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IRRADIATION EFFECTS ON UC_2 DISPERSED IN
GRAPHITE — FINAL REPORT

J. G. Morgan
M. F. Osborne

OAK RIDGE NATIONAL LABORATORY

operated by

UNION CARBIDE CORPORATION

for the

U.S. ATOMIC ENERGY COMMISSION

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ABSTRACT

Postirradiation examinations were performed on four fuel cylinders containing UC_2 dispersed in graphite and sealed in low permeability graphite cans irradiated in the MTR. In all but one experiment, a flowing stream of helium passed over the outside of the graphite cans. The estimated fuel cylinder central temperatures ranged from 2500°F to 3500°F, and the maximum U^{235} burnup was 21%. The most important radiation effects were fuel dimensional change, fission product and uranium migration, and microscopic structural changes. The fuel cylinders, in general, decreased in diameter and increased in length. The decrease in diameter was a function of fuel burnup. A 4.5% decrease in diameter was observed at a burnup of 6×10^{19} fissions/cm³ of fuel dispersion.

Uranium had migrated out of the fuel cylinders into the graphite cans. Fission products likewise, were found throughout the walls of the graphite can, with steep concentration gradients near the inside surface of the can wall. The isotopes Zr^{95} and Ce^{144} were more abundant near the outside wall surface than at mid-wall. There was no corresponding rise in the concentrations of Sr^{90} and Cs^{137} near the outside surface.

Microstructural changes were observed in the UC_2 particles which were a function of burnup. At around 4 atom % U burnup the particles

became porous and began to lose their angular shape. At 21 atom % U burnup, the particles had spheroidized and had begun to diffuse into the surrounding graphite matrix.

INTRODUCTION

Fuel materials studies under the Gas-Cooled Reactor Project have included a series of irradiations on UC_2 dispersed in graphite. The fuel cylinders were sealed in a low permeability graphite can and irradiated in the MTR. The purpose of these tests was twofold: 1) to determine the dispersed fuel stability at temperatures up to 3500°F and burnups of up to 21 atom % U, and 2) to study the fission gas escape rates through low permeability graphite at temperatures of 1500°F.

Because leaks developed in the low permeability graphite can seals, fission gas escape vs. irradiation time could not be accurately determined. However, upper burnup limits were established on the fuel dispersion, and fission product gradients through the graphite can were measured.

SPECIMEN DESCRIPTION AND FABRICATION

The fueled graphite was prepared by admixture of UO_2 spherical shot (104-147 μ dia.) with a previously prepared carbonaceous mix followed by molding to a cylindrical shape, and baking. The molding pressure was parallel to the axis of the cylinders, thus the radial direction is with the grain. Final baking temperatures of 2350° to 2800°C converted the UO_2 to UC_2 in situ. Some particle enlargement occurs in this conversion. The final particle ranged from 160 to 260 μ .

The distribution of particles was quite uniform throughout the fuel cylinder and extended to the surface. Fully enriched uranium (93.12 w/o U^{235}) was used in all the experiments, and the fuel loading was varied from sample to sample. The low permeability graphite can contained from one to four fuel cylinders, and one or two cans were irradiated in each test. Fig. 1 shows a cross section of test 48-1 which contained two graphite cans each containing one fuel cylinder. The end plugs of the graphite cans were sealed with Si-SiC. The spacers between the cans and at the ends were either porous carbon or graphite. Axial holes in the walls of the graphite cans accommodated thermocouples and flux monitor wires.

IRRADIATION CONDITIONS

The irradiations were carried out in beamhole HB-3 of the Material Test Reactor, Idaho. As seen in Fig. 1, the test assembly was inserted horizontally in a water cooled liner. Because of a flux gradient along the assembly, the uranium loading was increased in the rear fuel cylinder to help maintain uniform power generation in both cylinders. With the exception of 48-1, a helium purge was used to sweep the fission gas from each experiment, and the fission gas release rate was determined by gamma ray analysis of samples from the gas stream. The temperature of the graphite can wall was controlled during irradiation by inserting or withdrawing the test assembly to vary the neutron flux. Fuel loading and burnup for the four irradiations are compared in Table 1. With the exception of 48-1, there was one graphite can per experiment, and the central fuel temperature is a calculated number. The graphite wall temperature as measured by thermocouples is listed in Table 2.

Fig. 1. Experimental Assembly for Irradiation of Graphite-Clad Fuel Elements.

Table 1. Fabrication and Operating Data for
Fueled Graphite Experiments

Expt. No.	Fuel Cylinder	U ²³⁵ Density (g/cc)	Avg. Fuel ^a Power Density w/cc	Estimated Central Temp. °F	U ²³⁵ Burnup % ^b
48-1	A	0.168	280	3500	13.1
	B	0.330	260	3200	4.9
48-2	A	0.085	140	2500	21.4
	B	0.123	-	2500	19.5
48-3	A	0.174	205	2500	1.96
	B	0.253	195	2400	0.98
	C	0.360	190	2300	-
	D	0.509	170	2100	0.55
48-4	A	0.169	230	2800	3.46
	B	0.249	215	2700	2.35
	C	0.359	215	2700	1.41
	D	0.517	205	2500	0.85

^aBased on measured temperatures and geometry.

