2-

**IRRADIATION BEHAVIOR
OF ZIRCALOY-2 CLAD
THORIUM-URANIUM-ZIRCONIUM
FUEL ELEMENTS
INTERIM REPORT 1**

J. W. GOFFARD
R. K. MARSHALL

SEPTEMBER, 1967

**AEC RESEARCH &
DEVELOPMENT REPORT**

ROUTE TO	FILE NO.	LOCATION	FILE/ROUTE DATE
DON for	60008	703	JAN 22 1968
L H RICE	51583	3703	1-29-68

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

PACIFIC NORTHWEST LABORATORY

RICHLAND, WASHINGTON

operated by

BATTELLE MEMORIAL INSTITUTE

for the

UNITED STATES ATOMIC ENERGY COMMISSION UNDER CONTRACT AT(45-1)-1830

PRINTED BY/ FOR THE U. S. ATOMIC ENERGY COMMISSION

3 3679 00060 6147

BNWL-479
UC-25, Metals, Ceramics,
and Materials

IRRADIATION BEHAVIOR OF ZIRCALLOY-2 CLAD
THORIUM-URANIUM-ZIRCONIUM FUEL ELEMENTS
INTERIM REPORT 1

By

J. W. Goffard and R. K. Marshall

Process Metallurgy Section
Metallurgy Department

September, 1967

RECEIVED
DISTRIBUTION DATE 001 23 '67

PACIFIC NORTHWEST LABORATORY
RICHLAND, WASHINGTON

Printed in the United States of America
Available from
Clearinghouse for Federal Scientific and Technical Information
National Bureau of Standards, U.S. Department of Commerce
Springfield, Virginia 22151
Price: Printed Copy \$3.00; Microfiche \$0.65

TABLE OF CONTENTS

LIST OF FIGURES	iv
LIST OF TABLES.	iv
ABSTRACT.	1
INTRODUCTION.	1
SUMMARY AND CONCLUSIONS	2
BACKGROUND.	3
FUEL ELEMENT FABRICATION.	5
FUEL ELEMENT IRRADIATION.	5
Test Facilities.	5
Test Assembly.	5
Interim Examinations	7
Current Test Status.	7
POSTIRRADIATION EVALUATION.	12
Visual Examination	12
Simulated Rupture Test	14
Metallographic Studies	14
Fuel Density	17
Postirradiation Anneal	21
Fuel Hardness.	24
Notch-Fracture Test.	24
Fuel Burnup and Isotopic Analysis.	24
DISCUSSION.	26
REFERENCES.	27

LIST OF FIGURES

1	Test Elements	6
2	Test Assembly Hardware with Aluminum Dummies	8
3	Swelling Behavior of Th-U-Zr Fuel Elements	10
4	As-received Irradiated Fuel Element GEH-10-66	13
5	Simulated Rupture Test Behavior	15
6	Pre- and Postirradiation Microstructure	16
7	Electron Micrograph of Irradiated Th-U-Zr Alloy Fuel, 4480X	18
8	Electron Micrograph of Irradiated Th-U-Zr Alloy Fuel, 14400X	19
9	Photomicrograph of 0.0013 in. Thick Oxide Film on Clad	20
10	Composite Photograph of Bond, Hydride Precipitates and Oxide Film	21
11	Irradiated Fuel After Vacuum Anneal	22
12	Photomicrographs Showing Gas Porosity After Vacuum Anneal	23
13	Microphotographs of Notch-Fracture Sample	25

LIST OF TABLES

I	Summary of Capsule Irradiation Experiments	4
II	Experimental Conditions and Facility	7
III	Irradiation Data on Th-2.5 wt% U-1 wt% Zr Fuel Elements	9
IV	Summary of Swelling Data of the Th-U-Zr Fuel Element GEH-10-66	22
V	Comparison of Pre- and Post Hardness	24
VI	Burnup and Uranium Isotopic Analysis--Fuel Element GEH-10-66	26

IRRADIATION BEHAVIOR OF ZIRCALOY-2 CLAD
THORIUM-URANIUM-ZIRCONIUM FUEL ELEMENTS
INTERIM REPORT 1

J. W. Goffard and R. K. Marshall

ABSTRACT

Seven tubular Th-2.5 wt% enriched U-1.0 wt% Zr alloy fuel elements are being irradiated under water cooled power reactor conditions. Irradiation performance of these Zircaloy-2 clad elements has been excellent to burnups of 2.1 at.% of the total atoms (18,600 MWd/ton). Measured volume expansion of the alloy fuel has been at a rate approximately equal to that expected from the solid fission fragments.

One element was destructively examined after an exposure of 1.4 at.% burnup (12,000 MWd/ton). No evidence of fuel porosity was found, and little evidence of crystallographic damage was noted in the structure of the fuel.

It is expected from existing data that the fuel will readily achieve 3.0 at. % burnup under water cooled power reactor conditions. Irradiation is continuing toward this goal exposure.

INTRODUCTION

This report describes the performance and evaluation of high burnup, metallic, thorium-uranium-zirconium alloy fuel elements irradiated at power reactor conditions. The metallic tubular elements, which have been clad with and bonded to Zircaloy-2 by the coextrusion process, are being irradiated in a high temperature, pressurized water environment in the Engineering Test Reactor (ETR)* to a goal exposure of 3.0 at.% burnup, and

have performed successfully to two-thirds of that goal. Destructive evaluation has been completed on an element that had attained about 1.4 at.% burnup.

