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by

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ABSTRACT

A specimen of cast thorium-5 w/o plutonium and one of thorium-10 w/o plutonium were irradiated to total atom burnups of 1.9 and 2.6 per cent, respectively, at maximum fuel temperatures of approximately 450°C. Both alloys displayed excellent dimensional stability with volume increases of 0.8 and 1.2 per cent per atom per cent burnup, respectively. Three cold-rolled specimens of zirconium-5 w/o plutonium and one cold-rolled specimen of zirconium-7 w/o plutonium were also irradiated. The zirconium-plutonium alloy specimens all showed extremely poor dimensional stability, with anisotropic elongations ranging from approximately 100 to 500 per cent. The irradiation growth coefficients for these specimens ranged from 90 to 210 microinches per inch per atom per cent burnup. The poor dimensional stability of the zirconium-plutonium alloy specimens is attributed to a highly preferred grain orientation that presumably developed during cold rolling.

INTRODUCTION

In the fuel alloy-development program for fast breeder reactors at Argonne National Laboratory, considerable emphasis has been placed on the study of the dimensional stability of plutonium-containing fuel alloys under irradiation. In a recent experiment, specimens of 2 thorium-plutonium alloys and 2 zirconium-plutonium alloys were irradiated at the MTR. This report describes the effects of irradiation at moderate temperatures on the binary alloys zirconium-5 w/o plutonium, zirconium-7 w/o plutonium, thorium-5 w/o plutonium, and thorium-10 w/o plutonium. Three specimens of the zirconium-5 w/o plutonium were irradiated; only a single specimen of each of the other alloys was available. The effects of irradiation on some ternary and quaternary alloys containing uranium, plutonium, and the "fissium" elements are described separately.[1]

The irradiations were intended to be a preliminary, qualitative screening test to determine which of the alloys are most promising for further development and to obtain preliminary information regarding temperature and burnup limits.

The thorium-plutonium alloy specimens were studied to provide information about the dimensional stability of this material under irradiation. This alloy system is of interest for breeding purposes, particularly in reactor systems which have 2-region fast and thermal cores.

In addition, the excellent irradiation stability of the thorium base thorium-uranium alloys in the temperature region from 600 to 700°C[2] suggested that the thorium base thorium-plutonium alloys might have a high degree of dimensional stability at elevated temperatures. Thorium is capable of dissolving up to approximately 47 atomic per cent plutonium at 619°C,[3,4] which is in the temperature range of current interest for most metal-fueled power reactors.

Fabrication tests with the zirconium-plutonium alloys indicated that these alloys were easy to fabricate. Arc-melted and cast specimens of the zirconium-5 w/o plutonium alloy had a density of 6.70 gm/cc which is within 1 per cent of the calculated density. The as-cast optical metallographic structure appeared to be alpha-phase zirconium-plutonium solid solution. One specimen of the alloy was reduced 62 per cent in thickness by hot pressing at 730°C; another specimen was reduced 36 per cent in thickness at 530°C. A third specimen was reduced 11 per cent at 25°C. The hot pressing was performed with a Riehle testing machine which has a load limit of 60,000 lb. It is reasonable to assume that further reductions in thickness could be obtained by hot pressing with equipment which is capable of applying a greater load to the specimens.

Following the hot pressing to a reduction of 62 per cent in thickness the specimen was cold rolled an additional 97.5 per cent. This degree of cold rolling is about the maximum cold reduction possible in unalloyed zirconium. The hardness of the cast alloy was increased from 43 R_A to 53 R_A by a 50 per cent reduction by cold rolling. The relative ease of fabricating this alloy made it worthwhile to obtain knowledge about the dimensional stability of the material under irradiation.

SPECIMEN MATERIAL AND PREPARATION OF IRRADIATION SPECIMENS

The chemical analyses of the thorium and plutonium used to make the thorium-plutonium alloys are contained in Tables I and II, respectively. The specimens consisted of 5 and 10 nominal w/o plutonium dissolved in thorium. The alloys were induction melted under vacuum in a high-purity thoria crucible; the melt was top poured at a temperature of 1800°C into a graphite mold.