^bBy mass spectrometric analysis of uranium, U²³⁵/U²³⁶.

Table 2. ORNL-MTR-48-1 thru 4 In-Pile
Temperature History

Test	Hrs. at Temperature	Graphite Wall Temperature, °F	
		A Element	B Element
48-1	1379.5	1579	1372
	20.5	1080	840
48-2	2466.0	1497	
	302.5	1072	
	26.0	1259	
48-3	1.0	1438	
	248.0	1026	
48-4	15.5	1416	
	759.5	1156	

POSTIRRADIATION EXAMINATIONS

Gamma Scans

The gamma radioactivity of each experiment was measured and plotted vs. capsule length. The gamma scan device is illustrated in Fig. 2. The capsule was moved very slowly past the steel collimator, which was mounted in the cell wall. The dimensions of the collimator slit are 0.020 in. by 1.0 in. by 36 in. long. A NaI (Tl) scintillator, mounted at the other end of the collimator, detected the radioactivity. The signal from the photomultiplier was amplified and transmitted to a count rate meter and a strip chart recorder. In general, a discriminator was used to exclude signals from weak or scattered gamma rays. The minimum energy recorded was about 0.65 mev, which included such abundant fission products as Zr^{95} , Ba^{137} , and Pr^{144} . The experiments were scanned both before and after removal of the graphite fuel assembly from the stainless steel containment vessel. The distribution of fission product deposition was explored through gamma scans of the metal components. However, due to the neutron activation of the stainless steel, these data were inconclusive. Duplicate gamma profiles always were made to verify results.

Representative gamma scans for these experiments are shown in Figs. 3 and 4. The curves indicate relative fuel burnup, which reflects the power generation. The fuel loading was increased with distance from the reactor, in an effort to maintain relatively constant heat generation. The effect of the different loading in each fuel cylinder is apparent from the stepped shape of the curve in Fig. 3.

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Fig. 2. In-Cell Portion of Gamma Scan Device.

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Fig. 3. Gamma Radioactivity Scan for MTR-48-1.

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Fig. 4. Gamma Radioactivity Scan of MTR-48-3 Showing Correlation With Fuel Pellets.

Visual Observations of Fuel Assemblies

The appearance of the graphite fuel containers was unchanged. The two fuel assemblies and the porous graphite spacers from experiment MTR-48-1 are shown in Fig. 5. An end view of one fuel assembly (Fig. 6), shows the Si-SiC seal area, and the holes drilled in the wall of the graphite can for six thermocouples and three flux monitor wires. The end spacers in experiment MTR-48-2 were made of porous carbon. These spacers shrank during irradiation and were broken during the process of removal from the end projections of the graphite cans, as shown in Fig. 7.

The appearance of the graphite fuel cylinders, before and after irradiation, is illustrated in Fig. 8. The fuel cylinders from only one experiment, MTR-48-2, had changed in appearance during irradiation. As shown in Fig. 9, these two fuel cylinders (one of which was much shorter than the other) were stuck together. In addition, there were many droplets of some unfamiliar material adhering to the outside surfaces. Similar droplets were present on the inside surfaces of the graphite can. These droplets were silvery in appearance, resembling mercury, and did not wet the graphite. Several small samples were collected in a vacuum bottle for radiochemical analysis. The droplets reacted vigorously with water, leaving a fine black powder. Although this material was never completely identified, the radioactive constituents were the common fission products, principally Ce^{144} and uranium.

Experiments MTR-48-3 and -4 contained four fuel cylinders each, as illustrated in Fig. 10. The fuel cylinders in -3 were similar to

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Fig. 5. Irradiated Fuel Elements from MTR-48-1.

Fig. 6. Si-SiC Seal Area of Graphite Can B, MTR-48-1.

Fig. 7. Broken Carbon End Spacer from MTR-48-2.

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Fig. 8. Appearance of Irradiated and Unirradiated Fuel Cylinders.

Fig. 9. Fuel Cylinders from MTR-48-2.. Note droplets adhering to surface.

