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Compiled by
S. E. Bronisz

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Los Alamos Los Alamos National Laboratory
Los Alamos, New Mexico 87545

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ABSTRACT

This technical monthly report covers studies related to the use of $^{238}\text{PuO}_2$ in radioisotope power systems carried out for the Office of Coordination and Special Projects of the US Department of Energy by Los Alamos National Laboratory.

Most of the studies discussed here are ongoing. Results and conclusions described may change as the work continues. Published reference of the results cited in this report should not be made without the explicit permission of the person in charge of the work.

I. GENERAL-PURPOSE HEAT SOURCE (GPHS)

A. Impact Testing (R. Zocher)

The third design iteration test, DIT-3, is designed to expose weld-cracked clads in a GPHS module to an impact after suitable aging. The test conditions specified by G. L. Bennett¹ of the US DOE will be as follows.

Impact velocity: 58 m/s

Impact temperature: 930°C

Impact angle: 30° (GIS* axes to target)

The velocity and temperature were selected to match those of tests DIT-1 and DIT-2. The angle was chosen to place the maximum bending stress on the clad closure weld, within the range of possible impact angles.

The four fueled clads to be used were recommended by Savannah River Plant² and accepted by DOE.³ They are listed in Table I. Clads 251 and 317 will be in the lead positions during impact; 127 and 140 will be in the rear positions.

*Graphite impact shell (GIS).

Unlike the iridium clads used in DIT-1 and DIT-2, which were aged for 20 h at 1500°C before welding to simulate the effects of 6 months at the 1310°C GPHS operating temperature, the clads to be used in DIT-3 were not preaged. It will be necessary to age them as fueled clads, but the aging treatment has not been determined.

TABLE I. Fueled Clads for DIT-4 Impact

Clad No.	Iridium Source ^a	Pellet Coordination ^b	Crack Description ^c
127	NR/NR	1	9.0
140	NR/N	3	11.5
251	PR/PR	1	8.0
317	Q/Q	4	10.4

^aThe first letter refers to the iridium powder batch and the R indicates remelting.

^bThe number of pieces that the pellet was in at the time of welding.

^cMagnitude of the reflection of the ultrasonic signal used in the examination of closure-weld integrity.

B. Fragment Testing (R. Zocher)

A typical array of components to be used in the second phase of the frequent impact test series is shown in Fig. 1. The partial aeroshell containing a single impact shell and two iridium-clad UO_2 pellets is in the center layer. It is backed by a bulk graphite piece containing a tantalum mass and sandwiched by two module-sized bulk graphite blocks, each containing a tantalum mass simulant. Each layer has a mass equivalent to a real GPHS module.

C. Early Compatibility Test

The accumulated exposure time for this test assembly, as of May 1, 1982, was 1570 h. Continuous monitoring of the helium release from the assembly indicated a sharp drop of the signal to approximately 50% of the generation rate at 1323 h exposure. This condition prevailed for 66 h when a large burst was observed. The signal then returned to a level of approximately the generation rate.

Fig. 1. The bullet-fragment test will be conducted with a partial module bracketed by two mass simulants.

Two periods of 41 h and 66 h have been observed when the helium release rate was about equal to 50% of the total generation rate, indicating that the vent of one capsule was closed.

D. Reduction of GPHS Fuel

Several GPHS modules recently have been exposed to CO at Mound Facility in an attempt to lower the O/Pu ratio in the fuel. A letter⁴ dated March 25, 1982, by E. Johnson of Mound presents results from this treatment. The process and results were analyzed thermodynamically this month. Kubaschewski and Alcock⁵ provided the properties for the $\text{CO}/\text{CO}_2/\text{C}$ equilibria, and Ackerman, Faircloth, and Rand⁶ for the Pu/O_{2-x} system.

The relative CO_2 pressures in equilibrium with the fuel and the graphite, respectively, determine the extent of reduction. Experimental factors that influence these relative pressures so as to limit reduction are increases in the $(\text{CO} + \text{CO}_2)$ pressure, lowering of the O/Pu ratio in the fuel, and decreases in the fuel and graphite temperatures.

