PLUTONIA/CURIA COMPATIBILITY TESTING

JULY - SEPTEMBER 1972
QUARTERLY REPORT NO. 16
J. D. WATROUS

PREPARED FOR THE ATOMIC ENERGY COMMISSION
DIVISION OF SPACE NUCLEAR SYSTEMS
UNDER CONTRACT NO. AT(45-1)-2138

DATE PUBLISHED - JANUARY 1973

Donald W. Douglas Laboratories
Richland, Washington

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SUMMARY

Chemical analyses of control specimens from early compatibility work in the program have been completed. Volatile impurities were removed from refractory metal alloys after more than a year at 1800°C, thereby purifying the alloys. Titanium, zirconium, and hafnium transferred between adjacent refractory metal alloys at 1800° and 2000°C but not at 1500°C. Mass transfer and volatility of refractory metal alloys is not a problem for current thermoelectric systems.

Several conclusions relevant to helium release, dimensional changes, and structural stability have been derived from results of the plutonia fuel aging experiments where curia-242 was added to plutonia-238 to accelerate helium generation. Fuel form quality and reactions with container materials made interpretation difficult. The helium released from both plutonia and plutonia molybdenum cermet (PMC) fuel forms, with and without curia additions, appeared to be related to chronological or pseudo-chronological age and thermal treatment. Almost total helium release occurred in plutonia at 850°C but not in PMC aged at the same temperature. Total helium release occurred in 1200°C aging. The PMC fuel forms swelled during aging from the as-fabricated 89% to 92% of theoretical density. The plutonia exhibited shrinkage during aging from the as-fabricated 52% to 74% of theoretical density. Plutonia fuel forms, with and without curia additions, exhibited roughly comparable structural changes under similar thermal treatment. The PMC+Cm fuel form had an inferior initial structure resulting in indeterminate aging results. Accelerating plutonia fuel aging by the addition of curia-242 appears technically sound, provided that adequate quality fuel forms are available as starting material.

In support of the multi-hundred watt radioisotope thermoelectric generator (MHW-RTG) program, seven plutonia-238 fueled and six control specimens have been assembled and are undergoing exposure in an effort to determine systems interactions. Short-time exposure (1000 to 1500 hr) will be completed during the next quarter at a maximum temperature of 1440°C. Test assemblies include all materials used in the MHW heat source, together with selected specimens in a comparable thermal gradient intended to mock-up total system variables. Tensile specimens have been included for post-test evaluation of iridium cladding using a DWDL-developed high-strain-rate tensile testing device. This device has been checked and is ready for use in the program.

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Section 1

INTRODUCTION

Use of plutonium-238 and curium-244 in radioisotopic heat sources requires absolute containment during the life cycle of the radioisotope thermoelectric generators (RTG). Radioisotopic fuels for space applications are currently based on oxide forms constrained in metallic containers. Reliability guarantees to users require that potential detrimental reactions to the containers and degradation in the fuel be determined in detail. Possible interaction of fuel with containers is influenced by temperature, thermal gradients, accessibility, and relative area or volume ratios of various system components. The gross effects are discernable in simple low-cost test configurations such as a miniature fuel pellet in a monometallic capsule. However, more complex configurations are needed to provide engineering data such as possible mass transport, structural changes in a larger fuel bulk, and potential mechanical property changes of the various containers. The DWDL compatibility testing program has evolved from the original simplistic tests to systems-oriented configurations now being used to provide engineering data.

Over a period of four years, this work has grown into five program tasks. The Task 1 effort studied plutonia-238 and curia-244 pellets in single containers and determined the stability of a plutonia-molybdenum cermet fuel (PMC precursor), later modified for use in Pioneer and transit RTGs. Task 2 was structured to determine stability of the later PMC and solid solution cermet (SSC) fuel forms, both Pu-238 base and on a small scale evaluate the interrelationship of double containment materials combinations as used in practice. Task 3 involved studying a system having plutonia in noble metal containers with barriers and external oxygen sinks and was designed to give early information on the multi-hundred watt (MHW) system. Task 4 was added to study fuel aging and structural stability using accelerated helium generation via Cm-242 additions in plutonia (PPO) and PMC fuel forms. Task 5 is to study the MHW-RTG (multi-hundred watt) systems interrelationships mocked-up in a sub-scale configuration.

Original goals for this program were to evaluate the compatibility of a broad range of refractory alloy containers for both plutonia and curia at thermionic and very high thermoelectric temperatures (1800° and 2000°C), and to determine the rates at which plutonia and curia might interact with these container materials. The intent was to back extrapolate reaction rates to lower temperatures and longer times for practical thermoelectric device utilization. The test configuration placed plutonia and curia in contact with the walls of a monometallic capsule containing compatibility discs in intimate contact with the fuel.

Early in the program which started in 1968, 18 plutonia-refractory alloy capsules were fabricated using SNAP-27 production grade plutonia cold pressed into pellets and contained approximately 1% nonactinide cationic impurities. Evaluation of these tests essentially is complete. A matched set of higher-purity (~0.23% nonactinide cationic impurities) plutonia/refractory metal specimens was added to the program as AEC fuel production processing improved. Effort on the higher purity plutonia specimens has been essentially completed. Eighteen curia-refractory metal capsules were also fabricated and exposed; 12 have been evaluated while the remaining six were contingency capsules whose evaluation was not required based on results obtained from the first 12. A supplemental effort was added in 1969 to evaluate high-temperature stability of plutonia-molybdenum cermetts fabricated at Battelle-Columbus Laboratories. Six of these precursor to PMC fuel pellets were encapsulated in W-25Re, a relatively non-reactive material, and exposed at 1800° and 2000°C for 1000 to 10,000 hours. Two control specimens which were not exposed were evaluated to determine the effect of long-term storage. This work and the original effort to define the best refractory alloy containers for plutonia and curia and determining interaction rates have been identified as Task 1.

Task 1 effort has been completed, with the exception of microprobe examination to be performed at Westinghouse-Hanford Company. During this quarter, a radioactive spill required extensive clean-up. Further effort has been delayed to permit approval of any experimental procedures to preclude recurrence of the accident. It is expected that further evaluation will be underway during the next quarter.

Task 2 was designed to evaluate the structural stability of double-containment refractory-alloy materials combinations for PMC using a more systems-oriented liner/strength member combination in the testing configuration. Tests with SSC were included to provide comparative information as to differences in stability and compatibility between the two fuel forms. Sixteen PMC and four SSC test specimens have been exposed at 1500°, 1800°, and 2000°C for times from 500 to 5000 hours. Evaluation has been completed, with the exception of microprobe examination.

Task 3 involved evaluating potential barrier materials between pressed plutonium oxide (PPO), the latest AEC/SNS fuel form, and iridium chosen as the post impact containment shell for the MHW-RTG. Evaluation has been completed on the set of 10 test capsules exposed at 1500°C for 1000 and 5000 hours, with the exception of microprobe analysis.

Task 4 is a highly experimental effort to determine the effects of accelerated plutonia fuel aging. The objective was to produce an equivalent of approximately 2-1/2 years of helium generated from the plutonium in 6 months by adding shorter-lived curium-242. Both PPO and PMC fuel forms were held at 850° and 1200°C for seven months prior to heating to simulate a reentry thermal pulse. The original plan included impact testing at Los Alamos Scientific Laboratory, but variable fuel quality negated the potential value of the impact effort and a portion of the post test standard technical analysis originally planned. A reduced-scope post-test activity has been completed during the current quarter.

Task 5, a followon to Task 3, is designed to provide a systems-oriented test configuration analogous to the MHW-RTG heat source. Heat source materials volumes and thermal conditions are to be reasonably simulated, along with insertion of iridium tensile specimens to determine mechanical behavior in a systems configuration. Four PPO-fueled and three control (non-fueled) thermal-gradient test specimens containing iridium microsize tensile specimens, some adjacent to the fuel and others in contact with either the graphitic impact liner or graphite ablator materials, are to be evaluated. Three plutonia powder fueled and three control uniform-temperature test capsules containing subsize iridium tensile specimens will also be evaluated. Maximum effort is being made to provide significant results to the MHW-RTG program office prior to the end of this calendar year, and in conjunction with that program's design freeze.