The fabrication history, the irradiation history, and the current status of the seven elements in this test are presented. One of the fuel elements has been returned to Battelle Northwest for a thorough postirradiation examination and evaluation to confirm the exposure and fuel swelling data and to determine the effect of irradiation and operation history upon the character and properties of the element. Initial studies were visual examination, simulated rupture test, and metallographic

* ETR is at National Reactor Testing Station near Idaho Falls, Idaho.

examination. Additional studies were made of fuel hardness, the fuel-to-clad bond character, and the fuel response to a high temperature vacuum anneal. Burnup analyses and uranium isotopic analyses completed the postirradiation evaluation.

The present program of testing and evaluating prototype thorium-uranium fuel elements under power operating conditions is intended to furnish some of the needed technical and operational data to permit the design of thorium-containing fuel systems for lowest possible costs.

SUMMARY AND CONCLUSIONS

Six test elements are under irradiation in the ETR with maximum fuel temperatures ranging from 350 to 600 °C. A maximum of 2.1 at.% burnup has been attained. The fuel volume increase for the highest exposure element in test is only 3.4%, and this amount of fuel swelling has been readily accommodated by the element. This fuel volume increase is equivalent to a calculated volume increase based on the conversion of thorium atoms to uranium atoms and the accumulation of solid fission products from the total fuel burnup. Indications are that the goal burnup of 3.0 at.% is realistic and will be readily attained by these fuel elements.

A test element (one of the seven elements) was returned to Battelle-Northwest from the test reactor after attaining 1.4 at.% burnup and incurring an indicated 1.6% fuel volume increase. This element has been studied in great detail, including rupture testing at simulated power reactor conditions.

Visual examination revealed no superficial changes in the element but did show some spalling of clad oxide film from the outer surface. A 1% length increase and a 0.4% outside diameter increase were noted.

The suitability of the fuel element to power reactor service conditions was demonstrated by rupture testing in a high temperature, pressurized, flowing water facility. Even though material properties were altered by the irradiation, failure damage developed slowly and fuel losses from the element were small.

Optical metallography of the fuel indicated an essentially unaltered appearance to the structure. The clad, however, was changed by the exposure-induced development of a 1.3 mil thick oxide layer on the coolant surface and by an internal hydride content that was consistent with a hot vacuum extraction analysis of 150 ppm hydrogen. Electron microscopy did not yield evidence of porosity or crystallographic damage in the thorium matrix of the fuel alloy. The dispersed enriched uranium phase which suffered very high burnup (~50%) showed severe damage in high resolution electron micrographs.

Fuel swelling in this element was indicated to be 1.6% on the basis of interim element bulk density measurements. Postirradiation density determinations on fuel samples averaged 2.6% volume increase. A correction to the element bulk density for the observed 1.3 mil thick clad oxide layer yielded a perfectly agreeing swelling value of 2.6%. Postirradiation vacuum annealing for 100 hr at 800 °C was performed on the fuel, and a total swelling of

22.5% was incurred by the development of grain boundary porosity and cracking.

Irradiation and fission product effects in the fuel alloy have caused a considerable degree of hardening as shown by the change in Rockwell B values from 12 to 91. Notch-fracture testing of a segment of the coextruded fuel element tube wall demonstrated that a strong fuel-to-clad bond still exists even though the fuel has suffered the loss of some ductility.

Burnup analysis and test loop operating data yielded fuel exposure values differing from each other by only 6%. Isotopic analyses of the irradiated fuel confirm that the fertile thorium is being transmuted to fissionable uranium in accordance with the designed intentions of the experiment.

The outstanding performance of the fuel elements is demonstrated by low values of fuel swelling, by good dimensional stability, by a stable metallurgical structure and by good behavior during simulated rupture testing under water-cooled power reactor conditions.

BACKGROUND

The prospects for long range nuclear power production depend upon our proper utilization of nature's more abundant fertile materials, which can be converted into fissile isotopes, in conjunction with the much less abundant fissile materials. The application of fertile thorium as a fertile material in a nuclear fuel requiring long service life, stable reactivity, and a constant high power capability has long been considered. In the final analysis,

however, the usefulness of thorium to power reactor fuels technology will be a matter of economics. Many studies⁽¹⁻³⁾ have been made on economics of thorium utilization, but supporting technical and operational data are needed to permit the design of systems for lowest possible costs. The present program of testing and evaluating prototype thorium-uranium fuel elements under power reactor operating conditions is intended to furnish some of the needed technical and operational data.

Inherent high density, mechanical strength, high thermal conductivity, and low fabrication costs are some of the advantages of a metal system which warrant the continuing development of metallic fuels for power reactor applications.⁽⁴⁾ Metallic thorium offers not only its important nuclear characteristics but also its many desirable physical and mechanical properties to a nuclear fuel. Some of the desirable aspects of metallic thorium are:

1. The isotropic crystal structure obviates concern over irradiation "growth" or "growth induced" swelling, e.g., that which occurs in the anisotropic structure of uranium.
2. The high melting point ($\sim 1750^\circ\text{C}$) of thorium permits the attainment of high heat generation and transient fuel temperatures without danger of melting. Also, fission gas swelling would be expected to be minimal, below about 800°C (~ 0.5 of the melting point in degrees Kelvin).
3. High conductivity permits operation at high specific powers and at high surface heat fluxes without danger of excessive fuel temperatures.

