-42-8-2	Preirradiation	-	0.74	65.7	0.33	33.2
	Postirradiation	0.93	0.76	61.3	1.60	35.5
ANL-42-8-5	Preirradiation	-	0.95	93.3	0.40	5.37
	Postirradiation	0.23	0.94	91.7	1.44	5.67

The appearance of typical specimens from each alloy group is shown in Figures 10 through 14. Significant distortion or surface roughening did not develop in most of the specimens containing 20 w/o uranium or less. Swelling was observed at the extreme upper ends of a few of these specimens as a result of locally high temperatures (see Figure 15). It is believed

Negative No.

26692

26673

27696

27427

Specimen No.

ANL-42-8-1

ANL-42-2-1

ANL-42-3-1

ANL-42-5-1

Burnup, a/o

0.90

2.2

2.9

4.0

Max Irradiation Temp, °C

290

680

380

560

 $\frac{\% \Delta \text{Vol}}$

1.4

4.3

1.9

2.0

a/o Burnup

Figure 10. Postirradiation Condition of Typical Cast Thorium-10 w/o Uranium Alloy Specimens.
Magnification 2X.

Negative No.

EI-890

26681

27697

27428

Specimen No.

CP-11-2

ANL-42-4-2

ANL-42-3-2

ANL-42-5-2

Burnup, a/o

0.47

1.4

3.3

4.5

Max Irradiation Temp, °C

665

410

450

640

 $\frac{\% \Delta \text{Vol}}$

3.9

2.2

1.8

2.5

a/o Burnup

Figure 11. Postirradiation Condition of Typical Cast Thorium-15 w/o Uranium Alloy Specimens.
Magnification 2X.

Negative No.

EI-891

26682

27698

27429

Specimen No.

CP-11-5

ANL-42-4-3

ANL-42-3-3

ANL-42-5-3

Burnup, a/o

0.46

1.5

3.5

4.7

Max Irradiation Temp, °C

540

420

460

650

 $\frac{\% \Delta Vol}{a/o Burnup}$

4.0

1.7

2.2

2.9

a/o Burnup

Figure 12. Postirradiation Condition of Typical Cast Thorium-20 w/o Uranium Alloy Specimens.
Magnification 2X.

Negative No.

26695

26683

27436

27693

Specimen No.

ANL-42-8-4

ANL-42-4-4

ANL-42-7-4

ANL-42-1-4

Burnup, a/o

0.85

2.0

3.4

4.7

Max Irradiation Temp, °C

260

450

450

670

 $\frac{\% \Delta Vol}{a/o Burnup}$

2.2

1.2

2.8

3.9

a/o Burnup

Figure 13. Postirradiation Condition of Typical Cast Thorium-25 w/o Uranium Alloy Specimens.
Magnification 2X.

Negative No.	26696	26684	27700	27694

Specimen No.	ANL-42-8-5	ANL-42-4-5	ANL-42-3-5	ANL-42-1-5
Burnup, a/o	1.7	3.4	6.5	10.1
Max Irradiation Temp, °C	510	720	720	>1000
$\frac{\% \Delta Vol}{a/o \text{ Burnup}}$	2.5	1.1	5.6	8.4

Figure 14. Postirradiation Condition of Typical Cast Thorium-31 w/o Uranium Alloy Specimens. Magnification 2X.

Negative No.	26686	26687	26674	26688	26675

Specimen No.	ANL-42-6-1	ANL-42-6-2	ANL-42-2-2	ANL-42-6-3	ANL-42-2-3
Uranium, w/o	10	15	15	20	20
Burnup, a/o	1.6	1.8	2.6	1.9	2.7
Max Irradiation Temp, °C ^(a)	470	540	750	560	770
$\frac{\% \Delta Vol^{(b)}}{a/o \text{ Burnup}}$	12	2.1	4.8	2.2	5.2

(a) Does not apply to upper swelled end of specimen.

(b) Measurement taken after removal of upper swelled end of specimen.