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Section 2

RESULTS

Chemical analyses were completed on control specimens from Tasks 1, 2, and 3 to supplement results reported previously. Microprobe analysis was initiated at Westinghouse-Hanford Company on specimens from Tasks 1, 2, and 3, but has been delayed because of a radioactive materials spill in their microprobe facility. Metallographic evaluation was completed on Task 4 fuel aging specimens. Test capsules were assembled and exposure is about to begin on the Task 5 MHW mockup test effort. The high-strain-rate tensile test machine was assembled and successfully demonstrated using microsize iridium specimens resistively heated to 1370°C.

2.1 TASK 1 - PLUTONIA/CURIA COMPATIBILITY AND BCL-PMC STABILITY

Results of the original plutonia (~1 w/o metallic impurities) and improved purity plutonia (~0.23 w/o metallic impurities) short-term tests (1000 hours at 2000°C and 2000 hours at 1800°C) have been reported (Reference 1). Long-term test results (15,000 and 18,000 hours at 1800°C) were discussed in the 15th quarterly report (Reference 2). Semiquantitative emission spectrochemical analyses were completed by Ledoux and Company, Teaneck, New Jersey, during this quarter on control capsule materials which had been exposed 18,000 hours at 1800°C in an ion-pumped vacuum of approximately 10^{-8} torr. These chemical analyses (Table 2-1) indicate a reduction in the amount of volatile species such as chromium, iron, nickel, silicon, and possibly aluminum and titanium to a nondetectable level. This is in agreement with Bourgette's work on superalloys (Reference 3). There was an increase in molybdenum content in the three nonmolybdenum-containing alloys because of the high (4×10^{-7} torr) vapor pressure of molybdenum at 1800°C. Fueled specimens would not have been affected because two guard capsules surrounded each specimen thereby protecting the inner container from molybdenum transport. The control specimens were exposed without external guard capsules to minimize cost and to provide maximum interaction with the external vacuum.

Table 2-1
ORIGINAL PLUTONIA CONTROL CAPSULE CHEMICAL ANALYSES
(Impurities Expressed in Parts Per Million)

Impurity	Tungsten		W-25Re Post	Rhenium		Mo-46Re		Molybdenum		W-30Mo-30Re	
	Pre	Post		Pre	Post	Pre	Post	Pre	Post	Pre	Post
Aluminum	<10	<10	<10	<10	<10	<10	<10	10	<10	<10	<10
Chromium	<10	<10	<10	30	<10	<10	<10	10	<10	<10	<10
Iron	<10	<10	<10	100	<10	40	<10	30	<10	10	<10
Nickel	<10	<10	<10	20	<10	<10	<10	<10	<10	<10	<10
Silicon	<10	<10	<10	<40	<10	10	<10	70	<10	<10	<10
Titanium	<10	<10	<10	10	<10	10	<10	<10	<10	<10	<10
Molybdenum	10	100	20	50	200	High	High	High	High	High	High
Rhenium	ND	ND	High	High	High	High	High	ND	ND	High	High
Tungsten	High	High	High	<500	<500	<500	<500	<500	<500	High	High

NOTE:

High - 10% to 100%

ND - Not detected (no detection limit stated)

Detection limits for other elements analyzed for but not detected:

<10 ppm - Ag, Ba, Be, Ga, Ge, In, Mg, Mn, Sn, Sr, V, Zr

<30 ppm - B, Ca, Co, Cu, Nb, Pb,

<50 ppm - Sb

<100 ppm - Bi

<300 ppm - As, Zn

<500 ppm - Hf, Ta

Microprobe analysis at Westinghouse-Hanford Company was completed on two specimens in August after which radioactive contamination was found on the floor of the laboratory. Extensive cleanup was required. Handling procedures have been detailed prior to proceeding with with further examination during the next quarter. Specimens from Tasks 2 and 3 have also been delayed because of this spill.

Experimental work was previously completed on the curia-244 and Battelle-Columbus Laboratories plutonia-molybdenum cermet subtasks.

2.2 TASK 2 - PMC AND SSC TESTING PROGRAM

Twenty refractory alloy capsules containing PMC (plutonia-molybdenum cermet) or SSC (plutonia-thoria-molybdenum solid-solution cermet) fuel pellets were exposed at 1500°, 1800°, and 2000°C for times from 500 to 5000 hours. Results are included in the last five quarterly reports (References 2, 4, 5, 6, and 7).

Chemical analyses were completed on seven sets of control specimens (Table 2-2). Arrows between columns indicate expected direction of mass transfer between the inner and outer containers. Underlined values indicate the actual amount of mass transfer that occurred between containers. Intercapsule transfer did not occur in the Mo-46Re/T-111 capsule exposed at 1500°C for 5000 hours. There was no potential for transfer in the TZM/TZM capsule exposed at 1800°C for 1000 hours. Only hafnium, titanium, and zirconium were transferred in three capsules (TZM/Mo-46Re, Mo-46Re/TZM, and W-25Re/T-111) exposed at 1800°C for 5000 hours. Titanium transferred from TZM to Mo-46Re in two cases, whereas zirconium was only detected when transferred from the massive outer TZM container to the less massive Mo-46Re inner container. Both hafnium and zirconium were transferred from T-111 to the W-25Re container. In the TZM/W-25Re capsule exposed at 2000°C for 1000 hours, both titanium and molybdenum transferred, although to a very minor extent. Tungsten, Tantalum, and rhenium did not transfer in analyzable quantities. All quantities transferred were small and would have only minor effects on structural properties of pure refractory metals or solution-strengthened refractory alloys such as Mo-46Re and W-25Re but could eventually cause decreased strength in precipitation-strengthened alloys such as TZM (Mo-0.5%Ti-0.08% Zr).

Table 2-2

PMC-SSC CONTROL CAPSULE POST TEST CHEMICAL ANALYSES
(Impurities Expressed in Parts Per Million)

Temperature (°C) Time (Hours) Layer Material	1500° 5000		1800° 1000		1800° 5000		1800° 5000		1800° 5000		2000° 1000		2000° 1000	
	Inner Mo46Re	Outer T111	Inner TZM	Outer TZM	Inner TZM	Outer Mo46Re	Inner Mo46Re	Outer TZM	Inner W25Re	Outer T111	Inner W25Re	Outer W25Re	Inner TZM	Outer W25Re
Impurity:														
Iron	<10	<10	<10	10	<10	<10	<10	<10	<10	<10	10	<10	<10	<10
Hafnium	<500	← Med	<500	<500	<500	<500	<500	<500	<u>700</u>	← Med	<500	<500	<500	<500
Molybdenum	High	→ <50	High	High	High	High	High	High	<20	<50	<20	<20	High	→ <u>20</u>
Columbium	<30	50	<30	<30	<30	<30	<30	<30	<30	50	<30	<30	<30	<30
Tantalum	<500	← High	<500	<500	<500	<500	<500	<500	<500	← High	<500	<500	<500	<500
Titanium	<10	<10	4000	4000	4000	→ <u>400</u>	800	← 4000	<10	<10	<10	<10	4000	→ <u>10</u>
Tungsten	<500	← MH	<500	<500	<500	<500	<500	<500	H	MH	High	High	<500	← High
Zirconium	<10	← 400	500	500	500	→ <10	<u>50</u>	← 500	<u>30</u>	← 400	<10	<10	500	→ <10
Rhenium	High	ND	ND	ND	ND	→ High	High	ND	H	ND	High	High	ND	← High

Note:

1. High - 10% to 100%
2. MH - 10%
3. Med - 1% to 10%
4. ND - Not detected (no detection limit stated)
5. Detection limits for other elements analyzed for but not detected:
 <10 ppm - Ag, Al, Ba, Be, Cr, Fe, Ga, Ge, In, Mg, Mn, Ni, Si, Sn, Sr, V
 <30 ppm - B, Ca, Co, Cu, Pb
 <50 ppm - Sb
 <100 ppm - B
 <300 ppm - As, Zn
6. ← → Expected direction of mass transfer
7. xx Actual mass transfer amount

Microprobe analyses were completed on two specimens from this task, which resulted in extensive contamination in the laboratory as discussed under Task 1. Further effort will commence during the next quarter.