Table I

ANALYSES OF THE THORIUM USED TO MAKE THE THORIUM-PLUTONIUM ALLOYS

Element	Parts per Million
By Spectrographic Analysis	
Iron	110
Manganese	2
Copper	30
Aluminum	45
Beryllium	150
Silicon	< 50
Magnesium	< 20
Boron	< 20
Cadmium	< 20
Zinc	< 20
By Chemical Analysis	
Nitrogen	110
Carbon	370

Table II

ANALYSES OF THE PLUTONIUM USED TO MAKE THE THORIUM-PLUTONIUM AND ZIRCONIUM-PLUTONIUM ALLOYS

Element	Parts per Million
By Spectrographic Analysis	
Aluminum	150
Boron	2 5
Barium	1
Beryllium	<0.01
Calcium	250
Cadmium	<10
Cobalt	15
Chromium	250
Copper	75
Iron	500
Gallium	250
Hafnium	<2.5
Potassium	5
Lithium	0 05
Magnesium	250
Manganese	50
Molybdenum	10
Sodium	5
Nickel	500
Lead	100
Tin	<5
Thorium	<2.5
Titanium	<2.5
Zinc	~50
Zirconium	100
By Chemical Analysis	
Oxygen	429
Carbon	99

The castings were then machined into specimens which were a nominal 0.875 in. long by 0.144 in. in diameter. According to the equilibrium diagram, the thorium-plutonium alloys were presumably single-phase solid solutions of plutonium dissolved in face-centered-cubic thorium.

The zirconium-plutonium alloys were made from Grade I crystal bar zirconium and the plutonium described in Table II. The alloys consisted of 5 and 7 nominal w/o plutonium dissolved in zirconium. The alloying was performed by arc melting in a helium atmosphere. Prior to melting the zirconium and plutonium, the static helium atmosphere was cleaned up by melting several zirconium "getter" buttons. The arc melting produced zirconium-plutonium alloy buttons approximately $\frac{5}{8}$ in. in diameter and approximately $\frac{5}{16}$ in. thick. The as-cast buttons were forged at room temperature with a hammer to a rhombohedral cross section. The forging operation produced a shape that would enter the rolling mill without undue difficulty. After forging, the specimens were rolled at room temperature to produce rods 0.160 in. in diameter. The total reduction in area produced by the forging and rolling was approximately 90 per cent. The specimens were subsequently machined into irradiation specimens which were a nominally one inch long and 0.144 in. in diameter.

The metallographic structure, as shown by polarized light, of the as-cast zirconium-5 w/o plutonium alloys is shown in Figure 1. The etchant used was 2 parts hydrofluoric acid, one part nitric acid, and 20 parts glycerol. The structure appeared to be a single-phase solid solution of plutonium dissolved in hexagonal close-packed zirconium, with some twinning present in each grain. The anisotropic behavior of the structure under polarized light suggested that the structure was close-packed hexagonal alpha zirconium. Preliminary irradiation results of the zirconium-plutonium alloys have been reported elsewhere.[5]

EXPERIMENTAL PROCEDURES

Prior to irradiation, the thorium-plutonium alloy specimens were thermally cycled 200 times as follows: They were transferred mechanically from a sodium bath held at 50°C to one held at 500°C within a transfer time of one minute, held at 500°C for 5 min, returned to the bath at 50°C within one minute, and held at 50°C for 5 min; this cycle was repeated for a total of 200 times. Unfortunately, the thermal-cycling apparatus was disassembled prior to the preparation of the zirconium-plutonium alloys; hence, these specimens were not tested for thermal-cycling stability prior to irradiation.

218 75X

Figure 1. Metallographic structure as revealed by polarized light of zirconium-5 w/o plutonium alloy in the as-cast condition.

The following properties of the specimens were measured prior to irradiation:

1. dimensions to 0.0001 in.;
2. weights to 0.1 mg;
3. density to 0.05 per cent, by immersion in CCl_4;
4. mass spectrographic analysis for concentration of plutonium isotope.

The typical preirradiation appearance of the specimens is shown in Figure 2.

27548 2X

Figure 2

Typical preirradiation appearance of thorium-plutonium and zirconium-plutonium alloy specimens.

The specimens were placed in irradiation capsules of zirconium. The capsules were evacuated and the specimens were covered with sufficient eutectic NaK to provide adequate heat transfer from the fuel to the process coolant water. The gas pressure which existed above the NaK in the capsules after they were filled was 1.4×10^{-4} mm of mercury. Each irradiation capsule contained 3 specimens, located 120° apart, as shown in Figure 3.