① POROUS CARBON SPACER	⑤ INNER CONTAINMENT VESSEL, TYPE 304 STAINLESS STEEL
② LOW-PERMEABILITY GRAPHITE CAN	⑥ OUTSIDE CONTAINMENT VESSEL, TYPE 1100 ALUMINUM
③ U^{235} -FUELED GRAPHITE MATRIX	⑦ HELIUM INLET LINE
④ SHEATHED THERMOCOUPLE	⑧ GRAPHITE PLUG, SEALED WITH Si-SiC

Fig. 10. Experimental Assembly Used in MTR-48-3 and MTR-48-4.

those in -1 and -2, while those in -4 were coated with pyrolytic carbon to a thickness of about two mils. As seen in Fig. 11, there was no gross damage to any of the fuel cylinders, or to the coatings on the -4 cylinders. A magnified view of the fuel from a mid-radius region of the -4 experiment is shown in Fig. 12. The voids adjacent to the fuel particles are the result of the formation of UC_2 , from the UO_2 particles and the graphite, during fabrication of the fuel cylinders.¹

Dimensional Stability

The dimensions of the graphite containers and the UC_2 -graphite fuel cylinders were measured with a calibrated dial indicator and with a standard micrometer. Several measurements were made at various circumferential positions and averaged to obtain the recorded diameter. Length measurements were made at both center and edge positions. In three of the five containers there was no measurable change. As shown in Table 3, the maximum change was +0.3%, which was observed in the diameter of the MTR-48-3 container. In both cases where diameter changes were found, the changes occurred at the rear end of the container, while no change was measured at the front end where the exposure to radiation was significantly higher.

There were appreciable changes (>1%) in the dimensions of all the fuel cylinders. These data are shown in Table 4. In all cases, the diameters decreased during irradiation. In general, there were larger changes at the higher burnups, as shown in Fig. 13. In the first two experiments, all four fuel cylinders increased in length, while all

¹T. M. Benziger and R. K. Rohwer, "Graphite-Matrix Fuel Bodies," *Nucleonics* 19, No. 5, p 84 (1961).

Uncoated

Coated

Fig. 11. Fuel Cylinders from Experiments MTR-48-3 (Uncoated) and MTR-48-4 (Coated). 1.7X.

Fig. 12. Structure of Fueled Graphite Irradiated in MTR-48-4.
As-polished. 50X.

Table 3. Dimensional Data for Graphite Fuel Containers, Major Diameter

Experiment No.	Avg. Length, in.		% Change	Avg. Diameter, in.		% Change	
	Pre- Irradiation	Post- Irradiation		Pre- Irradiation	Post- Irradiation		
MTR-48-1,A	2.5055	2.506	-	1.8753	1.875	-	
-1,B	2.5006	2.501	-	1.8752	1.875	-	
-2	2.509	2.509	-	1.875	1.875	-	(Front)
				1.876	1.876	-	(Rear)
-3	6.017	6.024	+0.1	1.8826	1.882	-	(Front)
				1.8821	1.884	+0.1	(Middle)
				1.8814	1.886	+0.3	(Rear)
-4	6.031	...	...	1.8806	1.880	-	(Front)
					1.877	-0.2	(Rear)

- No significant change.

... No measurement.

Table 4. Dimensional Data for UC₂-Graphite Fuel Cylinders

Experiment No.	Cylinder No.	Avg. Length, in.		% Change	Avg. Diameter, in.		% Change		
		Pre-Irradiation*	Post-Irradiation		Pre-Irradiation*	Post-Irradiation			
MTR-48-1	A	1.468	1.508(min.)	+2.7	0.996	0.966	-3.0	(Rear)	
			1.544(max.)	+5.2		0.962	-3.4	(Middle)	
						0.954	-4.2	(Front)	
	B	1.468	1.521	+3.6	0.997	0.946	-5.1	(Rear)	
						0.963	-3.4	(Middle)	
						0.973	-2.4	(Front)	
MTR-48-2	A	1.235	1.271(min.)	+2.9	0.996	0.948	-4.8	(Rear)	
			1.276(max.)	+3.3		0.952	-4.4	(Middle)	
						0.951	-4.5	(Front)	
	B	0.233	0.236(min.)	+1.3	0.995	0.951	-4.4		
			0.246(max.)	+5.6					
MTR-48-3	A	1.2347	No length measurements due to sectioning		0.9958	0.984	-1.2	(Front)	
	B	1.2350			0.9968	0.986	-1.0	(Rear)	
						0.987	-1.0	(Front)	
	C	1.2352			0.9964	0.989	-0.8	(Rear)	
						0.991	-0.5	(Front)	
	D	1.2345			0.9963	0.989	-0.7	(Rear)	
						0.992	-0.4	(Front)	
	D	1.2345							
MTR-48-4	A	1.236	1.217	-1.5	0.999	0.972	-2.7		
	B	1.236	1.218	-1.5	1.000	0.973	-2.7		
	C	1.237	1.217	-1.6	0.998	0.980	-1.8		
	D	1.235	1.221	-1.1	1.000	0.985	-1.5		

* Only one value is shown for preirradiation dimensions; it is an average of several measurements.

Fig. 13. Diameter Decrease vs. Burnup for UC_2 -Graphite Dispersion Fuel Cylinders.

four fuel cylinders in MTR-48-4 decreased in length. The reason for this contradictory behavior is not apparent. According to the manufacturer, the fabrication technique was such that a decrease in diameter and an increase in length was expected for all fuel cylinders.