2.3 TASK 3 - MHW-RTG BARRIER TEST

Ten complex test capsules containing PPO (pressed plutonium oxide) with two oxygen content levels, (PuO_2 and $\text{PuO } 1.85$), barriers (Mo foil/Ir foil or Mo foil/ HfO_2), noble metal containers (Ir, Pt-20Rh, or Pt-26Rh-8W), and oxygen getters (graphite or Ta-10W) were exposed at 1500°C for 1000 or 5000 hours. Results have been reported in prior quarterlies (References 4, 5, and 6).

Chemical analyses of the iridium control specimens exposed at 1500°C for 5000 hours are listed in Table 2-3. Results are representative of current production quality iridium. Neither molybdenum nor hafnium were detected, indicating that the effect of the presence of molybdenum foil (in 33C) and hafnia barriers (in 29C and 31C) was negligible on the bulk properties of iridium.

The two iridium containers to be examined by microprobe analysis continue to await action.

2.4 TASK 4 - PLUTONIA FUEL AGING

The objective of the plutonia fuel aging effort was to determine the extent of structural damage to fuel forms having the equivalent of several years helium generation in the fuel. Damage had been displayed previously in fuels aged for several months, but program schedules precluded study to expected system lifetimes. In concept, curium-242 can be added to the plutonium-238 to artificially accelerate helium generation without changing the structural characteristics of the fuel. The use of approximately 3% Cm-242 in Pu-238 would result in the equivalent of 2-1/2 years of helium generation in six months. Both PMC and PPO fuel forms were to be studied using standard fuel forms as reference material. Aging temperatures of 850° and 1200°C were selected as representative of the operating conditions for Transit/Pioneer and an early version of the multi-hundred watt heat sources, respectively. It was originally intended to study only the effect of aging as compared to aging

Table 2-3
MHW BARRIER IRIIDIUM CONTROL CAPSULE
POST-TEST CHEMICAL ANALYSES
(Impurities Expressed in Parts per Million)

	Capsule No.		
	29C	31C	33C
Copper	10	10	10
Iron	10	20	20
Silicon	<10	<10	10
Tungsten	1500	1500	1500
Platinum	20	70	20

Note: Detection limits for other elements analyzed for but not detected:

<10 ppm - Ag, Al, B, Va, Be, Bi, Co, Cr, Ga, Ge, In, Mg,
Mn, Nb, Ni, Sn, Sr, Ti, V, Zr
<30 ppm - Pb
<50 ppm - Cd, Mo, Sb
<300 ppm - As, Zn
<500 ppm - Hf, Ta

plus a typical reentry thermal pulse and subsequent impact. However, variability of the fuel forms fabricated for the program at ORNL resulted in a decision to forgo impact testing. Accompanying this decision was a modification in scope of the evaluation effort to those specimens expected to provide the most information relevant to heat source applications.

All fuel forms were encapsulated in Ta-10W and T-111 containers typical of the materials used in Transit and Pioneer heat sources. Pre-test specimens were maintained under ambient conditions throughout the aging period. These specimens were then subjected to reentry thermal pulses along with the thermally aged specimens.

Macroscopic damage mechanisms were to be evaluated by dimensional measurement and indirectly by helium release. Specimens were assembled with at least 5% allowable diametral gap to permit swelling prior to sticking in the container. Helium release provides a qualitative measure of the structural openness of the fuel. Metallographic examination was to be used as the primary means to determine microscopic damage mechanisms such as helium void distribution, metal network stability, and structural degradation within the plutonia. More sophisticated techniques such as scanning electron microscopy (SEM) or electron beam microprobe analysis would have been used wherever useful.

The ambient aged specimens were originally intended as pre-test reference samples. Postponement of evaluation to the end of the program to minimize dose problems resulted in a decision to perform reentry thermal pulses on these specimens. The thermal pulse was to represent long-time storage followed by an immediate operational abort. These specimens, therefore, became non-representative as reference specimens.

Evaluation has been completed on selected fuel aging specimens (Table 2-4). Furnaces containing 18 fuel aging specimens were turned off on July 3 after seven months exposure at 850° and 1200°C. Seven test specimens were thermally cycled on July 11 through the Transit reentry thermal pulse listed in Table 2-5, reaching a maximum temperature of 1425°C. Seven other test specimens were thermally cycled on July 13 through the MHW reentry thermal pulse listed in Table 2-6, reaching a maximum temperature of 1850°C.

Table 2-4
TASK 4 - FUEL AGING CAPSULE TEST STATUS

DWDL Capsule Designation	Fuel Form	Container Materials		Exposure		Reentry Simulation ^(a)	Status (10/1/72) ^(b)
		Liner	Structural Member	Temp. (°C)	Time (mo)		
420	PMC	Ta-10W	T-111	Ambient	7	T/P	Met
416	↓	↓	↓	850	↓	None	Store
417				850		T/P	Met, He, Intact
418				1200		None	Store
419				1200		MHW	Met
425	PMC + Cm			Ambient		T/P	Met
422	↓			850		None	Store, He,
421				850		T/P	Store, He
423				1200		None	Store
424				1200		MHW	Store, He
428	PPO (HP) ^(d)			Ambient		MHW	Met
427	↓			850		None	Met, Intact
426				850		T/P	Store, Intact
430				1200		None	Met, He
429				1200		MHW	Met
431	PPO + Cm			Ambient		MHW	Met
433	↓			850		None	Store, He,
432				850		T/P	Store, Intact
434		1200	None	Met, He, Intact			
435		1200	MHW	Met, He			
436	PPO (CPS) ^(c)	Ta-10W	850	T/P	Store, Intact		
437	PPO (CPS) ^(c)	Ta-10W	1200	MHW	Met		

a. T/P is a Transit/Pioneer thermal reentry transient, 1425°C max temperature.
MHW is a Multihundred Watt thermal reentry transient, 1850°C max temperature.

b. Met - metallography performed.
Store - specimen stored without metallography.
He - helium release measured.
Intact - fuel removed intact, all others stuck in container or pulverized on attempting to remove.

c. CPS - cold pressed and sintered

d. HP - hot pressed

Table 2-5
TRANSIT REENTRY THERMAL PULSE

Elapsed Time (min)	Temperature (°C)	Comments
0	850	Heating started
10	1100	
12	1370	
13	1425	Furnace turned down
14	1370	
16	1315	
20	850	Furnace turned off

Note: Furnace equilibrated 15 min at 850°C prior to start.
Manual furnace control provided smooth temperature transients within $\pm 25^\circ\text{C}$ throughout run.

Table 2-6
MHW REENTRY THERMAL PULSE

Elapsed Time (min)	Temperature (°C)	Comments
0	1200	Rapid heating started
3	1700	
6	1850	Held for 4 min
10	1850	Furnace turned off
12	1200	

Note: Furnace equilibrated 15 min at 1200°C prior to start
Manual furnace control provided smooth temperature transients and hold within $\pm 50^\circ\text{C}$ throughout run.

Helium-release measurements were made on eight selected specimens. Metallography was completed on 10 of 15 specimens selected for examination. The remaining five either pulverized prior to mounting or did not polish after mounting.