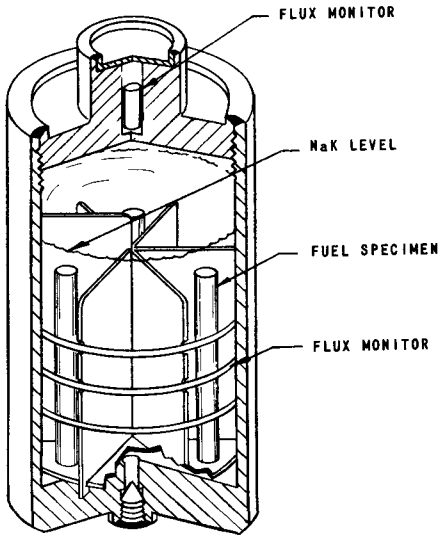

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Figure 3. Typical irradiation capsule assembly. The capsule is 3-1/8 in. long and 1-1/8 in. in diameter.

Each capsule contained 2 aluminum-0.5 w/o cobalt-0.5 w/o manganese wires, which were included for neutron dosimetry. The integrated neutron fluxes indicated by the dosimeters were used in computing preliminary temperature and burnup data on the specimens after corrections for resonance activation of the cobalt were made. Mass spectrographic isotopic analyses for the plutonium isotope distributions were also performed for 3 of the 6 specimens before and after irradiation. The preirradiation and postirradiation plutonium isotope compositions of these 3 specimens are contained in Table III. In addition to providing the best available measurement of the burnup and temperature experienced by the specimen, these specimens also provided a calibration for the dosimeter-indicated burnup and temperature for the other specimens in the same irradiation capsule.

Table III

PLUTONIUM ISOTOPE COMPOSITION OF SPECIMENS ANALYZED MASS SPECTROGRAPHICALLY BEFORE AND AFTER IRRADIATION

Specimen Number	Preirradiation Plutonium Composition Mole Per Cent				Postirradiation Plutonium Compositon, Mole Per Cent			
	Pu^{239}	Pu^{240}	Pu^{241}	Pu^{242}	Pu^{239}	Pu^{240}	Pu^{241}	Pu^{242}
ANL-36-12-1	94 48 ± 0 05	5 16 ± 0 05	0 342 ± 0 005	0 0140 ± 0 0004	69 51 ± 0 13	26 17 ± 0 13	3 73 ± 0 05	0 583 ± 0 009
ANL-36-12-2	94 48 ± 0 05	5 16 ± 0 05	0 342 ± 0 005	0 0140 ± 0 0004	77 95 ± 0 09	19 89 ± 0 09	2 00 ± 0 02	0 237 ± 0 003
ANL-36-13-3	94 48 ± 0 05	5 16 ± 0 05	0 342 ± 0 005	0 0140 ± 0 0004	58 9 ± 0 2	32 2 ± 0 2	7 02 ± 0 04	1 81 ± 0 02

The burnups were computed by the first method presented in IDO-16620.[6] The nomenclature has been changed from that in the reference to that as follows:

$$\% \text{ Pu burnup} = \frac{(1+\alpha)(Pu^{239}{}_b - Pu^{239}{}_a)}{Pu^{239}{}_b\,(1+\alpha - Pu^{239}{}_a)} \times 100 \quad , \qquad (1)$$

where

Pu^{239}_b = fraction of the plutonium present which is Pu^{239} before irradiation,

Pu^{239}_a = fraction of the plutonium present which is Pu^{239} after irradiation,

$\alpha = \sigma_c/\sigma_f = 0.38$,

and

σ_c = nonfission capture cross section (280×10^{-24} cm^2)

σ_f = fission cross section (746×10^{-24} cm^2).

From the burnup values obtained by this method, the average perturbed fluxes necessary to induce the burnups were computed by use of the equation

$$\text{Total a/o burnup} = Af \frac{\sigma_f}{\sigma_a} [1 - \exp(-\phi t \sigma_a)] \quad ,$$

where

A = atomic per cent plutonium in fuel

f = fraction of the plutonium which is fissionable

σ_a = absorption cross section (1026×10^{-24} cm^2)

ϕ = neutron flux (neutrons/cm^2-sec)

t = irradiation time (seconds).

All values for nuclear cross sections were taken from reference 7.