Density

The bulk density of the fuel cylinders was determined from weights and dimensions. Small weight losses were observed, as would be expected due to the migration of uranium and fission products from the fuel cylinder to the graphite container. However, the shrinkage of the fuel cylinders was sufficient to cause a consistent density increase of about 5% (shown in Table 5).

Table 5. Density of Fuel Cylinders

Experiment No.	Density, g/cm ³		Increase in Density %
	Preirradiation	Postirradiation	
48-1-A	1.887	1.930 ^a	2.28
B	2.017	2.120 ^a	5.11
2-A	1.802	1.908	5.88
B	1.825	1.920	5.21
4-A	1.859	1.970	5.97
B	1.938	2.052	5.88
C	2.012	2.106	4.67
D	2.145	2.227	3.82

^a Thought to be low, due to loss of fuel particles from the surface.

Uranium Burnup

Complete transverse sections of the fuel cylinders were used to determine uranium burnup. After dissolution, small samples were analyzed for U^{235} , U^{236} , and U^{238} by mass spectrometry. The fraction of the U^{235} fissioned was calculated from the ratio of U^{235} -to- U^{236} , before and after irradiation. These data are compared to values calculated from neutron flux measurements and heat generation data in Table 6. The agreement between these three sets of numbers is only fair. The data obtained by mass spectrometry are considered to be the most accurate. Therefore, these data were used in correlating the observed changes in fuel microstructure which will be discussed later.

Fission Product and Uranium Migration in Graphite Cans

The fission product concentration gradient across the wall of the graphite can was determined for each experiment. Small tubular core drills were used in a miniature drill press (Fig. 14) to obtain graphite samples which were about 0.040 in. in diameter by about 1/4 in. long. Dial indicators mounted on the drill press located the sample positions with a precision of ± 0.001 in.. Samples were selected radially at intervals of about 0.1 in. as shown in Fig. 15. The graphite cores were dissolved, stable carriers were added to the solutions, and the elements to be counted were isolated by chemical separation. The fission product concentrations were determined by counting with a 256 channel analyzer (Zr^{95} and Cs^{137}) and a gas flow proportional counter (Ce^{144} - Pr^{144} and Sr^{89}). The results were corrected for decay, both during and after irradiation. Additional

Table 6. Comparison of Burnup Data for Fueled Graphite Experiments

Expt. No.	Burnup, atom % U ²³⁵ (by fission)			Burnup, fission/ cm ³ x 10 ¹⁹
	(by Co ⁶⁰) ^a	(by heat measurements)	(by mass spectrometry)	
48-1-A	15.	12.	13.1	5.63
-B	7.0	5.3	4.9	4.14
48-2-A	16.	15-22	21.4	4.67
-B	15.	-	19.5	6.16
48-3-A	1.05	1.4	1.96	0.87
-B	0.54	0.9	0.98	0.63
-C	0.43	0.6	-	-
-D	0.31	0.4	0.55	0.71
48-4-A	6.4	5.2	3.46	1.50
-B	3.2	3.3	2.35	1.50
-C	1.9	2.3	1.41	1.30
-D	1.4	1.5	0.85	1.11

^a
Computed from values obtained from stainless steel and Inconel monitors, including flux depression across fuel pellet.

Fig. 14. Miniature Drill Press and Core Drills Used to Obtain Graphite Samples.

Fig. 15. Holes Showing Distribution of Radial Sampling by Core Drilling. (a) Graphite can. (b) UC₂-graphite fuel cylinder.

fission products which were looked for, but not found in quantities sufficient for analysis, included Ru^{106} , Ba^{140} , and I^{131} . The uranium concentrations were determined by fluorimetric analysis.

The results of these measurements are shown in Table 7. The fission product and uranium concentrations for a typical experiment, MTR-48-2, are plotted as a function of radial position in Fig. 16. There was a significant quantity of uranium found in the graphite can. The amount found in the 48-2 can represented a migration of 7% of the original uranium from the fuel cylinder. Only a very small fraction of the fission products found in the can walls originated with the fissioning of this uranium, the majority had escaped from the fuel cylinder. In all experiments the fission product concentration gradient was quite steep near the inside surface of the graphite can wall, then flattened out near mid-wall. The isotopes Zr^{95} and Ce^{144} were more abundant near the outside wall surface than at mid-wall. There was no corresponding rise in the concentrations of Sr^{90} and Cs^{137} near the outside surface. This difference in behavior is illustrated in Figs. 17 and 18, in which the radial distributions of Cs^{137} and Ce^{144} are compared.

Walton² of Harwell has reported similar increases in fission product concentration near the outside surface of graphite can walls, except that all the fission products (Sr^{90} , Cs^{137} , I^{131} , and Ru^{106} in addition to Zr^{95} and Ce^{144}) appeared to be distributed similarly. Walton attributes this increase in concentration near the outer surface

²G. N. Walton, Nuc. Eng. 7, 70, (March, 1962).