4. An absence of allotropy below 1400 °C (~0.82 of the melting point in degrees Kelvin) eliminates possible influences of transformation on irradiation behavior kinetics.

J. H. Kittell⁽⁵⁾ has reported experimental results which verify some of the advantages of thorium-uranium alloys. The results of three capsule irradiation experiments performed over a period of twelve years on thorium-uranium alloys are summarized in Table I.

The experiments showed that the rates of volume increase of irradiated thorium-uranium alloys were about 1% per 1 at.% burnup. This minimal amount of fuel swelling is a decided asset in the application of Th-U alloys to high

burnup power reactor elements.

Th-2.5 wt% U (93.2% enriched)-1.0 wt% Zr fuel alloy was fabricated into Zircaloy-2 clad tubular fuel elements for irradiation testing in high-temperature, high-pressure water loops in the ETR. Fuel alloy ingots were prepared by double vacuum arc melting, and the clad tubular shape was produced by coextrusion at 760 °C. Element fabrication was completed by Be-Zr eutectic brazing of end caps into the ends of tubular sections followed by electron beam welding as a final seal. Seven elements have been involved in the long-range testing program to evaluate the performance of these candidate power reactor fuel elements.

TABLE I. Summary of Capsule Irradiation Experiments⁽⁵⁾

Specimen	Burnup, at. %	Temperature, °C	Results
Th-5 wt% U alloy rolled plates	1.5	200	No anisotropic growth volume increase of 1% per at.% burnup
15 swaged specimens Th-0.1 wt% U; Th-1.4 wt% U; and Th-5.5 wt% U	0.3- 3.6	45-200	No anisotropic growth volume increase of 1% per at.% burnup
44 chill-cast specimens of thorium alloys, containing 10, 15, 20, 25, 31 wt% U	0.16- 10.1	260- 1000	Volume increases of 1% per at.% burnup at lower tem- peratures; 2.5% per at.% burnup at 650 °C; 6% per at.% burnup at 800 °C.

FUEL ELEMENT FABRICATION

The fuel elements were fabricated at Battelle-Northwest, Richland, Washington, by the Metal Fabrication Development Operation⁽⁶⁾. Thorium-2.5 wt% U (93.2% ^{235}U)-1.0 wt% Zr fuel alloy was fabricated into Zircaloy-2 clad tubular fuel elements.

The 1.0% zirconium was added to the base fuel to improve the surface quality of the arc cast ingot, and to lower the room temperature hardness of the fuel. The fuel elements are 1.750 in. OD x 1.050 in. ID x 8 1/2 in. long with 0.025 in. thick clad (Figure 1).

The fuel elements were produced from two double vacuum arc-melted ingots which were coextruded with Zircaloy-2 at 760 °C on a 2750 ton horizontal hydraulic extrusion press. Fuel sections prepared from these extrusions were heat-treated for 1 hr at 750 °C in vacuum and furnace-cooled. Uniform clad-core diffusion was observed, and the total bond width after heat treatment was approximately 0.0007 in. The thorium alloy was almost completely recrystallized as a result of the heat treatment. Uranium, in excess of that soluble in thorium, was precipitated as small particles of alpha uranium distributed nearly at random in the structure.

End closures were made by brazing Zircaloy-2 end caps into chemically milled and machine flattened end recesses. Zircaloy-2-5.0 wt% Be braze alloy was used; the brazing was followed by an electron beam welding pass to seal the exposed braze line.

FUEL ELEMENT IRRADIATION

TEST FACILITIES

The test is being performed in the P-7 and M-3 loop facilities in the ETR. The reactor consists of a fuel core region which is encased by a beryllium reflector. Surrounding the beryllium reflector and enclosed in the reactor tank is an aluminum reflector. Both loops are located in the aluminum reflector and are adjacent to the beryllium reflector. The test conditions provided by the facilities are shown in Table II.

The length of test space available in each loop is 34 in.; the inside diameters of the P-7 and M-3 loop tube are 2.700 and 3.440 in. respectively. Both loop pressure tubes are vertical and are made from Zircaloy-2.

TEST ASSEMBLY

Three fuel elements are irradiated at a time in a vertical column in a test assembly which, during reactor shutdowns, permits easy removal of the fuel elements for examination and reinsertion for further irradiation. The test assembly hardware consists of a Zircaloy-2 tube containing the three fuel elements, a flow restrictor rod which extends through the bore of the fuel elements, and a quick disconnecting device located at the top of the assembly. The annular coolant flow passages are maintained by spacers located between each fuel element and

FIGURE 1. Test Element

TABLE II. Experimental Conditions and Facility

Condition	Loop	
	P-7	M-3
Volume average thermal neutron flux in fuel, n/cm ² -sec	3.5 x 10 ¹³	2.0 x 10 ¹³
Ratio of maximum axial neutron flux to average flux	1.2	1.2
Ratio of maximum radial neutron flux to average flux	1.5	1.5
Bulk outlet water temperature (max.), °C	260	260
Pressure, psi	1600	2000
Coolant flow rate, gal/min	82	170
pH	9-10	9-10
pH adjuster	LiOH	NH ₄ OH

at the top and bottom of the fuel element column. Figure 2 shows the test assembly hardware with aluminum dummy fuel elements.