From the results obtained from the 3 specimens subjected to mass spectrographic analyses, the average perturbed fluxes incident upon the other 3 adjacent specimens could also be computed. The fluxes obtained by this method were used to compute the burnup in the remaining 3 specimens. The temperatures which existed in all of the specimens during the irradiation were determined with the aid of an electrical-geometrical analogue.[8]

The same properties measured prior to irradiation were measured after irradiation on the thorium-plutonium alloy specimens, with the exception of hardness. The only measurements made with the zirconium-plutonium alloy specimens after irradiation were weight and density. Length and diameter measurements were not possible because of the shape of these specimens after irradiation. Length changes for these specimens were estimated from photographs of the specimens at a known magnification.

RESULTS AND DISCUSSION

The results of thermal cycling of the thorium-plutonium alloy specimens are shown in Table IV. The dimensions of both specimens were relatively unaffected by the cycling tests. As might be expected, the changes that were observed were larger in the specimen containing the greater amount of plutonium.

Table IV

EFFECTS OF THERMAL CYCLING OF THORIUM-PLUTONIUM ALLOY SPECIMENS[a]

	Specimens	
	ANL-36-12-1	ANL-36-12-2
Composition, w/o	Th-5 Pu	Th-10 Pu
Weight Change, %	0.04	-0.14
Length Change, %	0.05	0.19
Mean Diameter Change, %	-0.14	-0.42
Density Change, %	-0.06	-0.41

[a]Each specimen was thermally cycled 200 times in sodium between 50 and 500°C.

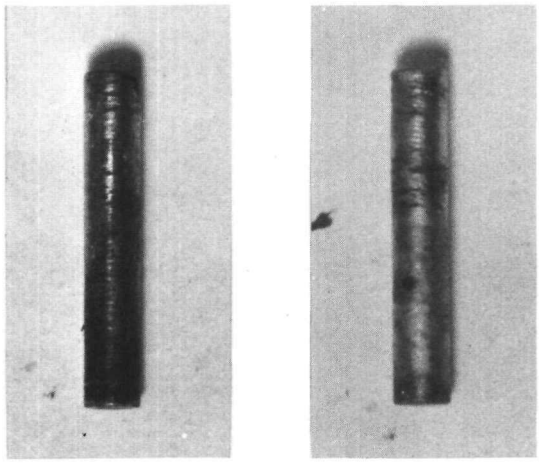
Table V is a summation of the irradiation data obtained on all of the specimens. Figure 4 shows the postirradiation appearance of the thorium-plutonium alloy specimens. The circumferential striations on both of the specimens are machining marks which were present prior to irradiation. The thorium-plutonium alloys showed excellent dimensional behavior to burnups from 1.4 to 2.6 a/o at maximum calculated fuel temperatures of approximately 450°C.

Table V

EFFECTS OF IRRADIATION OF THORIUM-PLUTONIUM AND ZIRCONIUM-PLUTONIUM ALLOYS

Specimen No	Composition	Burnup, a/o	Max Fuel Temp, °C		Length Change %	G_f microinches/in / fission/10^6 total atoms	Diameter Change %	Density Decrease, %	% ΔV / a/o Burnup	Weight Change mg
			Center	Surface						
ANL-36-12-1	Th 5 w/o Pu	1 9	440	420	0	0	1 2	1 6	0 8	-0 3
ANL-36-12-2	Th-10 w/o Pu	2 6	460	440	0 9	0 35	0 8	3 1	1 2	1 9
ANL-36-12-3	Zr-5 w/o Pu	0 8	430	410	100	85	(a)	2 6	3 3	-8 4
ANL-36-13-1	Zr-5 w/o Pu	0 9	530	510	250	140	(a)	3 0	3 3	-361 2
ANL-36-13-3	Zr-5 w/o Pu	0 9	530	510	500	200	(a)	24[b]	32[b]	26 5
ANL-36-13-2	Zr-7 w/o Pu	1 3	530	510	200	85	(a)	1 3	1 0	15 0

[a]Measurements not obtained due to the postirradiation shape of the specimens
[b]Includes globular mass