Table 7. Fission Product and Uranium Concentrations in Graphite Cans

Experiment No.	Sample Position (inches from inside surface)	Concentration (atoms/mg of Graphite)				
		U	Sr ⁸⁹	Zr ⁹⁵	Cs ¹³⁷	Ce ¹⁴⁴
MTR-48-1A	0.01	1.6x10 ¹⁶	1.2x10 ¹⁶	3.4x10 ¹⁴	1.2x10 ¹⁶	5.6x10 ¹⁵
	0.10	3.4x10 ¹⁵	9.7x10 ¹³	8.0x10 ¹¹	7.2x10 ¹⁴	2.1x10 ¹¹
	0.20	4.8x10 ¹⁵	1.4x10 ¹⁴	3.9x10 ¹⁰	1.7x10 ¹⁴	2.0x10 ¹¹
	0.30	4.4x10 ¹⁵	2.8x10 ¹³	2.3x10 ¹⁰	6.5x10 ¹³	1.2x10 ¹¹
	0.42	3.6x10 ¹⁴	-	3.6x10 ¹¹	8.3x10 ¹²	6.8x10 ¹³
MTR-48-1B	0.02	3.6x10 ¹⁵	1.5x10 ¹⁶	4.2x10 ¹³	1.5x10 ¹⁵	4.6x10 ¹⁵
	0.09	2.8x10 ¹⁵	1.1x10 ¹³	8.1x10 ¹⁰	6.4x10 ¹⁴	5.9x10 ¹¹
	0.28	1.8x10 ¹⁴	2.0x10 ¹²	8.9x10 ¹⁰	1.0x10 ¹²	1.0x10 ¹¹
	0.37	1.5x10 ¹⁴	1.2x10 ¹²	7.4x10 ¹⁰	4.6x10 ¹¹	9.5x10 ¹⁰
MTR-48-2	0.01	1.0x10 ¹⁶	2.1x10 ¹⁵	2.2x10 ¹⁴	2.2x10 ¹⁵	6.6x10 ¹⁵
	0.08	4.7x10 ¹⁵	1.4x10 ¹⁴	4.7x10 ¹⁰	7.6x10 ¹⁴	5.9x10 ¹²
	0.18	4.2x10 ¹⁵	4.5x10 ¹¹	1.9x10 ¹⁰	6.7x10 ¹¹	4.6x10 ¹¹
	0.36	3.7x10 ¹⁵	1.7x10 ¹¹	1.8x10 ¹⁰	4.4x10 ¹¹	2.4x10 ¹¹
	0.42	1.6x10 ¹⁴	-	1.1x10 ¹¹	2.8x10 ¹¹	4.5x10 ¹²
MTR-48-3	0.01	8.7x10 ¹⁴	3.2x10 ¹¹	2.0x10 ¹¹	1.2x10 ¹³	2.6x10 ¹¹
	0.08	9.1x10 ¹⁴	2.3x10 ⁹	4.1x10 ⁸	1.3x10 ¹⁰	3.8x10 ⁹
	0.18	6.6x10 ¹⁴	2.0x10 ⁹	5.1x10 ⁹	3.8x10 ¹⁰	6.7x10 ⁹
	0.36	5.3x10 ¹⁴	2.4x10 ⁹	4.0x10 ⁸	1.2x10 ¹⁰	3.5x10 ⁹
	0.42	2.4x10 ¹⁴	-	-	1.7x10 ¹⁰	2.6x10 ¹⁰
MTR-48-4	0.01	2.1x10 ¹⁵	-	-	3.4x10 ¹⁴	1.1x10 ¹⁴
	0.18	1.4x10 ¹⁴	-	-	7.0x10 ¹²	1.0x10 ¹⁰
	0.27	2.5x10 ¹⁴	-	-	1.5x10 ¹²	7.4x10 ⁹
	0.36	2.6x10 ¹⁴	-	-	3.1x10 ¹²	1.1x10 ⁹
	0.43	1.6x10 ¹⁵	-	-	1.5x10 ¹¹	4.8x10 ¹⁰

Fig. 16. Uranium and Fission Product Concentrations Across Wall of Graphite Can of Capsule MTR-48-2.

Fig. 17. Distribution of Cs^{137} Across Wall of Graphite Can.

Fig. 18. Distribution of Ce^{144} Across Wall of Graphite Can.

to high diffusion rates along the machined surfaces of the graphite, rather than through the wall. This explanation is based on the assumption that the machining process opens many pores at and near the graphite surface, thereby greatly increasing the effective surface area available for adsorption.

With the exception of MTR-48-3, which was irradiated for a comparatively short time, the concentration of Ce^{144} decreased to a significantly lower level (Table 7) compared to the maximum than that of Cs^{137} and Sr^{90} . The distribution of Zr^{95} was similar to that of Ce^{144} . This behavior is consistent with the tendency of cerium and zirconium to form more stable carbide compounds than do strontium and cesium. Thus, the latter would be expected to be more mobile in graphite.

This fission product concentration data was compared with the temperature histories of the experiments and with the measured permeabilities of the graphite cans. No correlation was apparent.