We calculated the CO_2 pressures in equilibrium with the fuel at selected $(\text{CO} + \text{CO}_2)$ pressures, fuel compositions, and temperatures by considering the reaction

We calculated the effective temperature of the graphite parts from measured CO and CO_2 pressures by considering reaction

E. Johnson reported results from two series of tests conducted at Mound.⁷ The first series consisting of five gas taps was performed with modules contained in closed cans. The second series consisting of four gas taps was performed with modules contained in cans open to a manifold. The CO and CO_2 pressures measured at Mound are shown in Table II. The CO_2 pressures in equilibrium with the fuel and the effective graphite temperature were calculated from the measured CO and CO_2 pressures, assuming a 1137°C fuel temperature⁷ and a plutonia O/M ratio of 2.00 (Table II). (These values are upper limits because, as the fuel is reduced, the equivalent CO_2 pressure decreases.) The CO_2 calculated

TABLE II. Measured CO and CO₂ Pressures from Mound Facility Gas Taps and Corresponding Calculated Graphite Temperatures

	Tap	PCO (atm)	PCO ₂ (atm)	Calculated ^a	T _c (°C)
				PCO ₂ (atm)	
Series 1	V-1	3.257E-2	3.089E-2	1.138E-2	570
	V-2	3.958E-2	1.589E-2	0.995E-2	608
	V-3	1.974E-2	3.75E-3	4.214E-3	610
	V-4	7.501E-3	8.88E-4	1.505E-3	592
	V-5	1.57E-3	9.87E-5	2.993E-4	559
Series 2	-1	1.963E-1	2.760E-2	2.70E-3	721
	-2	7.889E-2	6.808E-2	1.035E-3	701
	-3	3.357E-2	1.679E-3	4.256E-4	687
	-4	2.564E-2	4.149E-4	3.148E-4	727

^aAssumes fuel composition of PuO_{2.00} and fuel temperature of 1137°C.

pressures are lower than the measured CO₂ pressures for the first two gas taps in series 1 and for all gas taps in series 2, indicating that no reduction took place in these cases. If the fuel temperature were higher than the assumed value, the fuel could have been reduced. The higher calculated graphite temperatures for series 2 suggest that the fuel was hotter than the assumed 1137°C.

The primary limitation on fuel reduction is the low graphite temperature. The influence of the graphite temperature on the extent of fuel reduction is depicted in Fig. 2. The CO₂ pressures over the fuel at a total (CO + CO₂) pressure of 0.1 atm are plotted as a function of the O/Pu ratio at fuel temperatures corresponding to no insulation, one layer, and two layers. These curves are correlated with CO₂ pressures in equilibrium with graphite at temperatures between 600 and 900°C. No reduction would occur at a graphite temperature of 600°C with no insulation, and very little would occur with one or two layers. As the graphite temperature is increased, the extent of reduction also increases. With one layer of insulation and a graphite temperature of 700°C, the fuel is reduced to PuO_{1.995}. With two layers of insulation and a graphite temperature of 800°C, a fuel composition of PuO_{1.964} could be attained with repeated evacuations.

Another approach that should be considered is the substitution of an inert material for the outer layer of graphite in the can. This change would raise the average graphite temperature without affecting the fuel temperature.

II. MULTI-HUNDRED WATT (D. Pavone)

Additional postmortem results were obtained for two Multi-hundred Watt Fueled Sphere Assemblies (FSA), MHFT-73 and MHFT-76. Both had been aged for 1 yr at the operating temperature (1210°C on the graphite surface and 1330°C on the iridium surface). After aging, the spheres were subjected to an orbital-decay reentry heating simulation (1500°C peak temperature) and impacted at 82 m/s at 1440°C (iridium).

Fig. 2. Dependence of CO₂ pressure on fuel and graphite temperatures and O/Pu ratio at a total (CO + CO₂) pressure of 0.1 atm. No insulation (-----), one layer (————), two layers (— · — · —), graphite temp (————).