Post-test helium release measurements were made to determine the effects of curium additions and thermal treatment on the amount of helium released from the fuel structure into a closed container. The standard fuel forms averaged 0.75 ± 0.03 yr from fabrication to the end of aging or thermal pulsing. The curium-spiked fuel forms averaged a pseudo-age of 4.10 ± 0.05 yr (chronological age also 0.75 yr) from fabrication to the end of aging or thermal pulsing. Emphasis was on PMC after 850°C aging and PPO after 1200°C aging because of current systems applications. Table 2-7 lists the data obtained.

Evaluation of helium release from the PPO and PPO+Cm fuel forms indicate essentially no difference between the two. Directly comparable specimens aged at 1200°C (specimen 430: PPO, and 434: PPO+Cm) both released about 95% of the helium generated. The gas mass spectrometry sample for specimen 434 was lost, resulting in a best estimate that 2.00 ± 0.09 cc/g of helium was released. The corresponding 95% $\pm 4\%$ release of the helium generated provides reasonable correlation with the unspiked specimen. Residual helium storage, calculated as the difference between generated and released helium, is estimated as 0.10 ± 0.08 cc/g. The minimum estimated for the spiked PPO, therefore, is the same as unspiked material (0.02 cc/g) with a reasonable probability that the helium stored in the spiked PPO is somewhat higher than for the unspiked PPO. Helium release data for a PPO+Cm specimen aged at 850°C shows a 93% release, which is comparable to those specimens aged at 1200°C . It appears that a somewhat higher level of helium may remain stored in the structure (0.15 cc/g at 850°C compared with 0.10 ± 0.08 cc/g at 1200°C). More complete data are necessary to confirm these observations, but it is reasonable that helium retention in the structure is related more to helium overpressure (PMC+Cm has higher pressure than PMC) than to temperature (1200°C results in less storage than 850°C).

Evaluation of helium release from the PMC and PMC+Cm fuel forms indicates that the curia had no effect beyond that of natural aging of standard PMC fuel forms. In unreported work currently underway at Los Alamos Scientific

Table 2-7

HELIUM RELEASE VALUES FOR FUEL AGING SPECIMENS

Specimen No.	Fuel Form	Exposure Conditions		Estimated Helium Storage As-Fabricated (cc/g) ^(a)	Helium Generation from Fabrication to Test Completion (cc/g)	Total Helium Storage (cc/g)	Post-Test Helium Release		Estimated Residual Helium Storage (cc/g)
		Temp for 7 mo (°C)	Reentry Thermal Pulse (°C)				(cc/g)	(%)	
430	PPO	1200	None	0	0.40	0.04	0.38	94	0.02
434	PPO+Cm	1200	None	0	2.10	2.10	2.00 ^(b)	95 ^(b)	0.10 ^(b)
435	PPO+Cm	1200	1850	0	2.14	2.14	0.31 ^(c)	(c)	(c)
433	PPO+Cm	850	None	0	2.10	2.10	1.95	93	0.15
417	PMC	850	1425	0.12	0.37	0.49	0.30	62	0.19
422	PMC+Cm	850	None	0.12	2.10	2.22	1.24	56	0.98
421	PMC+Cm	850	1425	0.12	2.14	2.26	1.63	72	0.63
424	PMC+Cm	1200	1850	0.12	2.15	2.27	2.26	100	0.01

a. It is assumed that all helium is released from the plutonia fuel form as fabricated but that 0.1 cc/gm of cermet is stored in the PMC fuel forms as fabricated.

b. Gas mass spectrometry sample lost. Values listed are probably accurate within ± 0.08 cc/g helium and $\pm 4\%$ helium released.

c. Container apparently leaked helium to the next level of containment.

Laboratory, helium release begins relatively slowly and gradually increases to the generation rate when held at 850°C and remains at about half the generation rate when held at 800°C. Post-test results on PMC+Cm specimen 422 aged at 850°C show a helium release of 56%. The addition of a 1425°C thermal pulse increased release to 72% for the curium-spiked PMC specimen 421. The comparable aged and pulsed PMC specimen (417) released 62% of that stored. The difference is more likely attributable to age (0.75 yr for PMC and 4.1 pseudo-yr for PMC+Cm) than to any form of degradation. Aging at 1200°C followed by an 1850°C thermal pulse resulted in total helium release in a PMC+Cm specimen (424). This was expected. Helium storage is a reciprocal to helium release. Essentially no storage occurred in the 1200°C age plus 1850°C thermal pulse PMC+Cm specimen. The 850°C plus 1425°C thermal pulse PMC specimen stored only slightly more helium after exposure than after fabrication (0.19 cc/g after exposure, 0.12 cc/g after fabrication). The comparable curium-spiked specimen stored more helium after exposure (0.63 cc/g) with even more stored in the specimen not pulsed (0.98 cc/g). Helium overpressure, generated to a greater extent in curium-spiked fuels, results in somewhat increased storage, with the short thermal pulse tending to drive out some of the stored helium.

Specimen 435 with a discolored oval area on the outer surface was smear free on that surface, but upon penetration for helium measurement, evolved a much smaller-than-expected gas volume. It appears that helium leaked from the liner containers into the safety container thereby reducing the stored gas content. The discoloration was most likely associated with leakage of oxygen along with the helium.

The fuel-aging capsule design is shown in Figure 2-1. Each of the 22 capsules was sectioned near the top of the capsule so as to permit removal of the fuel pellets. Only eight of the pellets were removable intact. The remainder stuck in their respective capsules, some because of interaction with the tantalum-10% tungsten container and others because of fuel swelling. All five PPO or PPO+Cm specimens aged at 850°C were removable. Only one other PPO+Cm (1200°C, no thermal pulse), one PMC (850°C, 1425°C thermal pulse), and one PMC+Cm (850°C, no thermal pulse) specimens were removable intact. Attempts were made to examine three of the intact PMC+Cm or PPO+Cm specimens without success because of pulverizing before or after mounting for metallography.

Figure 2-1. Fuel Aging Capsule Design (SNS/DWDL Configuration 7)

Metallography was completed on 10 specimens and limited observations were made on the remaining 12 specimens. Emphasis was directed toward thermal pulsed specimens, particularly PMC after 850°C aging and PPO after aging at 1200°C.

In specimen 420 (PMC, ambient storage, 1425°C thermal pulse), the fuel pellet was stuck in its capsule as shown in A, Figure 2-2. The capsule appeared clean with only minor discoloration. Metallography showed that the gross metal-oxide structure was relatively typical of a coated-shard hot-pressed product (B, Figure 2-2). The oxide particles were highly fractured into smaller particles. An acicular medium gray second phase in the oxide is indicative of the monotectoid decomposition product (C, Figure 2-2). The darkest gray areas in C, Figure 2-2 are artifact pseudo-phases present in voids and fractures and are most likely related to a mounting compound reaction from the alpha radiation. There are fine metallic precipitates in the oxide and in D, Figure 2-2, a large number of oxide appearing precipitates are present in the molybdenum metallic phase. Precipitates in the metal

A. MACROGRAPH OF SECTIONED CAPSULE

B. CENTER
50x (20 MILS)

C. CENTER
500x (2 MILS)

D. CENTER
500x (2 MILS)

Figure 2-2. 420: PMC, Ambient Storage, 1425°C Thermal Pulse

phase show dramatically using an alumina relief polish but tend to disappear on polishing with diamond. The structure of this specimen appears to have been degraded considerably, probably caused by the rapid thermal pulse forcing the stored helium out of the particles in an uncontrollable manner. Comparable testing on a Task 1 BCL-PMC specimen produced similar results.

The specimen 416 (PMC, 850°C, no thermal pulse) fuel pellet was stuck in the capsule. The capsule was clean. This specimen was not examined because specimen 417 (with a thermal pulse) was available for examination.