Figure 15. Cast Thorium-Uranium Alloy Specimens which Developed Swelling in Upper End during Irradiation. Magnification 2X.

that the overheating developed from temperature stratification at the top of the NaK surrounding the specimens. A similar condition was observed in some of the thorium-uranium alloy specimens irradiated in capsules by Atomics International.(11,12)

Of greatest interest are the relatively low swelling rates shown by the specimens. The rates of volume change are shown in Table IV. In none of the alloys was a threshold burnup found beyond which the rate of volume increase changed significantly, i.e., density changes were generally linear with increasing burnup. Such a threshold, if it does exist, is beyond 5 a/o burnup for alloys containing 25 w/o uranium or less, and 8 a/o burnup for the 31 w/o uranium alloy.

The effect of temperature on the rate of volume increase is shown in Figure 16. Between 100 and 650°C the average rate of volume increase increases slowly from approximately 1% volume increase per a/o burnup to a value of 2.5. Thereafter, the swelling rate increases at a greater rate to a value of approximately 6% volume increase per a/o burnup at 800°C. Above this temperature, for which the temperature calculations were less accurate, the maximum swelling rate was 8.5% volume increase per a/o burnup.

106-7101 Rev.

Figure 16. Effect of Irradiation Temperature on the Swelling Rate of Thorium and Thorium-Uranium Alloys.

As mentioned earlier, the alloys with the higher uranium contents showed significant distortion and surface roughening. The swelling rates of all of the alloys irradiated were surprisingly similar, however, including those with the higher uranium contents. Figure 17 shows a comparison of the swelling rates of the cast thorium-uranium alloys used in the present study compared with reported swelling rates of various other thorium and uranium-base alloys.

106-7271

Figure 17. Comparison of the Swelling Rate of the Cast Thorium-Uranium Alloys Used in the Present Study (Curve 6) Compared with the Swelling Rates Reported for Various Other Uranium and Thorium-base Alloys.

The excellent swelling resistance of the specimens containing 25 w/o uranium or less has been recently confirmed in a series of post-irradiation annealing experiments.⁽¹³⁾ In these experiments, a specimen with at least 4.0 a/o burnup irradiated at 640°C or lower from each of the alloys containing 10, 15, 20, and 25 w/o uranium, was subjected to a series of 100-hr anneals at progressively higher temperatures. The annealing treatments were started at 550°C. After 100 hr at an annealing temperature of 775°C, plus 600 hr prior annealing at temperatures between 550 and 775°C, the maximum cumulative volume increase observed was 3.7% volume increase per a/o burnup.

Metallographic sections were made from at least one irradiated specimen from each alloy composition. The polished sections were electrolytically etched with a 5:4:5 mixture of phosphoric acid, ethylene glycol, and ethyl alcohol. The changes in microstructure for each alloy are shown in Figures 18 through 22. All the alloys but that with 15 w/o uranium showed grain-boundary agglomeration of the uranium phase as a result of irradiation. This was particularly evident in the 25 and 31 w/o alloys. Some cracking was also observed in the 31 w/o alloy (see Figure 23). Figure 21 shows an area in the 25 w/o alloy where particles of the uranium phase happened to have been removed by etching. The resulting voids should not be attributed to swelling produced by fission gas (see also reference 12).

EI-1

250X

a. Before Irradiation

29212

250X

b. After 4.0 a/o Burnup at 560°C
(Specimen ANL-42-5-1)

Figure 18. Effect of Irradiation on the Microstructure of Thorium-10 w/o Uranium Alloy from Melt No. C16F-221.

EI-2

250X

a. Before Irradiation

29213

250X

b. After 4.5 a/o Burnup at 640°C
(Specimen ANL-42-5-2)

Figure 19. Effect of Irradiation on the Microstructure of Thorium-15 w/o Uranium Alloy from Melt No. C16F-218.

EI-4

250X

a. Before Irradiation

29214

250X

b. After 4.7 a/o Burnup at 650°C
(Specimen ANL-42-5-3)

Figure 20. Effect of Irradiation on the Microstructure of Thorium-20 w/o Uranium Alloy from Melt No. C16F-229.

EI-7

a. Before Irradiation

250X

29211

b. After 2.5 a/o Burnup at 650°C
(Specimen ANL-42-2-4)

250X

Figure 21. Effect of Irradiation on the Microstructure of Thorium-25 w/o Uranium Alloy from Melt No. C16F-220. The Voids Resulted from Overetching of the Uranium Phase, and Not From Swelling.

35440

250X

a. Before Irradiation

29216

250X

b. After 7.6 a/o Burnup at 860°C
(Specimen ANL-42-7-5)

Figure 22. Effect of Irradiation on the Microstructure of Thorium-31 w/o Uranium Alloy from Melt No. Y16F-190.