INTERIM EXAMINATIONS

Every six weeks, during reactor shutdown, the test assembly is removed from the reactor and disassembled. Each fuel element is visually examined and weighed under water with a Mastergram balance having an estimated precision of 1/3 g. The volume of each fuel element, determined before irradiation by weighing in air and water, was about 200 cm³; thus, when weighed in water having a density of 1 g/cm³, a weight change of 1 g represents a corresponding volume change of 1 cm³, or approximately 1/2%. A correction is made for the volume of the clad and of the end caps to give the reported values in terms of fuel swelling only.

CURRENT TEST STATUS

The current status of the seven test elements is summarized in Table III. The accumulated exposures vary from 18,600 to 2,500 MWd/ton with corresponding volume changes from 3.4 to 0.1%.

Fuel element GEH-10-66, after reaching an exposure of 12,000 MWd/ton was returned to Battelle-Northwest for metallurgical examination. Examination of the element revealed a 0.0013 in. thick layer of ZrO₂ on the surface of the clad which possibly caused the clad surface temperature to increase from 300 to 350 °C. To avoid the possibility that such a temperature increase might result in excessive clad corrosion and prohibit achieving goal exposure, the loop water temperature was recently reduced from 254 to 204 °C. Maintaining the clad temperature at 300 °C is in keeping with the original objectives of the test.

(a)

(b)

FIGURE 2. *Test Assembly Hardware
With Aluminum Dummies*

The temperature data for fuel elements GEH-10-64, 65, and 71 listed in Table III are based on the reduced loop water temperature and a 50 °C temperature rise across the oxide. The data taken before cycle 85, which was the first cycle of operation at the lower water temperature, are based on a loop water temperature of 254 °C and on the assumption that no oxide build-up has occurred. The swelling data reported in Table III has not been corrected for the oxide layer.

The temperature history and cumulative swelling as functions of exposure are shown in Figure 3 for the four fuel elements having the highest expo-

sure. A trend for the low exposure elements is not as yet evident.

The element with the maximum exposure (GEH-10-65) has operated most of the time with the maximum core temperature between 400 and 600 °C although for several reactor cycles this temperature was 350 and 400 °C due to flux depression from adjacent tests. This fuel element has experienced more than 740 days of full power reactor operation and at the beginning of the test was operating at a specific power of 69 W/g with a surface heat flux of 1.0×10^6 Btu/ft²-hr.

During the times that interim weight measurements were made, four mishandling

TABLE III. Irradiation Data on Th-2.5 wt% U-1 wt% Zr Fuel Elements

Fuel Element Number GEH-10	Percent Fuel Swelling	Burnup		Surface Temp., °C	Maximum Core Temp., °C	Specific Power, W/g	Surface Heat Flux Btu/ft ² -hr	Thermal Cycles ^(d)
		Fissions/cm ³ (MWd/ton)	at. %					
65(a)	3.4	6.3 x 10 ²⁰ (18,600)	2.1	295	460	39	5.7 x 10 ⁵	384
64(a)	1.7	4.4 x 10 ²⁰ (13,000)	1.5	285	420	31	4.5 x 10 ⁵	323
71(a)	1.3	3.2 x 10 ²⁰ (9,400)	1.1	295	480	44	6.4 x 10 ⁵	184
72(b)	0.1	1.5 x 10 ²⁰ (4,300)	0.5	300	490	43	6.2 x 10 ⁵	103
70(b)	-0.5	1.3 x 10 ²⁰ (3,900)	0.4	295	470	39	5.6 x 10 ⁵	103
84(b)	0.1	0.9 x 10 ²⁰ (2,500)	0.3	290	440	33	4.8 x 10 ⁵	58
66(c)	1.6	4.1 x 10 ²⁰ (12,000)	1.4	295	445	36	5.4 x 10 ⁵	291

(a) Temperatures, corrected for oxide buildup, and heat generation conditions during ETR Cycle 89.

(b) Temperatures, not corrected for oxide buildup, and heat generation conditions during ETR Cycle 84.

(c) Temperatures, not corrected for oxide buildup, and heat generation conditions during ETR Cycle 77.

(d) A thermal cycle is defined as a change from 90 to 100% of maximum power to 0 to 10% of reactor power and return to 90 to 100% of reactor power.

Fuel Element GEH-10-65

Fuel Element GEH-10-64

FIGURE 3. Swelling Behavior of TH-U-Zr Fuel Elements.

Fuel Element GEH-10-66

Fuel Element GEH-10-71

FIGURE 3. (Contd).

accidents occurred. In all of these accidents the test assembly hardware was damaged to such an extent that it had to be replaced, but in only one instance was a fuel element damaged. This fuel element was returned to BNWL for examination. These accidents, which certainly were undesirable, demonstrate the structural strength and ruggedness of the fuel elements and the high integrity of the end closure welds--these attributes are highly desirable in a power reactor fuel element.