Fuel from specimen 417 (PMC, 850°C, 1425°C thermal pulse) came out of the capsule intact as shown in A, Figure 2-3. Pellet dimensions were 0.192-in. pretest length, 0.201-in. post-test length, 0.184-in. pretest diameter, and 0.190-in. post-test diameter for a volumetric expansion of approximately 11%, from about 91% of theoretical density before exposure to 82% after. The weight remained unchanged. The capsule was clean. Metallography showed the general cermet structure to have remained intact with major fracturing of the plutonia into subgrains (B, Figure 2-3). Higher magnification photomicrographs show the metal areas with nonmetallic precipitates present and the oxide with metal precipitates (C, Figure 2-3). As shown in D, Figure 2-3, the oxide may be somewhat substoichiometric. The general structure is very similar to specimen 420 (ambient aged), exhibiting essentially no microstructural damage caused by aging PMC at 850°C for seven months.

Specimen 418 (PMC, 1200°C, no thermal pulse) fuel fractured with approximately half sticking to the tantalum hold-down disc; the remainder stuck in the capsule. The capsule had a matte surface finish inside. This specimen was not examined because specimen 419 exposed at 1200°C with a subsequent 1850°C thermal pulse was available for examination.

Specimen 419 (PMC, 1200°C, 1850°C thermal pulse) was sectioned transversely through the fuel end of the capsule. The fuel pellet remained firmly lodged in the capsule. The cermet structure was more porous than those aged and thermally pulsed at lower temperatures. In A, Figure 2-4, the porosity is shown as well as a loss in the continuous nature of the molybdenum metal

Figure 2-3. 417: PMC, 850°C, 7 Months, 1425°C Thermal Pulse

network. At higher magnifications (B and C, Figure 2-4), the small grain size of the plutonia is clearly shown. The blackest areas are voids, the acicular dark gray is either grain boundaries or monotectoid (or both), and the white areas are metallic precipitates in the oxide and metal network. There is a definite tendency for the metal network to break up and coalesce into less angular shapes, particularly compared to specimens heated at lower temperature.

In 425 (PMC+Cm, ambient aged, 1425°C thermal pulse) the fuel remained intact and relatively undamaged (A and B, Figure 2-5). The capsule had minor discoloration on the wall as shown in B, Figure 2-5. In C, Figure 2-5, the cermet structure was highly irregular and probably representative of the as-fabricated pellet which had fractured transversely sometime after hot pressing. The metallic network is very uneven in content and contains irregularly shaped very fine particles as shown in D, Figure 2-5. A massive amount of metal precipitates is present in the plutonia and much oxide precipitation is present in the metal network. High magnification shows a basically single phase fine-grain structure, with a second dark gray phase at the grain boundaries, and a small amount of porosity (E, Figure 2-5). Comparison with specimen 420 (no curia addition) indicates that the initial structure of specimen 425 was very inferior to standard PMC, but that the 1425°C pulse seemed to have caused less severe damage to the PMC+Cm than to the PMC alone which showed a higher level of fracturing within the plutonia

Specimen 422 (PMC+Cm, 850°C, no thermal pulse) fuel pellet fell out and crumbled to a coarse powder. The pretest appearance is shown in A, Figure 2-6, as the larger piece in the back of the photograph.

Exposure at 850°C resulted in the tantalum hold-down plug (which replaced the hold-down disc in PMC+Cm specimens because of the limited height of the pellets) being coated with an irregular gray to black deposit. No attempts were made to analyze the deposit which is probably a combination of both molybdenum and plutonia. Small fragments of the fuel pellet were mounted for metallography but polishing was unsuccessful.

Figure 2-4. 419: PMC, 1200°C, 7 Months, 1850°C Thermal Pulse

A. PRETEST PELLET

B. SECTIONED CAPSULE

PMC
→

C. MOUNTING MATERIAL

50x (20 MILS)

D. CENTER

200x (5 MILS)

E. CENTER

1000x (1 MIL)

Figure 2-5. 425: PMC+Cm, Ambient Storage, 1425°C Thermal Pulse

Specimen 421 (PMC+Cm, 850°C, 1425°C thermal pulse) behaved very similar to specimen 422, crumbling to a powder. Therefore, no metallography was attempted.

Specimen 423 (PMC+Cm, 1200°C, no thermal pulse) fuel pellet stuck in the capsule and crumbled on attempting to remove it from the capsule. The pre-test pellet is shown in Figure 2-7.

Specimen 424 (PMC+Cm, 1200°C, 1850°C thermal pulse) partially stuck to the hold-down plug. The remainder pulverized on slight prodding with tweezers. The capsule had a very dull appearance. The pre-test pellet is shown in Figure 2-8.

Only the ambient aged plus 1425°C thermal pulse PMC+Cm specimen exhibited sufficient integrity after seven months to be sectioned and polished for examination. None of the 850° or 1200°C aged specimens retained any semblance of structural integrity. It is undeterminable at this time whether this was caused by poor initial structure, thermal stresses caused by the increased heating from the curium-242, or from the presence of helium equivalent to four years decay of plutonia-238. Based on information obtained on the plutonia specimens, It is likely that the poor initial structure had the greatest influence on structural integrity.

Five of the PPO specimens were made by hot pressing (HP) techniques as were the PPO+Cm specimens. Typical PPO (HP) pre-test specimens are shown in Figure 2-9. These pellets were hot pressed in graphite dies and subsequently heated to burn out the graphite. It is apparent that the hot-pressed PPO used in this program was inferior to current products. Two extra PPO pellets (specimens 436 and 437) were made by cold pressing and sintering (CPS) and had a much better appearance and overall structure.

Specimen 428 (PPO(HP), ambient aged, 1850°C thermal pulse) remained stuck in the capsule as shown in A, Figure 2-10. The capsule exhibited dull areas on the wall, a powdery deposit, and apparent melting around the periphery of the conical pellet recess. The oxide structure was very porous with only about half the area being polished satisfactorily (B, Figure 2-10). Portions of the plutonia had the appearance of fine particles with spherical voids, separated from each other (the gray is mounting compound) as shown in C, Figure 2-10.

A. PRETEST SPECIMEN

B. HOLD-DOWN PLUG AFTER EXPOSURE

Figure 2-6. 422: PMC+Cm, 850°C, 7 Months, No Thermal Pulse

Figure 2-7. 423: PMC+Cm, Pre-Test

Figure 2-8. 424: PMC+Cm, Pre-Test

Figure 2-9. Typical PPO (HP) Specimens Before Exposure

A. MACROGRAPH

B. CENTER

50x (20 MILS)

C. CENTER TYPICAL

500x (2 MILS)

D. EDGE

200x (5 MILS)

Figure 2-10. 428· PPO(HP), Ambient Storage, 1850°C Thermal Pulse

The relief polished structure of the plutonia in C, Figure 2-10, is indicative of quite substoichiometric plutonia. Other areas of the plutonia appeared well sintered such as in D, Figure 2-10. The white areas are metal precipitates that appear to delineate grain boundaries and may well have been liquid at temperature. This structure could have been a result of interaction with the tantalum-10% tungsten container or the result of coalescing original impurities into smaller volumes during the thermal pulse, with the former being more likely. Appearance of the Ta-10W container bottom is shown in Figure 2-11 where a 3-mil reaction layer has been formed in the capsule bottom. The structure of the plutonia has been damaged by the thermal pulse in some manner as is obvious when compared with the structure in 427 (Figure 2-12).

The PPO pellet in 427 (PPO(HP), 850°C, no thermal pulse) came out reasonably intact as shown in A, Figure 2-12. Some loss of loose particles occurred as indicated in a weight change from 0.724 g prior to exposure to 0.700 g after exposure. The length was measured as 0.217 in. before exposure and 0.215 in.