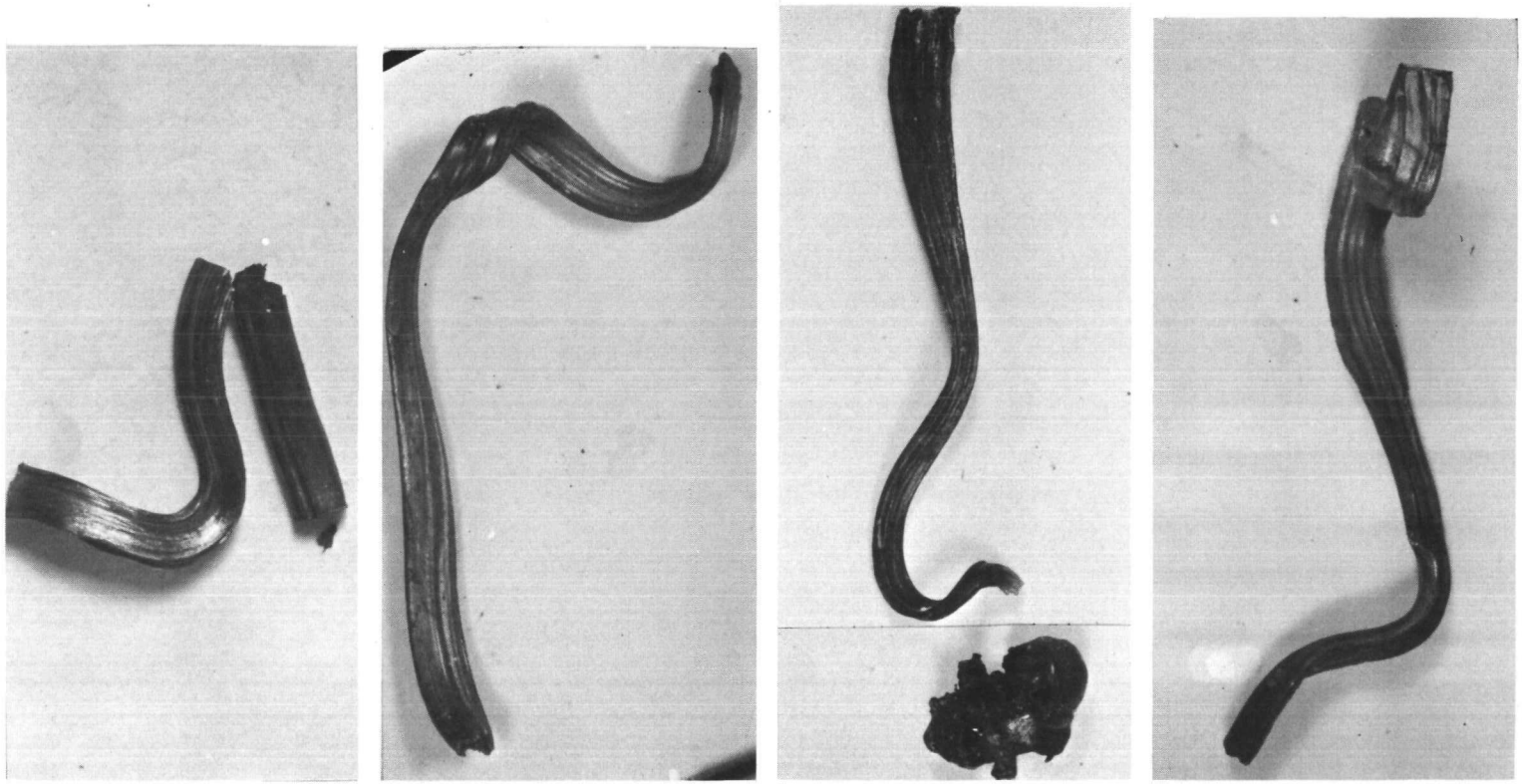


Neg. No.	27254	27255
Specimen No.	ANL-36-12-1	ANL-36-12-2
Composition	Th-5 w/o Pu	Th-10 w/o Pu
Burnup, a/o	1.9	2.6
Max Fuel Temp, °C	440	460
% $\Delta V/a/o$ Burnup	0.8	1.2

Figure 4. Postirradiation appearance of cast thorium-plutonium alloy specimens. Magnification 2X.

This behavior is even more encouraging when one considers the recent work of Pugh at Harwell.[9] In the irradiation experiments conducted at Harwell, the only experiments in which large amounts of irradiation-induced swelling were observed were those in which the irradiation capsules were partially evacuated. Film boiling on the surface of the specimens with resulting high specimen temperature was considered to be the cause of the large amounts of swelling observed in these cases. As previously mentioned, the pressure in the present capsules was 1.4×10^{-4} mm of Hg. At 227°C, which is estimated to be near the average NaK temperature which existed in the capsules during irradiation, NaK has a vapor pressure of 1.8×10^{-3} mm of Hg.[10] This is more than 10 times the pressure which existed in these capsules. It is believed that film boiling on the surface of the specimens is quite likely to have occurred under these conditions and that at least some parts of the specimens may well have been considerably hotter than the calculated 450°C mentioned above.