POSTIRRADIATION EVALUATION

Fuel element GEH-10-66, which was involved in the most damaging of the several handling accidents, was returned to Battelle-Northwest for a thorough postirradiation examination and evaluation. Test loop operational data indicated that the element had accumulated an exposure of 12,000 MWd/ton (approximately 1.4 at.% burnup), and interim bulk density measurements revealed a 1.6% increase in fuel volume. The objective of the postirradiation evaluation was to confirm the exposure and fuel swelling data and to determine the effect of the irradiation and operation history upon the character and properties of the element. Following visual examination and measurement of the element, the rupture performance was determined by defect testing the element at simulated power reactor conditions in the Irradiated Rupture Prototype (IRP) facility⁽⁷⁾. Rupture behavior was compared to that of an unirradiated control element. After the simulated rupture test, metallographic examination of the fuel element was pursued to determine the effects of

the test environment and burnup upon the element and its component materials. Additional studies were made of the fuel hardness, the fuel-to-clad bond character, and the fuel response to a high temperature vacuum anneal. Burnup analyses and uranium isotopic analyses completed the postirradiation evaluation.

VISUAL EXAMINATION

The appearance of test element GEH-10-66 is shown in Figure 4. It is unwarped and free of surface irregularities such as bumps, wrinkles, or circumferential creases at the cap-core junction of the end closures. The variously shaded circumferential bands on the element that have developed at the ends delineate heat-affected zones of the clad associated with the 1050 °C closure brazing process. Longitudinal ridges and grooves on the element are the original as-fabricated coextrusion striations and appear to have been unaltered by the irradiation testing. A view of one end shows the special tapered end cap and portions of the inner and outer welds. The welds, super-imposed on the Be-Zr eutectic braze joints between the sides of the ring-cap and the inner and outer clads, show no indication of any unusual corrosion behavior. Areas of spalled surface film resulting from the handling incidents are evident on the two photos of the element. An enlarged view of the edge of one of these spalled areas is also shown in Figure 4. The surface film was subsequently determined to be ZrO_2 accumulated during the extended exposure.

Neg D5652

(a)

2/3X

Neg D5645

(b)

1 1/4X

ETR Photo

(c)

~15X

FIGURE 4. As-Received Irradiated Fuel Element GEH-10-66. [(a) and (b) Condition of fuel element at Battelle-Northwest Radiometallurgy Facility with arrow indicating a spalled area. (c) Magnified view of spalled surface film resulting from handling accidents during irradiation testing]

Measurements made on the element indicate an average outside diameter increase of 0.007 in. and a length increase of 0.084 in. Inside diameter measurements on the tubular element were not made, but the tube bore was free of any observable changes. The dimensional changes are compatible with the fuel swelling as determined from interim fuel element bulk density measurements.

SIMULATED RUPTURE TEST

The rupture behavior of the irradiated element was demonstrated by defecting the outer clad with a 0.025 in. diameter hole and exposing the element to high temperature, pressurized water in the out-of-reactor IRP facility.* After 2 1/4 hr of testing the rise of activity in the IRP loop filter indicated that the clad of the defected element had ruptured. One half hour later the test was terminated. Examination of the element showed a blister at the defect with a 2/3 in. longitudinal split through its center. There was no damage or distortion to the inner bore of the tubular element nor was there any gross cracking or fragmentations of the corroded fuel. Less than an 8 gram weight loss was suffered by the element.

An unirradiated control element was also rupture tested in the IRP facility for direct comparison with the performance of the irradiated element. Twelve hours were required to attain rupture damage comparable to that experienced by the irradiated element during its 2 3/4 hr test. Fuel corrosion in the control element progressed on a uniform front. The bond's resistance to the propagation of rupture damage was excel-

lent, and the ductility of the clad permitted the development of a large blister. In contrast, the fuel in the irradiated element corroded in an intergranular manner; the resistance to rupture propagation along the bond zone was decreased; and reduced clad ductility permitted the blister to fracture and release corrosion products. The behavior of the irradiated and the control elements in the simulated rupture test are shown in Figure 5.

The comparative rupture tests have shown that material properties and fuel element rupture behavior have been degraded by irradiation. However, it is believed that the slow rupture development of the defected element with a minor amount of fuel loss and damage demonstrates the suitability of these fuel elements to power reactor service conditions. The simulated rupture test is discussed in greater detail in another report.⁽⁷⁾

METALLOGRAPHIC STUDIES

Following the rupture test and evaluation of the rupture performance of the fuel element, metallographic studies were made to determine the effects of the irradiation history on the fuel element.

A comparison of the pre- and post-irradiation fuel microstructure is made in Figure 6. Both photographs are of longitudinal sections (direction of extrusion) of the Th-2 1/2 wt% U-1 wt% Zr fuel alloy and show a recrystallized alloy matrix with ThO₂ stringers. The top photograph shows the preirradiation microstructure after an electrolytic ethyl alcohol-perchloric acid etch.

* See page 12

Neg 556-6595

1.6X

(a)

Neg D6520

2.4X

(b)

FIGURE 5. Simulated Rupture Test Behavior. [(a) Section through blister developed on unirradiated control element after 12 hr in IRP loop. (b) Section through rupture tested irradiated element (GEH-10-66) after 2 1/2 hr in rupture test loop]

(a)

(b)

FIGURE 6. Pre- and Postirradiation Microstructure [(a) Preirradiated as-fabricated microstructure of Th-U-Zr alloy fuel showing stringers of ThO_2 in recrystallized alloy matrix. (b) Postirradiation microstructure showing essentially unaltered appearance]

The bottom photograph shows the post-irradiation microstructure after an HNO_3 -HF etch. This comparison reveals an essentially unaltered structure in the irradiated fuel.