Figure 2-11. 428: Bottom of Ta-10W Capsule Adjacent to PPO(HP) After 1850°C Thermal Pulse

A. MACROGRAPH OF PELLET

B. TYPICAL

50x (20 MILS)

C. TYPICAL

200x (5 MILS)

D. TYPICAL

500x (2 MILS)

Figure 2-12. 427: PPO(HP), 850°C, 7 Months, No Thermal Pulse

after exposure. The diameter was measured as 0.191/0.192 in. before exposure and 0.190 in. after exposure. It is probable that some small amount of sintering or shrinkage occurred during the thermal aging. The capsule was clean and the hold-down disc was tarnished. The plutonia structure shown at low magnification appears to have large cracks, many small voids, and no well defined structure (B, Figure 2-12). Higher magnification shows the cracking and voids in better detail (C, Figure 2-12). At still higher magnification, many small voids are shown to be present throughout the structure (D, Figure 2-12). There was no visible evidence of substoichiometry. Macroscopic damage did not occur during the 850°C aging. The extent of structural change during aging is unknown.

The specimen 426 (PPO(HP), 850°C, 1425°C thermal pulse) fuel pellet stuck but came free on cutting. The length of the pellet shrank from 0.220 in. before aging to 0.216 in. after aging. The diameter changed from 0.193 in. to 0.191 in. after aging for an estimated volumetric shrinkage of 3.9%. Pellet weight was not determined and metallography not performed because of the material inadvertently became mixed with scrap material and was removed from the gloved boxes to reduce personnel dose rates. The capsule was clean and no oxide had stuck to the disc.

The plutonia pellet from 436 (PPO(CPS), 850°C, 1425°C thermal pulse) came out intact except for a chip out of the top edge (Figure 2-13). The capsule was clean.

The plutonia pellet in 430 (PPO(HP), 1200°C, no thermal pulse) stuck in the capsule but came out during subsequent sectioning. The pellet as shown in A, Figure 2-14 exhibited no major macroscopic damage other than a spalling off of some of the surface material. The capsule had a dull dark gray appearance caused by oxidation of the Ta-10W capsule from the oxygen containing vapor species over the plutonia. Structure of this 1200°C aged specimen is different from 427 aged at 850°C. The higher temperature aging resulted in a greater coalescing of voids into stringers of voids throughout the structure and at grain boundaries (B, Figure 2-14). White metallic precipitates were readily observable in plutonia aged at the higher temperature (C, Figure 2-14) but not at the low temperature. Long thin precipitates in the plutonia with an alignment related to the parent crystal orientation are new observations. This may be a different form of the

monotectoid reaction product caused by different thermochemical phenomena. Mechanical performance of this material would have been degraded because of the presence of large numbers of voids in the grain boundaries of the plutonia.

The plutonia pellet stuck in 429 (PPO(HP), 1200°C, 1850°C thermal pulse) even after sectioning (A, Figure 2-15). The capsule had a dull matte finish but was relatively clean. Structurally, this specimen is very similar to 430 which did not have a thermal pulse. The voids have coalesced around the original grain boundaries as well as being distributed throughout the structure (B, Figure 2-15). There are metallic precipitates in the oxide. The only difference perhaps caused by the thermal pulse is the greater amount of the aligned widmanstatten (long, thin) precipitates in the plutonia (C, Figure 2-15). Again, this may be a different manifestation of the monotectoid decomposition product, but this remains unsure.

The cold pressed and sintered plutonia pellet in 437 (PPO(CPS), 1200°C, 1850°C thermal pulse), which was thermally treated the same as 429, stuck in the capsule as shown in A, Figure 2-16. The capsule appeared relatively clean with

Figure 2-13. 436: PPO(CPS), 850°C, 7 Months, 1425°C Thermal Pulse

A. MACROGRAPH OF SECTIONED CAPSULE

B. TYPICAL

50x (20 MILS)

C. TYPICAL

200x (5 MILS)

Figure 2-14. 430: PPO(HP), 1200°C, 7 Months, No Thermal Pulse

A. MACROGRAPH OF SECTIONED CAPSULE

B. TYPICAL

100x (10 MILS)

C. TYPICAL

200x (5 MILS)

Figure 2-15. 429: PPO(HP), 1200°C, 7 Months, 1850°C Thermal Pulse

A. MACROGRAPH OF SECTIONED CAPSULE

Figure 2-16. 437: PPO(CPS), 1200°C, 7 Months, 1850°C Thermal Pulse

signs of matte surface near the pellet. The pellet appeared porous and the plutonia reacted with the capsule to fill the void area between the conical plug and the capsule bottom. This is shown in B, Figure 2-16, where a medium-gray shell is present adjacent to the plug and capsule bottom. Plutonia adjacent to this shell did not polish and actually crumbled away during grinding. The Ta-10W material shows definite intergranular attack caused by oxygen from the plutonia. The plutonia shell adjacent to the capsule shows a multiphase structure consisting of white metallic precipitates, light gray single-phase PuO_2 , darker gray unknown phase, and black voids oriented along grain boundaries (C, Figure 2-16). The mottled appearing plutonia structure on the left side of C, Figure 2-16 has metallic precipitates and possibly substoichiometric appearance but the inability to produce a polished surface does not permit further speculation as to the structural integrity of this material. It is apparent from this specimen that Ta-10W intruded into the aging reactions and should not be used if the experiment is repeated.

Ambient aged PPO+Cm specimen 431 which was thermally pulsed at 1850°C showed major degradation as shown in the sectioned capsule macrograph (A, Figure 2-17). The capsule appeared relatively clean. The center of the plutonia appeared highly fractured and porous. The areas that polished up were mostly single-phase oxide in the observable areas (B and C, Figure 2-17). The dark mottled areas are the result of fracturing out of large areas during polishing. There were considerable metallic precipitates some of which appear to have resulted from a eutectic decomposition. There do not appear to be many voids in the polished areas inferring that the voids coalesced at grain boundaries and resulted in the inability to polish large areas. The plutonia appears to have a small amount of a slightly different hardness material which may be another form of monotectoid decomposition product. This material appears slightly lighter gray in the original photomicrograph (C, Figure 2-17). Structurally, this specimen is in poor condition to remain in one piece if impacted even at low velocity.

The pellet in 433 (PPO+ Cm, 850°C, no thermal pulse) was in poor condition as-fabricated (A, Figure 2-18) and in worse condition after aging (B, Figure 2-18). Spalling was already occurring between fabrication and assembly. Aging continued this degradation. The pellet crumbled into powder on attempting to handle it for measuring.

A. MACROGRAPH OF SECTIONED CAPSULE

B. NEAR EDGE

50x (20 MILS)

C. NEAR EDGE

200x (5 MILS)

Figure 2-17. 431: PPO+Cm, Ambient Storage, 1850°C Thermal Pulse

Figure 2-18. 433: PPO+Cm, 850°C, 7 Months, No Thermal Pulse

Upon removal from the capsule, the pellet in 432 (PPO+Cm, 850°C, 1425°C thermal pulse) appeared completely intact but porous (Figure 2-19). Attempts to measure the length resulted in the pellet crumbling to fine powder. Poking with tweezers showed a very low probability of successful polishing, and no metallography was performed. The capsule remained relatively clean after aging.

Specimen 434 (PPO+Cm, 1200°C, no thermal pulse) came out of the capsule relatively intact (Figure 2-20). It appeared that a shell had formed at the surface and that the inner material had the appearance of a porous, friable ceramic. Dimensions were successfully taken with the diameter having decreased from 0.205 in. to 0.201 in. during aging. The length was 0.143 in. after exposure compared to 0.272 in. before exposure, indicating a considerable loss in length attributable to fracturing. Fracturing did occur during measuring, but one piece was mounted for metallography. The specimen continued to disintegrate on attempting to grind prior to polishing. Efforts to polish were discontinued.