A. MHFT-73

The iridium cladding suffered a severe fuel push-through failure on the impact face and a hoop-crack failure on the side. The metallographic cross section through the hoop failure is shown in Fig. 3. In contrast to the ductile-shear fracture mode of the fuel push-through failure, the fracture mode at this location was brittle intergranular. The edges of the fracture do not match, suggesting that one or more grains fell out of the clad

during the impact. The grain size at this location was essentially one grain across the thickness.

Metallographic examination of cross sections through the vent assemblies revealed some unusual features. A photomicrograph of one of the vent cross sections is shown in Fig. 4. Plutonia deposits in the filter element appear as a ring surrounding the entrance to the vent hole, and the iridium of the filter element has been degraded by transport into the vent hole and onto the exterior surface of the clad surrounding the vent exit. The

Fig. 3. Metallographic cross section through the hoop failure in the clad of MHFT-73. The fracture mode was brittle intergranular. 40X.

Fig. 4. Metallographic cross section through one of the vent assemblies of the clad of MHFT-73. There was degradation of the iridium frit and deposition in the vent hole. 50X.

iridium filter element at the entrance to the vent assembly appeared to be of normal density, and the reason for the transport of materials is not apparent. The other vent assembly exhibited a similar degradation of the filter element structure, but to a lesser degree. Nonmetallic deposits in the venthole are illustrated in Fig. 5. The major phase present contained plutonium and oxygen with low concentrations of potassium and aluminum. The dark gray phase contained calcium and phosphorus with low concentrations of potassium, aluminum, and plutonium. Intermetallic reaction products observed on the exterior of the iridium clad are shown in Fig. 6. Elements identified in the phases of Fig. 6(a) were iridium, silicon, aluminum, plutonium, and oxygen; those in the light gray phase [Fig. 6(b)] were iridium, plutonium, and oxygen. The eutectic-like material in Fig. 6(c) contained iridium, plutonium, and probably oxygen. The dark gray material associated with the eutectic-like material contained only plutonium and oxygen. The occurrence of the eutectic-like constituent containing Ir-Pu-O is perplexing because it has not been observed on the interior of the clad and, therefore, is not the product of direct reaction of plutonia with iridium. Possibly other elements of low atomic number that are not readily identified by electron microprobe analysis, such as carbon, are also constituents in this material.

Emission spectrographic analysis of a plutonia sphere sample indicated the following elements to be present in amounts exceeding the limits of detection.

Al - 45 ppm	Ba - 35 ppm
Ta - 100 ppm	Ca - 500 ppm
Si - 85 ppm	Fe - 120 ppm
Cr - 25 ppm	Mg - 1 ppm
Mn - 1 ppm	Ti - 60 ppm
	Sr - 15 ppm

The calcium content exceeds its specification limit; all others that are included in the specification are well below their limits.

The phosphorus content of the plutonia, determined by a colorimetric procedure, was 50 ppm.

Analysis of the ash produced by combustion of the GIS debris indicated the total plutonium content was 0.961 g. A phosphorus content equivalent to 73 ppm, based upon the nominal 120-g GIS, was also determined.

B. MHFT-76

Photographs of the impacted fueled clad are shown in Fig. 7. The principal failure was an intermittent crack extending from the hoop region toward the back side of the iridium clad. The failure appeared to be associated with stretching over the edge of a large fuel fragment. Several other small hoop cracks also were present. No fingerprint cracks were observed, but an irregularly shaped fuel push-through displacement without severe deformation of the iridium was noted on the impact face. The areas surrounding the vent exits appeared to have large quantities of effusate deposited on the surface; a

Fig. 5. Nonmetallic deposits in the venthole of the clad of MHFT-73. Light gray—Pu and O with K and Al. Dark gray—Ca and P with K, Al, and Pu. 250X.

(a)

(b)

(c)

Fig. 6. Intermetallic reaction products on the exterior of the clad of MHFT-73. (a) Ir, Si, Al, Pu, and O (500X); (b) light gray—Ir, Pu, and O (500X); (c) eutectic-like material—Ir, Pu, and O; dark gray—Pu and O (500X).