The uranium concentration gradients across the fuel cylinders were determined for the first three experiments by the same core drilling technique. These data are shown in Table 8 and are plotted vs. radial position in Fig. 19. There is a tendency toward the expected decrease in concentration with distance from the center of the fuel cylinder, due to greater uranium burnup in the outer region.

Table 8. Uranium Concentration in Fuel Cylinders

Experiment No.	Sample Position (Inches from Center)	Uranium Concentration (atoms U/mg of fueled graphite x 10 ¹⁷)
MTR-48-1A	0.00	1.8
	0.20	2.7
	0.34	2.3
	0.42	2.0
	Avg. Preirradiation Value	2.4
MTR-48-1B	0.00	4.1
	0.20	4.0
	0.34	3.3
	0.42	3.3
	Avg. Preirradiation Value	4.5
MTR-48-2A	0.00	0.90
	0.10	0.65
	0.19	0.88
	0.38	0.98
	Avg. Preirradiation Value	1.30
MTR-48-2B	0.00	1.6
	0.10	1.5
	0.19	1.6
	0.38	1.0
	Avg. Preirradiation Value	1.86
MTR-48-3D (Fuel Pellet #1002)	0.00	7.2
	0.10	4.9
	0.29	5.5
	0.42	5.0
	Avg. Preirradiation Value	6.58

Fig. 19. Uranium Concentration Across Fuel Cylinders of MTR-48 Experiments.

Metallography Results

Structural Changes

MTR-48-1. In fabricating fuel pellets for the MTR-48-1 experiment, the UO_2 particles were converted to uranium carbide at 2800°C . As a result of high temperature conversion, most of the uranium carbide moved out of the space originally occupied by the UO_2 and into the graphite. Typical microstructures of an unirradiated control pellet for this experiment are shown in Fig. 20. The two fuel pellets, A and B (Figs. 21 and 22), received a burnup of 13.1 and 4.9 atom % U^{235} , respectively. Metallographic examination at low magnification revealed that the microstructures of the irradiated pellets were similar to the unirradiated control; however, some differences could be seen at high magnification. Typical microstructures at the centers and mid-radii of fuel pellets A and B are shown in Figs. 21 and 22. The irradiated uranium carbide particles were not as angular as those in the control pellet. There were no marked differences in the microstructures of the two fuel pellets.

MTR-48-2. The UO_2 particles were converted to UC_2 at a lower temperature than in the first experiment, MTR-48-1, and resulted in integral carbide fuel particles. The microstructure of the unirradiated control sample of the fuel pellets used in MTR-48-2 is shown in Fig. 23. Graphite crystals were present in the fuel particles.

The fuel pellets, A and B (Fig. 24), received a burnup of 21.4 and 19.5 atom % U^{235} , respectively. Metallographic examination showed that the microstructures no longer resembled the control material. Portions of the uranium carbide particles had migrated into the graphite matrix

Fig. 20. Unirradiated Control of Fuel Pellet for Capsule MTR-48-1. (a) Fine uranium carbide particles surrounded the large voids in the graphite matrix. As-polished. 100X. (b) Higher magnification of above area. Etched. 750X. Reduced 9%.

Fig. 21. Fuel Pellet A from Irradiated Capsule MTR-48-1. (a) Area near the center of the pellet. (b) Area near mid-radius of the pellet. As-polished. 500X.

Fig. 22. Fuel Pellet B from Irradiated Capsule MTR-48-1. (a) Area near the center of the pellet. (b) Area near mid-radius of the pellet. Etched. 500X.

Fig. 23. Unirradiated Control of Fuel Pellet B of Capsule MTR-48-2. Note graphite crystals in the uranium carbide particle. Etched. 250X. Reduced 6%.

Fig. 24. Areas of Fuel Pellets from Irradiated Capsule MTR-48-2. (a) Typical area from pellet A. The white phase is the uranium carbide fuel. As-polished. 250X. (b) Area near mid-radius of fuel pellet B. The fuel particle had spheroidized and the uranium carbide was migrated into the graphite matrix. As-polished. 500X.

and the remainder had spheroidized. Areas typical of pellets A and B are shown in Fig. 24. No differences were observed in the microstructures of the two pellets, nor between the center and O.D. regions of the pellets.

MTR-48-3. Although the MTR-48-2 experimental assembly was in the reactor only a short time, a fuel pellet was selected for comparison with pellets from other assemblies which had been irradiated to higher burnups but at similar temperatures. Fuel pellet D (Fig. 25), which had undergone a burnup of only 0.55 atom % U^{235} , was selected for metallography. As was expected for the short irradiation time (250 hrs.), the microstructure of the uranium carbide particles suffered little or no damage. A typical fuel particle that was located approximately .17 inches from the outer surface of the pellet is shown in Fig. 25.