28579

250X

Figure 23. Cracking in Thorium-31 w/o Uranium Alloy Irradiated to 4.1 a/o Burnup at 900°C. (Specimen ANL-42-6-5)

The rate of volume increase of thorium-uranium alloys under irradiation is no doubt dependent upon the size and distribution of the uranium phase, in which most of the fission events occur. If the maximum dimension of a uranium particle is less than the recoil range in uranium of the fission products, then all of the fission recoils will escape from the uranium particle into the adjoining thorium matrix. Under these conditions, anisotropic growth of the specimen would not be expected to occur because of the isotropic cubic lattice of thorium. More importantly, the rate of volume change would be less because the less densely packed thorium lattice presumably can accept interstitial impurity atoms with less lattice strain.

The probability $\bar{f}$ of escape of recoils with the range R in spherical particles of diameter D has been given as:⁽¹⁴⁾

$$\bar{f} = \frac{3}{4} \left(\frac{2R}{D} \right) - \frac{1}{16} \left(\frac{2R}{D} \right)^3 \quad (1)$$

The range of fission fragments in uranium is reported to be 12.6 mg/cm²,⁽¹⁵⁾ equal to a linear distance of 6.6 μ .

In thorium-uranium alloys, however, the uranium phase does not tend to occur in the form of discrete spherical particles, but rather as irregularly shaped particles that are thin relative to their length and width. In the higher uranium compositions studied in the present investigation, the uranium particles approached the form of complete grain-boundary

envelopes. The probability of recoil escape from particles with slab geometry and with thickness t is⁽¹⁶⁾

$$\bar{f} = R/2t \quad \text{if } t \geq R,$$

or

$$\bar{f} = 1 - \frac{t}{2R} \quad \text{if } t \leq R. \quad (2)$$

A plot of this function for uranium particles is shown in Figure 24.

Figure 24. Probability of Escape of Fission Recoils from Uranium Particles with Slab Geometry as a Function of Particle Thickness.

As has been stated earlier, the particle thickness in most of the present alloys was less than one micron. It is evident from Figure 24 that a large fraction of the fission recoils in these alloys escaped from the uranium particles into the thorium matrix. Whether or not they came to rest in adjoining uranium particles would be dependent upon the orientation and spacing of the particles and upon the range of the recoils in thorium. A search of the literature for the range of fission recoils in thorium was unsuccessful, so that the probability of a fission recoil coming to rest in an adjoining uranium particle was not calculated.

As indicated in Figure 17, the cast specimens in the present study showed significantly lower rates of volume change at irradiation temperatures above 600°C than did a group of Th-11 w/o U alloy specimens irradiated by Atomics International.^(11,12) A photomicrograph of their alloy, shown in reference 12, indicates that the thickness of the uranium particles was of the order of 5 to 10 μ . It is evident that a larger fraction of fission recoils would have been retained in the uranium particles in the Atomics International alloy than in the uranium particles in the Argonne alloys, so that this may account for the difference in behavior.

CONCLUSIONS

1. Wrought thorium and thorium-uranium alloys containing at least 5.5 w/o uranium show no evidence of anisotropic growth under irradiation.
2. Excellent surface smoothness is shown under irradiation by cast thorium-uranium alloys containing as much as 20 w/o uranium to total atom burnups of at least 5 percent.
3. Small-diameter castings of thorium-uranium alloys containing as much as 31 w/o uranium do not show excessive swelling rates at irradiation temperatures of 800°C or higher and to total atom burnups of 4 percent or higher.

ACKNOWLEDGEMENTS

The authors are indebted to A. B. Shuck, R. J. Dunworth, F. L. Yaggee, and W. R. Burt for preparing the experimental specimens. Measurements before and after irradiation were taken by R. Fousek, F. Pausche, A. C. Klank, D. A. Donahue, and H. E. Strohm. The metallographic preparation was done by R. Carlander, C. H. Gebo, and J. C. Florek. Radiochemistry and isotopic analyses were supplied by R. P. Larsen, P. Kafalas, C. M. Stevens, and the Nuclear Science and Engineering Corporation. Finally, the authors wish to acknowledge the helpful cooperation of the operating staffs at the NRX, MTR, and CP-5 reactors.

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