Figure 5 shows the postirradiation appearance of the zirconium-plutonium alloy specimens. Specimens ANL-36-13-1, -2, and -3 were irradiated to the same exposure at the same temperature. The irradiation temperature listed is that which existed at the beginning of the irradiation and is based on the initial cylindrical geometry. The temperature decreased as the specimens underwent the dimensional distortion illustrated.



Neg. No.	27262	25639	25641	25640
Specimen No.	ANL-36-12-3	ANL-36-13-1	ANL-36-13-3	ANL-36-13-2
Composition	Zr-5 w/o Pu	Zr-5 w/o Pu	Zr-5 w/o Pu	Zr-7 w/o Pu
Burnup, a/o	0.8	0.9	0.9	1.3
Max Fuel Temp, °C	430	530	530	530
% Δ V/a/o Burnup	3.3	3.3	32 (includes globular mass)	1.0

Figure 5. Postirradiation appearance of cold-rolled zirconium-plutonium alloy specimens. Magnification 2X.

Specimen 36-13-1 has anisotropically grown to approximately 3 in. long, with a corresponding decrease in cross section. The only volume change experienced by the specimen is that induced by the production of solid fission product atoms. One-fifth of the specimen was welded to the specimen holder and could not be removed. Therefore, in reality, 0.8 in. of the specimen elongated to 3 in., which resulted in a growth of from 200 to 250 per cent. The growth coefficient, G_i, was calculated from the relation

$$G_i = \frac{\ln L/L_0}{F} \quad ,$$

where

L_0 = preirradiation length of specimen

L = postirradiation length of specimen

F = fraction of all atoms which have fissioned.

For specimen 36-13-1, the value of G_i was 150 microinches/in. per fission/10^6 total atoms. Specimen 36-13-2 had elongated to approximately 3 in., which is a growth of approximately 200 per cent (G_i = 85). Approximately two-thirds of specimen 36-13-3 was welded to the specimen holder; however, this piece was broken free of the specimen holder, as shown in Figure 5. This portion of the specimen consists of several loops folded upon themselves. The remaining one-third of the specimen grew to a length of approximately 2 in., which is a growth of 500 per cent (G_i = 210).

The final specimen, 36-12-3, was irradiated to a lower exposure than the 3 previous specimens. This specimen grew to approximately 2 in. in length (G_i = 90) and contained a loop in the center of it before it fell apart during removal from the specimen holder. This loop is not clearly evident in Figure 5. Some evidence of the loop is shown by the large shadow adjacent to one portion of the specimen indicating that this portion of the specimen is in a plane above that of the rest of the specimen.

All of the zirconium-plutonium specimens developed a trapezoidal cross section and longitudinal striations running the length of the specimens. The trapezoidal cross sections which developed indicate that the thickness reductions were not uniform in all diametral directions. This is not completely unexpected, since the specimens had a rhombohedral cross section during the first few passes in the rolling mill.

The reactor was shut down or reduced to a lower power level 88 times during the period that these specimens were in the reactor. The thermal cycling produced by these shutdowns and power reductions and subsequent startups also may have contributed to the growth of these specimens. No particular differences were evident between the anisotropic growth characteristics of the 5 w/o plutonium alloy and the

7 w/o plutonium alloy. The irradiation behavior of these specimens is similar to that observed on unclad zirconium-7 and -8 w/o uranium alloys at Knolls Atomic Power Laboratory.[11]

The desirable properties of a cast, isotropic cubic structure compared with those of a highly anisotropic structure produced by cold working are clearly demonstrated by the excellent dimensional stability of the thorium-plutonium alloy specimens compared with the irradiation behavior of the zirconium-plutonium alloy specimens.

CONCLUSIONS

1. Cast alloys of thorium containing 5 and 10 w/o plutonium exhibit excellent dimensional stability to burnup levels of 1.9 to 2.6 a/o at maximum fuel temperatures of approximately 450°C.

2. Cold-rolled zirconium-5 and -7 w/o plutonium alloys have poor dimensional stability under irradiation. These materials appear to be of little use as a reactor fuel material unless preferred grain orientations are removed or unless they are adequately restrained by strong cladding.

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