MTR-48-4. The fuel cylinders in experiment MTR-48-4 were coated with pyrolytic carbon. The microstructure of the unirradiated control for this experiment is shown in Fig. 26. Fuel pellets A and D were examined metallographically. There were no visible changes after irradiation in the appearance of the microstructure of the uranium carbide particles in pellet D, as shown in Fig. 27. This pellet received a burnup of 0.85 atom % U^{235} . Pellet A received a burnup of 3.5 atom % U^{235} and showed a considerable change in microstructure, Fig. 28, as compared to the unirradiated control. Fine porosity and an unidentified grey precipitate were seen throughout the uranium carbide particles. Also the particles showed an increase in volume, had migrated into the graphite matrix in some areas, and were amorphous

Fig. 25. Typical Uranium Carbide Particle from Pellet D of Experimental Assembly MTR-48-3. There was no evidence of any microstructural changes after irradiation. Etched. 250X.

Fig. 26. Unirradiated Control of Fuel Pellets in Capsule MTR-48-4.
Etched. 250X. Reduced 7%.

Fig. 27. Typical Uranium Carbide Fuel Particles from Fuel Pellet D of MTR-48-4. Etched. 250X.

Fig. 28. Typical Uranium Carbide Particle from Pellet A of MTR-48-4. No additional microstructural details were developed after etching. Note general porosity and grey precipitate in the fuel particle. As-polished. 250X.

in appearance.

The pyrolytic graphite coating on the fuel pellets was either blistered or missing wherever a fuel particle was found at the surface of the graphite matrix. With the exception of the above areas, the pyrolytic coating remained in intimate contact with the surface of the pellet.

Conclusions. The first microstructural changes were observed in the uranium carbide particles at a burnup of approximately 3.5 atom % U^{235} . The particles exhibited an apparent increase in volume; also, voids and an unidentified grey precipitate were observed. At higher burnups, approximately 20 atom % U^{235} , the fuel particles had spheroidized and uranium carbide had begun to migrate into the graphite matrix. This resulted in a reduction in particle size to where only point contacts existed between the fuel particles and the graphite matrix.

The microstructural changes observed are believed to be primarily a result of irradiation rather than temperature. For example, the pellets that exhibited fuel particle spheroidization were not the pellets that had the highest central temperatures. Nor were there any marked microstructural differences in the uranium carbide particles in any one pellet, although temperature differences greater than 1000°F existed in some of the pellets.

The pyrolytic graphite coating on the fuel pellets in the MTR-48-4 experiments failed wherever it had been in intimate contact with a fuel particle.

Graphite Can Leak Tests and Seal Examinations

The first experiment was a static irradiation and no postirradiation leak tests were made on the graphite cans. In experiments 2, 3 and 4, however, it became apparent during operation that the encapsulating graphite can or seal was defective. Experiment No. 2 maintained what appeared to be a normal operation until very near the end of the test. At that time a sudden, large increase in activity of the purge gas indicated failure.³ Experiment No. 3 was irradiated for only one of the four scheduled MTR reactor cycles⁴ because of the same indication of failure. The fourth experiment released an excessive amount of fission gas after the first few hours of operation.⁵

Two methods of leak detection were used in the hot cell. The first was to submerge the unopened graphite can in hot silicon oil and observe bubbling at the point of failure. The other method was to drill into the interior of the can and, by use of a seal, pressurize the interior of the can and observe pressure drop as a function of time. The hot oil bubble test is effective if the defect is large enough to permit the bubbles to be resolved optically and if there is sufficient internal free volume to supply a continuous stream of bubbles for at least a few minutes.

When the graphite can from the second experiment was immersed in hot oil, a very fine stream of bubbles was observed coming from one of

³Gas-Cooled Reactor Quar. Prog. Rep. Dec. 31, 1960, ORNL-3049, p. 246.

⁴Gas-Cooled Reactor Quar. Prog. Rep. March 31, 1961, ORNL-3102, p. 154.

⁵Gas-Cooled Reactor Quar. Prog. Rep. June 30, 1961, ORNL-3166, p. 126.

the thermocouple holes. These holes were drilled down the mid-plane of the can wall. Sectioning away a part of the can revealed the location of the defect. Fig. 29 shows the graphite can wall. The path of the leak was from the interior of the can, up between the end plug and can wall, then out through a fine crack in the can wall itself. A slightly different method was used in locating the leak in the graphite can from Experiment No. 3. When the usual bubble test failed to locate the leak, the interior of the can was pressurized through a tube sealed in a hole drilled through the top of the can. The can was pressurized to 20 psig and immersed in alcohol. At least three fine bubble trails were observed coming from the seal between the end plug and the can wall. Upon metallographic examination, flaws were found in the thread seal. There was poor penetration of the silicon braze material along the threads and none of the roots of the threads were sealed. After additional polishing, a hairline fracture was found in the braze at the top portion of the seal, Fig. 30. The path from the interior of the can was as follows; first along the spiral thread path formed by the poor bond at the thread root, and then through the defects in the outermost seal.