(a)

(b)

Fig. 7. Photographs of the impacted fueled clad of MHFT-76. (a) Impact Face ($\sim 1X$), (b) back side ($\sim 1X$), and (c) profile view ($\sim 1X$).

(c)

similar small spot was on the impact face, associated with a small crack network. Details of the impact test are included in the Impact Test Summary in Table III.

The microstructure of the closure weld is shown in Fig. 8. Grain growth has obliterated much of the original microstructure, though an area of relatively small grains remains.

Typical microstructures of the iridium clad hemishells are shown in Fig. 9 and illustrate the very large grain size observed. The statistical average grain sizes were 2.9 and 3.0 grains across the thickness; however, this value is influenced by small grains encountered near the interior and exterior surfaces. Average grain diameters, determined by counting grain intercepts longitudinally at approximately 200 μm from each surface, yielded average grain diameters of 358 μm and 300 μm or approximately one-half the thickness of the clad.

The fracture mode of the primary hoop failure was brittle, as illustrated in Fig. 10. The principal fracture appears to have occurred after a limited reduction in thickness. The secondary fracture is through a small region of unusually fine grains. At no other location examined thus far was this structure encountered. The clad obviously was subjected to a complex set of bending and tensile and shear stresses at this site, and the observed microstructure probably resulted from dynamic recrystallization after failure, though the degree of plastic deformation is limited.

III. HELIUM RELEASE (D. Peterson, J. Starzynski, and J. Early)

Seven plutonia samples from the GPHS pellet GP-19 were exposed to thermal ramps during which the helium release rates were measured. Runs 58 and 59 involved a temperature increase at 53.3°C/min, and runs 60-62 used a rate of 26.6°C/min. In each case the sample was maintained at 1600°C following the ramp until the helium signal fell to background.

The temperature dependence of the diffusion constant was determined for the five exposures from analysis of the measured helium release rates using a simple diffusion model. The logarithm of the diffusion constant is plotted vs the reciprocal temperature in Fig. 11 for all five runs. Two definite regions of linearity were identified, 700–1160°C and 1300–1550°C. Each region was fitted by a linear least squares analysis to obtain the slope and intercept. The equations were solved simultaneously to determine the intercept temperature. The corresponding activation energy E_a , effective constant of diffusion D'_0 , and intercept temperature calculated for each exposure are listed in Table IV. The values of E_a and D'_0 for the low temperature region are the same within the standard deviations as those previously determined for faster 240 and 120°C/min pulses. Correlations of the data with respect to sample size, age, helium inventory, microstructure, and thermal pulse are continuing. Attempts at developing a theoretical model that includes grain boundary effects also are being pursued.

Fig. 8. Microstructure of the equatorial weld of the clad of MHFT-76. 50X.