Figure 2-19. 432: PPO+Cm, 850^oC, 7 Months, 1425^oC Thermal Pulse

Figure 2-20. 434: PPO+Cm, 1200^oC, 7 Months, No Thermal Pulse

Specimen 435 (PPO+Cm, 1200°C, 1850°C thermal pulse) remained intact upon sectioning (A, Figure 2-21). The capsule wall was dull and had deposits on it. The pellet appeared porous and massively fractured. Polishing was successful on this specimen. The fine grain size and fractured nature of the structure is shown in B, Figure 2-21. The white spots are metallic precipitates. The black areas are voids. At somewhat higher magnification (C and D, Figure 2-21), six different features become visible in the structure. The larger light-gray areas are basically PuO_2 . The white precipitate is metallic appearing, most likely was liquid during the thermal pulse, and is probably a $\text{Ta}_x\text{Pu}_x\text{O}$ compound. There is a small amount of darker gray material in the lighter gray matrix having an unknown composition. The angular dark gray material may be related to the monotectoid diffusion product, but this is uncertain. The mottled gray areas may be multiphase oxide or surface irregularity. The black areas are voids and fissures. This multiplicity of structures precludes positive conclusions as to modes of formation and degradation mechanism(s). It is apparent that the structural integrity of this specimen is poor; the reasons for this condition are unknown.

Quality of the initial material, both PPO(HP) and PPO+Cm, used in this experimental program was inferior to standard production-grade material. Helium release characteristics were as expected, apparently independent of the poor initial structure. Degradation was observable, but the extent and its effect on structural stability was undeterminable. The capsule material entered into the reactions to a varying extent, further compounding the difficulty in evaluation.

Control capsules were also exposed under the same conditions as the test specimens. No major compositional changes occurred during aging of these specimens which were not in contact with plutonia. The structure of the Ta-10W was unaffected by exposure. The T-111 appeared to have picked up a minor amount of precipitates.

A. MACROGRAPH

50x (20 MILS)

B. TYPICAL

C. TYPICAL

100x (10 MILS)

D. TYPICAL

200x (5 MILS)

Figure 2-21. 435: PPO+Cm, 1200°C, 7 Months, 1850°C Thermal Pulse

2.5 TASK 5 - MHW-RTG MOCKUP TESTS

Two different mockup test configurations are undergoing exposure prior to evaluation. The original thermal gradient set, designated "T" series, mocks up fuel, iridium claddings and graphite volumes, and associated thermal gradients. This series has micro-size iridium tensile specimens adjacent to standard MHW hot-pressed plutonia fuel, adjacent to the graphite impact material, and in the graphite reentry protection material. A matched set of control specimens without plutonia, designated as "C" series, provides reference data. A second configuration, designated "M" series, was added. This series contains larger sub-size iridium tensile specimens in contact with plutonia powder. The intent was to provide a higher level of assurance of data comparability on a standard tensile specimen under worst-case conditions of intimate contact with plutonia. This configuration has all the MHW materials but does not have a thermal gradient and does not mock up MHW materials volumes as well as the original configuration. A matched set of control specimens without plutonia, designated as "MC" series, provides reference data for this configuration.

Assembly of the seven fueled and six control specimens was completed in early October. Exposure was begun on one set on October 4 and the second set on October 11. Capsule status is listed in Table 2-8. The DWDL high-strain-rate tensile machine was successfully demonstrated for GE, AEC/SNS, and AEC/RLO personnel. Further work is underway to resolve minor problems with the apparatus.

Delays were encountered throughout the quarter on attempts to assemble the test specimens and start testing. The last critical delay was encountered in receiving the tungsten guard capsules. Although ordered in early July, the first partial shipment did not arrive until September 25; the second group arrived on October 4. Reasons for the delay included tungsten rejected because of cracking during welding, insufficient shipment of bar stock, and vendor errors in machining. Assembly was completed on the first group of three fueled and three control specimens on September 29; the remainder was completed on October 9.

Table 2-8

MHW-RTG MOCKUP TEST STATUS

Test Number	DWDL Number	Fuel Form	Tensile Specimen	Exposure Conditions		Reentry Thermal Pulse	Status (10-15-72)
				Time (hr)	Temperature (°C)		
T-1	566	Pellet	DWDL Micro	1500	1440/1100	No	260 hr
C-1	C-1	None	↓	1500	↓	No	260
T-2	567	Pellet	↓	Optional	↓	No	100
T-3	568	Pellet	↓	1500	↓	Yes	260
C-3	C-3	None	↓	1500	1440	Yes	260
T-4	569	Pellet	↓	Optional	↓	Yes	100
C-4	C-4	None	↓	Optional	↓	Yes	100
M-1	563	Powder	General Electric Subsize	1500	↓	No	260
MC-1	MC-1	None	↓	1500	↓	No	260
M-3	564	Powder	↓	1500	↓	Yes	100
MC-3	MC-3	None	↓	1500	↓	Yes	100
M-4	565	Powder	↓	Optional	↓	Yes	100
MC-4	MC-4	None	↓	Optional	↓	Yes	100

Components for the "T" series specimens are shown in Figure 2-22. The 10 DWDL micro-size tensile specimens were vacuum annealed at 1500°C prior to assembly. All other iridium parts were vacuum outgassed at 600°C. All graphite parts were vacuum outgassed at 2100°C. Plutonia pellets were hot pressed at LASL and had two flats to provide for intimate contact with four tensile specimens. The plutonia was further outgassed by DWDL at 1400°C in argon to produce a slightly substoichiometric composition. Iridium vent covers were supplied by GE with the central area of both surfaces covered with iridium powder sintered at 1850°C to provide adherence. Capsule lids had a 0.5-mil hole electron-beam-drilled in the center. The vent covers were spot welded to the lid to provide a vent configuration similar to that being used in the preliminary test units of the MHW source. Airflow through these vents typically varied from 50 to 250 cc/hr with one atmosphere pressure differential. One vent was considerably lower (13cc/hr) and one considerably higher (700 cc/hr). This variability could affect particulate retention but would not result in any pressure differential because the helium generation rate is only about 15×10^{-5} cc/min for these specimens. For each T unit, plutonia, four tensile specimens, and iridium foil specimen holders were assembled into the capsule and the lid was electron-beam welded. The large iridium capsule at the right in Figure 2-22 was assembled with the flat disc of ATJ graphite, the slotted cylindrical ATJ graphite, the slotted cylindrical ATJ graphite (originally intended as crushup graphite), the inner capsule assembly, four iridium tensile specimens adjacent to the capsule, a block of Hitco resin-impregnated Thornel-50 crush-up graphite, the slotted block of POCO AXF-5Q graphite, and two iridium tensile specimens for exposure at lower temperature. The lid with a 10-mil hole in the center was then electron-beam welded shut. Both a tungsten and a tantalum-10% tungsten guard capsule surrounded the inner assemblies with tungsten wire standoffs to minimize solid-state diffusion between layers. Control specimens ("C" series) had no plutonia, no vent cover (with the exception of C-4 which did), utilized an iridium foil sleeve and end discs in lieu of the outer iridium capsule (with the exception of C-4 which did), and used only a tungsten guard capsule (with the exception of C-4 which used only a Ta-10W guard capsule). These variations resulted from having only one spare vent cover (all supplied by GE) and having an extra iridium capsule, as well as schedule and cost constraints.

Components for the "M" series specimens are shown in Figure 2-23. The six GE sub-size tensile specimens were vacuum annealed at 600°C prior to

Figure 2-22. Components for MHW-RTG Mockup Test "T" Series Specimens

Figure 2-23. Components for MHW-RTG Mockup Test "M" Series Specimens

assembly. All other parts were treated the same as "T" series parts. Slotted iridium end discs were fixtured so that six iridium tensile specimens could be placed into the slots and a spot-welded iridium foil cylinder slid into place, then TIG welded to the two end discs. The tensile specimen subassembly was then vibratory filled with approximately 20 grams of plutonia powder supplied by LASL. The subassembly was heated to 1400°C for 6 hr in argon to outgas the fuel. The subassembly was handled as a fuel pellet and loaded into a long iridium capsule; the lid and vent cover combination was electron-beam welded. An ATJ-graphite disc, an ATJ graphite cylinder, the tensile specimen assembly, and a Hitco resin-impregnated Thornel-50 block were placed into the large iridium cylinder and electron-beam welded. Guard capsules of tungsten and Ta-10W were then placed over this assembly, the same as for the "T" series. Control capsules were the same, except for omission of plutonia and the inner iridium capsule (except for MC-4), an iridium foil cylinder and end discs in place of the outer iridium cylinder, and only tungsten guard capsules.