A study of the pre- and postirradiation fuel microstructure by electron microscopy was also made. Electron micrographs of unirradiated fuel were characterized by the presence of worked or smeared metal even after 2 hr of vacuum cathodic etching. Electron micrographs of the irradiated fuel after a 2 hr etch yield a work-free surface exhibiting grain boundaries as shown in Figure 7. There was no evidence of porosity or severe crystallographic damage in the structure. The surface irregularities are inclusions or other phases, including randomly dispersed uranium, in the Th-U-Zr matrix. A higher magnification study of the structure with special attention to the dispersed uranium phase (Figure 8) shows what is interpreted as severe damage to these high burnup, enriched uranium particles.

Optical metallography of the clad revealed a 0.0013 in. thick oxide layer on the surface which accumulated during the lengthy exposure in the ETR hot water loops. Prior evidence of this thick oxide is seen in Figure 4. Analysis of a clad sample by hot vacuum extraction indicated 150 ppm hydrogen content, and metallographic examination of the clad showing hydride disposition confirmed the content and revealed a fairly uniform distribution with a tendency for the hydride precipitates to be oriented in a radial direction. The oxide buildup and the hydrogen content of the Zircaloy-2 clad are comparable

to calculated values based upon the environmental conditions of time, temperature, pH and adjusting agent, loop oxygen content, and neutron flux. Heat transfer calculations indicated that a temperature drop in the range of 25 to 50 °C would exist across this oxide layer. The thick oxide layer developed on the clad surface is shown in cross section in Figure 9. A composite micrograph (Figure 10) displays the fuel and the diffusion heat treated bond, the clad and zirconium hydride precipitates, and the external oxide layer.

Fuel element diameter measurements indicated an average outer clad strain of 0.4% to have been experienced during the irradiation (see Visual Examination, above). Previous investigations with coextruded Zircaloy-2 clad fuel (uranium) have shown that, at mean clad temperatures below 325 to 350 °C, the limit on total clad strain before plastic instability and failure is approximately 1.5%⁽⁸⁾. However, the occurrence of localized straining and the onset of plastic instability can result in clad necking and fracture at relatively low total clad strain. Metallographic examination of fuel element cross sections showed that the 0.4% clad strain was uniformly distributed as there were no indications of localized straining or necking in the clad.

FUEL DENSITY

Fuel swelling was determined from fuel element bulk density measurements made during the course of the irradiation. The average fuel swelling experienced by the end of its irradiation

FIGURE 7. Electron Micrograph of Irradiated Th-U-Zr Alloy Fuel. There is no porosity or crystallographic damage evident

Neg 4340F

14400X

FIGURE 8. Electron Micrograph of Irradiated Th-U-Zr Alloy Fuel. This photo shows what may be dispersed uranium phase. Substructure within this phase may be irradiation damage in the high burnup enriched uranium

(a)

(b)

FIGURE 9. Photomicrograph of 0.0013 in. Thick Oxide Film on Clad. Photomicrographs of coolant side of outer Zr-2 clad of the Th-U-Zr fuel element showing the oxide layer developed during 468 days exposure in the ETR test loops. About 90% of the time the surface temperature was 300 °C or greater. The Zr-2 clad is at the bottom of each photo, the oxide layer is at the center and a special edge preserving mount material is at the top.

Neg 567-7042

240X

FIGURE 10. Composite Photograph of Bond, Hydride Precipitates and Oxide Film. A composite microphotograph showing [(A) Th-U-Zr fuel, (B) the 1+ mil fuel-to-clad diffusion bond, (C) clad with hydride needles, and (D) 1+ mil ZrO_2 corrosion film on clad surface]

exposure to 12,000 MWd/ton was 1.6 vol%. Density measurements made on samples of the fuel from the middle of the element indicate fuel swelling of 2.4 to 2.8 vol%. The data is summarized in Table IV. A discrepancy of about 1% existed between the fuel swelling using bulk fuel element density and fuel sample density data. A correction applied to the bulk fuel element data for the effect of the observed 1.3 mil oxide layer on the Zircaloy-2 clad yields a fuel swelling value of 2.6% which is in excellent agreement with the average swelling determined from two fuel samples. The observed fuel swelling is indeed minimal and has been readily accommodated by the tubular element.

POSTIRRADIATION ANNEAL

A segment of the fuel element was vacuum annealed at 800 °C for 100 hr to determine the higher temperature behavior of the highly irradiated Th-U-Zr alloy. After a slow cool from the annealing temperature, the fuel element sample exhibited multiple cracks in the longitudinal direction (direction of extrusion) and showed separation from its clad by failure of the bond (Figure 11). The specimen incurred 22.5% total swelling as listed in Table IV. Metallography has shown that cracking and swelling resulted from the development of generally elongated gas porosity at grain boundaries; the various microphotographs of Figure 12 illustrate this. Similar swelling has been observed previously in thorium Th-U specimens when annealed under similar conditions.⁽⁹⁾

TABLE IV. Summary Of Swelling Data of Th-U-Zr Fuel Element (GEH-10-66)