TABLE III. Impact Test Summary Fueled Sphere Assemblies

Assembly Id.	Aging Time (h)	Impact Test Conditions	Post-Impact Dimensions			Failure Type				Iridium Type
	1210°C-GIS ^a Vacuum	(Reentry T/Impact T Velocity)	Height (mm)	Diam (mm)	% Strain ^b Height/Diam	Hoop	Fingerprint ^c	Fuel Push-through	Other	
MHFT-61	8834	1550°C/1440°C 74 m/s	31.09	43.46	-23.5/+6.9		No Failures			DOP-26
MHFT-62	720	1550°C/1440°C 85 m/s	30.38	45.34	-25.6/+12.4	---	---	X	Weld bead back side	HDR
MHFT-64	720	1475°C/1300°C 85 m/s	29.03	45.11	-28.7/+10.8		(X)	---	---	DOP-26
MHFT-65	4320	1550°C/1440°C 85 m/s	28.55	43.84	-28.7/+8.0		(X)	X	If crack ex- tends hoop area	DOP-26
MHFT-66	720	1550°C/1440°C 85 m/s	30.68	43.64	-23.8/+6.9	---	X	---	---	HD
MHFT-67	100	1500°C/1430°C 74 m/s	29.64	43.66	-27.1/+7.4		No Failures			DOP-26
MHFT-68	110	1792°C/1579°C 82 m/s	30.07	43.66	-27.6/+7.4		No Failures			DOP-26
MHFT-69	100	---/1037°C 82 m/s	30.99	43.71	-23.8/+7.6	---	(X)	---	Weld bead crack-IF	DOP-26
MHFT-70	720	1500°C/1430°C 82 m/s	29.16	43.26	-28.3/+6.4	---	X	X	---	DOP-26
MHFT-72	720	1500°C/1430°C 82 m/s	30.43	43.76	-25.1/+7.6		No Failures			DOP-26
MHFT-74	720	1500°C/1430°C 81 m/s	29.74	43.54	-26.8/+7.1		No Failures			DOP-26
MHFT-75	720	1500°C/1430°C 81 m/s	30.07	43.23 44.07	-26.0/+6.6-8.3		No Failures			DOP-26
MHFT-71	9215	1550°C/1430°C 82 m/s	29.79	42.98	-26.7/+5.8	---	X	---	---	DOP-26
MHFT-73	8820	1500°C/1430°C 82 m/s	30.05	43.97	-26.1/+8.2	X	---	X	Reentrant Fold	DOP-26
MHFT-76	8820	1500°C/1430°C 82 m/s	30.84	43.61	-24.8/+7.3	X	---	---	---	DOP-26

^aGraphite impact shell (GIS) surface.^bBased upon nominal 40.64 mm diam except MHFT-62 through -66 based upon Mound Facility gaging.^cParentheses indicate penetration confirmed metallographically.

(a)

(b)

(c)

Fig. 9. Microstructures of the iridium clad of MHFT-76. Interior surface is at the bottom. 50X.

Fig. 10. Microstructure of the iridium clad of MHFT-76 at the hoop crack. 40X.

Fig. 11. Temperature dependence of diffusion constant for helium release from plutonia samples.

TABLE IV. Activation Energies E_a , Effective Constant of Diffusion D'_0 , and Transition Temperature for Helium Release from Plutonia

Run	Pulse (deg/min)	Low Temperature		High Temperature		Trans. T (°C)
		E_a (kcal/mol)	Log D'_0 (s ⁻¹)	E_a (kcal/mol)	Log D'_0 (s ⁻¹)	
58	53.3	45.7 ± 0.5	0.784 ± 0.084	127.3 ± 6.7	12.437 ± 0.864	1256
59	53.3	47.0 ± 0.3	0.660 ± 0.049	127.6 ± 2.9	12.286 ± 0.369	1242
60	26.6	51.3 ± 0.3	0.892 ± 0.051	130.3 ± 4.4	12.037 ± 0.565	1277
61	26.6	46.5 ± 0.3	0.319 ± 0.056	121.3 ± 1.7	10.902 ± 0.218	1271
62	26.6	45.1 ± 0.3	0.314 ± 0.053	123.4 ± 1.3	11.346 ± 0.162	1276

REFERENCES

1. G. L. Bennett, Subject: DIT-3 Test, TWX to S. Bronisz, March 10, 1982.
2. L. C. Sjostrom, Subject: GPHS Fueled Clads, TWX to G. L. Bennett, April 16, 1982.
3. G. L. Bennett, Subject: DIT-3 Test, TWX to S. Bronisz, April 22, 1982.
4. E. W. Johnson, Subject: Plutonium Oxide Reduction, Letter to D. Peterson, March 25, 1982.
5. O. Kubaschewski and C. B. Alcock, *Metallurgical Thermochemistry*, 5th Ed. (Pergamon Press, New York, 1979).
6. R. J. Ackerman, R. L. Faircloth, and M. H. Rand, "A Thermodynamic Study of the Vaporization Behavior of the Substoichiometric Plutonium Dioxide Phase," *J. Phys. Chem.* 70 (11), 3698-3706 (1966).
7. E. W. Johnson, "The Behavior of Oxygen Partial Pressure over Slightly Substoichiometric Plutonia at 1410 K," Mound Facility report to be published (August 1982).