The defect in the seal of the graphite can in Experiment No. 4 was much smaller than in the previous two. Bubble testing did not locate the leak. Pressurizing the interior and monitoring pressure drop vs. time gave results which were difficult to interpret. Metallographic examination of the seal region, however, showed the same type sealing results as in Experiment No. 3. The unfilled thread roots and fine cracks in the outside surface of the seal are shown in Fig. 31.

Fig. 29. Composite of Defect Fracture in Can Wall Near Seal. 100X. Reduced 24.5%.

Fig. 30. Longitudinal Sections Through the Threaded, Silicon-Sealed Plug of Fuel Can from Capsule MTR-48-3. (a) Note roots of threads not filled with silicon. As-polished. 50X. (b) Additional polishing revealed hairline fracture in silicon seal. As-polished. 250X. Reduced 30%.

Fig. 31. Portion of Threaded, Silicon-Sealed Plug from Experimental Assembly MTR-48-4. Note fine fracture in exterior portion of silicon seal and absence of silicon in the roots of the threads. As-polished. 50X. Reduced 24.5%.

Thermocouple Sheath Reactions

The thermocouples used to measure the graphite wall temperature were clad in either 316 stainless steel or tantalum. In general, these thermocouples gave satisfactory service for the duration of the experiment. Reactions with the stainless steel sheath resulted in carbide formation in the steel. Two transverse sections from a thermocouple sheath used in experiment MTR-48-2 are shown in Fig. 32. The (a) section was taken 5 in. above the bead and was not in contact with the graphite wall. There was no change in grain size compared with that of an unirradiated control specimen. There was, however, evidence of carbide formation in the grain boundaries. The (b) section was taken 1 in. above the T.C. bead and was in contact with the graphite wall. There was heavy carburization in this region, with practically a continuous carbide phase in the grain boundaries. General pitting of the outer surface was also noted. In the case of the tantalum sheathed thermocouples, reactions were also noted. These resulted in a swelling of the sheath so that, in a few cases, the thermocouple could not be removed from the hole in the graphite wall. Metallographic examination indicated that the reaction was oxidation of the tantalum.

Leach Results

Selected portions of the experiment assembly MTR-48-2 were leached in 1-1 HNO_3 solution to determine the fission product plate out. Helium was swept over the outside of the graphite can, in this experiment, and removed through a stainless steel capillary tube. The leach results are shown in Table 9. The top carbon spacer was at the highest temperature of the four leach samples and nearest the graphite can. Cs^{137} was

Fig. 32. Transverse Sections of Type 316 Stainless Steel Sheath of Thermocouple from Capsule MTR-48-2. (a) Section taken approximately 5 in. from thermocouple bead. (b) Section taken approximately 1 in. from thermocouple bead. Note carbide phase in grain boundaries and precipitate in grains. Etched. 250X. Reduced 5.5%.

Table 9. Fission Product Deposition MTR-48-2

Component	Distance from top of fuel can, in.	Atoms/in. ² of metal surface	
Top Carbon Spacer ^a	0	Cs ¹³⁷	9.4×10^{14}
		Ce ¹⁴⁴	8.8×10^{12}
		Zr ⁹⁵	1.0×10^{11}
Stainless Steel Containment Vessel	2 1/2	Cs ¹³⁷	Trace
		Ce ¹⁴⁴	2.3×10^{12}
		Zr ⁹⁵	3.8×10^{12}
Bottom of helium outlet line	8	Cs ¹³⁷	Trace
		Ce ¹⁴⁴	1.2×10^{12}
		Zr ⁹⁵	1.8×10^{12}
Top of helium outlet line	21	Cs ¹³⁷	Trace
		Ce ¹⁴⁴	4.1×10^{13}
		Zr ⁹⁵	4×10^{13}

^a Surface area unknown, total atoms in leach.

the predominant isotope found. The next sample from the containment vessel was at a lower temperature and further removed from the fuel. The sweep gas velocity was also reduced in this region. The Cs^{137} had apparently already settled out of the sweep stream and only a trace was found. The bottom of the helium outlet line was another five inches downstream and at this point the velocity of the sweep gas increases. Some thirteen inches further downstream another leach sample was obtained at the top of the helium outlet line. Here the temperature was lowest, and Ce^{144} and Zr^{95} were still being deposited from the sweep gas. The two most interesting results from this test were; a) the deposition of Zr^{95} and Ce^{144} tended to increase with distance from the hot zone of the capsule, and b) nearly all of the Cs^{137} was deposited on the porous top carbon spacer immediately adjacent to the fuel can.

CONCLUSIONS

The physical stability of both the graphite cans and the fueled graphite cylinders were considered to be satisfactory under these operating conditions. However, significant fractions of the uranium and fission products migrated from the fuel cylinder. The low permeability graphite cans were not effective barriers to this migration. Cracks in the graphite cans and in the Si-SiC thread seals obscured the evaluation of the fission gas retention property of the low permeability graphite. The fuel particles themselves were structurally stable up to about 4 atom % U^{235} burnup at temperatures of 3200°F .

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