	Density, g/cm ³	$\frac{\Delta V}{V}$, %	R (a)
Bulk Fuel Swelling	--	1.6	1.2
Corrected Bulk Fuel Swelling	--	2.6	1.9
Prefuel Sample	11.70	--	--
Postfuel Sample #1	11.38	2.81	2.1
Postfuel Sample #2	11.43	2.36	1.7
Postanneal Fuel Swelling (800 °C--100 hr)	9.56	22.5	--

$$(a) R = \frac{\% \Delta V / V}{\text{at.} \% \text{ burnup}}$$

$$\text{Calculated Theor. Minimum Swelling} = \frac{1.4\%}{\text{at.} \% \text{ burnup}}$$

$$\text{Fuel Element Exposure} = 12,000 \text{ MWd/ton} = 1.4 \text{ at.} \% \text{ burnup}$$

Neg D8961

3.40X

(a)

Neg D8964

3.40X

(b)

FIGURE 11. Irradiated Fuel after Vacuum Anneal. [(a) Transverse view of irradiated Th-U-Zr alloy fuel element section after 800 °C 100 hr vacuum anneal. ID clad is detached. (b) Longitudinal view of same section showing cracks extending in the direction of extrusion. Annealed fuel swelled 22.5% from its preirradiation condition]

Neg D9217

200X

(a)

Neg D9225

800X

(b)

Neg D9348

600X

(c)

FIGURE 12. Photomicrographs Showing Gas Porosity after Vacuum Anneal. [(a) and (b) Photomicrographs of post-irradiated annealed Th-U-Zr alloy fuel showing generated gas porosity (as-polished). (c) Photomicrograph of same with an electrolytic etch to reveal grain boundaries]

FUEL HARDNESS

The comparison of pre- and postirradiation hardness measurements taken on the fuel indicates that a considerable degree of hardening has resulted as a consequence of irradiation and fission product effects. The hardness values, which span the effective range of the Rockwell B Scale, average 12 preirradiation and 91 postirradiation, as shown in Table V.

NOTCH-FRACTURE TEST

Notch-fracture tests performed on samples prepared from both pre- and postirradiation fuel elements behaved in surprisingly similar fashion. Samples were prepared by notching about half way through a segment of the tube wall from the inside surface. Testing was accomplished by fracturing through the remainder of the tube wall at the root of the notch by bending the sample outward. Both the pre- and the post-samples fractured straight across the fuel-bond-clad composite structure. The unirradiated control sample showed some ductile yielding in the fuel before failing, while the irradiated sample displayed a brittle fracture in the fuel that propagated across the bonded

clad. This behavior of the irradiated piece demonstrates a strong fuel to clad bond. Microphotographs of the notch-fractured sample are shown in Figure 13.

FUEL BURNUP AND ISOTOPIC ANALYSIS

Chemical burnup analyses of the Th-U-Zr alloy fuel were made by the cesium fission-product method. The first analysis yielded a burnup value of 1.71 at.% as compared to a 1.4 at.% determined from the test loop operating data. However, discrepancy in the final uranium-to-thorium ratio was apparent because it was identical to the as-fabricated preirradiation uranium-to-thorium ratio. A study of the sampling technique and the analytical data led to the conclusion that some thorium precipitated from the dissolver solution. Careful sample preparation and reanalysis yielded a cesium fission-product burnup value of 1.46 at.% and a uranium-to-thorium ratio that was consistent with the burnup value. Uranium isotopic analyses made along with each of the chemical burnups were in excellent agreement and were consistent with the new burnup value. The analytical data are summarized in Table VI.

TABLE V. Comparison of pre- and posthardness

<u>Hardness Scale</u>	<u>Preirradiation</u>	<u>Postirradiation</u>
Rockwell B Scale of Th-U-Zr fuel alloy (average of three tests).	12	91

Neg D8677

1.0X

(a)

Neg D8679

2.40X

(b)

Fracture

Notch

Neg D8678

2.40X

(c)

FIGURE 13. Microphotographs of Notch-Fracture Sample. [(a) View of post-irradiation notch-fracture sample. (b) Closeup side view of fracture (left top of sample) showing straight fracture from root of notch through fuel and clad. (c) Closeup end view of fracture (left is fracture, right is machined notch) showing small grained fractured surface and intact clad-fuel bond]

TABLE VI. Burnup and Uranium Isotopic Analyses--Fuel Element GEH-10-66

	Preirradiation	Postirradiation	
		1st Analysis	2nd Analysis
U:Th Ratio	0.0259	0.0259	0.0212
Cesium Burnup	---	1.71 at. %	1.46 at. %
<u>Uranium Isotopic Analyses, %</u>			
²³² U	---	0.04	---
²³³ U	0.09	35.10	35.12
²³⁴ U	1.09	2.73	2.70
²³⁵ U	93.20	44.99	45.30
²³⁶ U	0.24	10.26	10.09
²³⁸ U	5.40	6.93	6.74
	100.00	100.05	99.95

DISCUSSION

The excellent irradiation performance of the fuel elements while achieving 65% of the 26,000 MWd/ton goal exposure under power reactor conditions indicates that the goal exposure is realistic and will be attained by the fuel elements.

The interim results of the test have verified the major predictions concerning the irradiation behavior of the thorium alloy fuel elements, namely, dimensional stability and the low rate of fuel swelling. The demonstrated uniform fuel volume increase and the absence of warping and bowing are basically due to the isotropic crystal structure of the fuel alloy. The fuel swelling predicted on the basis of the conversion of ²³²Th atoms to more dense ²³³U atoms and the conversion of uranium atoms to less dense fission product atoms for 1.4 at. % burnup

was 1.9%; the experimentally determined value is 2.6%. The agreement is reasonably good considering the simple model upon which the calculations are based.

The Dresden, Indian Point, Yankee, and Shipping Port power-producing reactors operate with maximum heat fluxes near 500,000 Btu/ft²-hr. The thorium alloy fuel element occupying the position of maximum power in this test operated at an initial surface heat flux of 1×10^6 Btu/ft²-hr, which decreased to an equilibrium value of about 450,000 Btu/ft²-hr. Thus, the test conditions have been comparable to those of current power reactors, and the observed performance is directly relatable to power reactor conditions.

The overall excellent performance of these fuels has demonstrated the technical capability of this fuel system to meet the performance demanded of a power reactor fuel.

REFERENCES

1. J. A. Lane. "The Economic Incentive for Thorium Reactor Development," The IAEA Panel on Utilization of Thorium in Power Reactors, Vienna, Austria, June 14-18, 1965.
2. M. W. Rosenthal, H. F. Bauman, L. L. Bennett, R. S. Carlsmith, D. R. Vondy. "The Technical and Economic Characteristics of Thorium Reactors," The IAEA Panel on Utilization of Thorium in Power Reactors, Vienna, Austria, June 14-18, 1965.
3. M. F. Duret, M. J. Halsall. "A Preliminary Assessment of Thorium as a Fuel for Thermal Reactors," The IAEA Panel on Utilization of Thorium in Power Reactors, Vienna, Austria, June 14-18, 1965.
4. A. R. Olsen, D. B. Trauger, W. O. Hamms, R. E. Adams, D. A. Douglas. "Irradiation Behavior of Thorium-Uranium Alloys and Compounds," The IAEA Panel on Utilization of Thorium in Power Reactors, Vienna, Austria, June 14-18, 1965.
5. J. H. Kittell, J. A. Horak, W. F. Murphy, S. H. Paine. Effects of Irradiation on Thorium and Thorium-Uranium Alloys, ANL-5674. Argonne National Laboratory, Lemont Illinois, April 1963.
6. R. S. Kemper, R. M. Johnson, J. E. Minor, R. G. Nelson. Fabrication of Zircaloy-2 Clad Thorium-Uranium Alloy Fuel Elements, HW-79843, Hanford Laboratories, Richland, Washington, March 1964.
7. J. W. Goffard. Unpublished Data. Pacific Northwest Laboratory, Richland, Washington, 1967. (Document in preparation)
8. J. W. Weber. "Plastic Stability of Zr-2 Fuel Cladding," BNWL-SA-653. 69th Annual Meeting of ASTM, Atlantic City, New Jersey, June 27-July 1, 1966.
9. R. D. Leggett. Physical Property Changes in Thorium Postirradiation Annealed to 950 °C, BNWL-24, Pacific Northwest Laboratory, Richland, Washington, January 1965.

DISTRIBUTIONNo. of
Copies

3	<u>AEC Library, Washington</u> <u>Reactor Development and Tech-</u> <u>nology</u> G. W. Cunningham D. K. Magnus J. M. Simmons	G. M. Dalen F. G. Dawson, Jr. D. R. de Halas D. E. Deonigi R. F. Dickerson R. L. Dillon E. A. Eschback E. A. Evans T. W. Evans J. R. Fishbaugher J. C. Fox H. R. Gardner S. M. Gill J. W. Goffard W. J. Gruber C. R. Hann L. A. Hartcorn H. Harty B. R. Hayward E. N. Heck P. L. Hoffman D. C. Kaulitz R. S. Kemper G. A. Last R. D. Leggett D. C. Lehfeldt R. K. Marshall (101) E. T. Merrill J. E. Minor W. I. Neef R. D. Nelson D. P. O'Keefe W. D. Richmond W. E. Roake C. A. Rohrmann F. R. Shober R. W. Stewart J. C. Tverberg J. B. Vetrano J. W. Weber R. G. Wheeler O. J. Wick F. W. Woodfield
5	<u>AEC Richland Operations Office</u> C. L. Robinson R. K. Sharp Technical Information Library	
2	<u>AEC RDT Site Rep - PNL, Richland</u> P. G. Holsted	
1	<u>Argonne National Laboratory</u> J. H. Kittel	
158	<u>Division of Technical Infor-</u> <u>mation Extension</u>	
1	<u>Division of Technical Infor-</u> <u>mation Extension</u> CCR Euratom, Ispra (Varese), Italy R. Lindner	
3	<u>Douglas United Nuclear</u> A. E. Guay M. Lewis J. W. Riches	
1	<u>Lawrence Radiation Laboratory,</u> <u>Livermore</u> Dr. J. Hadley	
158	<u>Battelle-Northwest</u> F. W. Albaugh E. R. Astley J. M. Batch A. L. Bement T. K. Bierlein S. H. Bush J. J. Cadwell T. T. Claudson	Technical Information Files (5) Technical Publications (2)