Four "T" and "C" thermal gradient specimens and two "M" and "MC" uniform temperature specimens were placed into one of the two Varian VF-400 ion-pumped furnaces modified specifically for this task. Four tantalum-sheathed W/W-25Re thermocouples were placed to measure the temperature of the uniform temperature capsules, the bottom and top of the thermal gradient capsules, and the top of the water-cooled copper chill block. Problems were encountered with water line leaks, thermocouple failure, and ion pump start-up which delayed the start of continuous exposure to October 4. The remaining specimens were loaded into the second furnace which started with minimal difficulty and both furnaces are now operating satisfactorily.

The DWDL high-strain-rate tensile test machine was demonstrated for GE (Paul Brown and Richard Mehan), AEC/SNS (Arnold Litman), and AEC/RLO (William Lotz and Jack Rhoades) personnel on August 24. Initial tests were on iridium micro-tensile specimens heated to 1370°C; average strain rates were in excess of 15,000 in./in.-min. Measured elongation values were 46% and 57% based on an effective gage length of 0.180 in. which closely approximate GE results at lower strain rates. Ultimate tensile strengths were estimated at 55 and 61 ksi, which are considerably higher than values obtained by GE. Three

possible reasons for the discrepancy have been explored. The first was that the load cell was out of calibration at the time of the demonstration. Recalibration showed that the load cell was providing correct readings. The second reason is that there may be some amount of hysteresis in the load cell resulting in the maximum recorded load occurring after the sample was broken. The first evidence of the sample being broken before maximum load was recorded was a spurious short-term transient superimposed on the load-time trace. This apparently occurred when the current path through the specimen was broken. This transient occurs between 0.2 and 0.5 ms prior to maximum load. No transient occurs on non-heated specimens as shown by the Ni sample (cold) in Figure 2-24. High-speed motion pictures wherein an oscilloscope trace of load was superimposed on pictures of the straining tensile specimens appeared to confirm this observation. However, superimposing the output of a small current through the specimen as a second signal channel showed that specimen breakage occurs at maximum load readout.

Figure 2-24. Strain Gage Load Cell Load-Time Recordings on Micro-Size Tensile Specimens

The third possible reason for load discrepancies is that the load cell dynamic response characteristics are inadequate for operation at the desired high strain rates. The strain gage load cell currently in use exhibits ringing characteristic of an underdamped system. Load rise time is only a factor of 2 to 5 slower than the resonant frequency of the load cell and its attendant hardware. The maximum load in an undamped system could be in error by as much as a factor of two. The probable error in the current system is less by an indeterminate amount. A high frequency piezoelectric load cell has been ordered so as to obviate the resonance problem and to provide correct readout at these high strain rates. Other investigators have successfully used piezoelectric transducers at deformation rates as high as 360 in. /sec.

Strain rate values were initially based on overall specimen deformation divided by the total time from the asymptotic point of load build-up to the maximum load. These averaged values for the two demonstration specimens were 46.7 and 51.9 in. /sec, which convert to 15,600 and 17,200 in. /in. -min (or min^{-1}) based on an effective gage length of 0.180 in. High speed motion pictures (Figure 2-25) confirm this deformation rate. This particular series was taken at a relatively slow 1000 frames per second to experiment with the superimposing of an oscilloscope load trace on the film (dotted line). Imposition of load occurred late in Frame 2 of Figure 2-25. Frames 3, 4, and 5 indicate deformation rates of 57, 67, and 73 in. /sec. Examination of higher speed ($\sim 10,000$ fps) films indicates that a relatively uniform deformation rate is attained in 0.5 ms or less with a relatively smooth transition from a zero strain rate to the average deformation rate. It appears that 10% or less of the total deformation occurs during this transitional deformation rate-time span. Based on information obtained to date, the average deformation rate on a heated micro-size iridium specimen, is approximately 60 in. /sec which is equivalent to an effective strain rate of $20,000 \text{ min}^{-1}$ on a specimen having a 0.180-in. gage length.

Resistance heating of the iridium test specimens resulted in a lower thermal gradient than that obtained on specimens at Del Research in work sponsored by GE/IPSO. Minor hardware modifications are underway to trigger the electronics package and to facilitate specimen handling when a gloved box is installed around the machine. Upon resolution of the breaking load discrepancy and

GRIP SEPARATION
BETWEEN FRAMES
(MILS)

LOAD ← 0

NONE

7

57

67

73

TOP GRIP
SPECIMEN

FRAME 1

BOTTOM GRIP

TIMING
MARKS

1 MILLISECOND

FRAME 2

OSCILLOSCOPE
LOAD TRACE

FRAME 3

FRAME 4

BREAK

FRAME 5

Figure 2-25. High Speed Pictures of Tensile Specimen Breaking

determination of the strain rate it was concluded in September by GE personnel that the DWDL high strain rate tensile unit will generate data closer to potential MHW impact strain rates than other devices in the MHW program.

The 1500 hour exposure of the first specimens is expected to be completed on December 6. Evaluation will then commence to provide engineering data to the MHW program prior to the end of December for use in a final design review meeting currently scheduled for early January 1973.

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Section 3

CONCLUSIONS

Evaluation of control capsules in the various tasks completed to date show that extended operation of refractory metal alloys in vacuum or in contact with other alloys at high temperatures results in compositional changes. Volatile impurities such as aluminum, iron, and silicon are lost at 1800°C and probably at considerably lower temperature. Removal of these specific constituents in all refractory alloys would not be detrimental and in fact, may be beneficial in producing enhanced ductility when cold and improved strength at elevated temperatures.

Molybdenum containing alloys lose molybdenum from the surface at 1800°C in a vacuum, at a rate of 10 mils per year, but appear to retain bulk properties. However, exposure of a molybdenum-containing alloy at 2000°C in a vacuum results in preferential volatilization of molybdenum leaving a porous degraded structure behind. A depth of over 0.1 in. was damaged in 10,000 hr. Other factors, such as strength, tend to eliminate the use of molybdenum-containing alloys at temperatures lower than that causing damage because of volatility of the molybdenum.

Alloys containing intentional additions of titanium and zirconium (TZM) or hafnium (T-111) may transfer these constituents to alloys not having these additions. Significant decreases of titanium and zirconium in TZM would degrade strength properties to that of unalloyed molybdenum. Loss of hafnium would have little or no effect on T-111 properties because hafnia is present as an oxygen getter for liquid metal systems and not for strength enhancement. Alloys picking up these constituents would probably be strengthened somewhat at the expense of decreased ductility. Transfer of these constituents occurred at 1800°C but was not observed at 1500°C. Therefore, for current thermoelectric systems mass transfer problems will not occur in at least 5000 hr and most likely will not be a factor to 5 yr.

Several conclusions have been reached from the fuel aging results although (1) quality of the initial fuel, (2) reaction of fuel with the container material, and (3) disintegration of several specimens which precluded metallographic examination all affected overall interpretation of results.

Only the standard PMC and PPO (CPS) appeared to meet current product standards. The PMC+Cm had a highly variable structure and was cracked. The PPO(HP) was low density (63% to 74% of theoretical density) and the PPO+Cm was even lower (52% to 60% of theoretical density) compared with standard products (80% to 85% TD).

The PPO+Cm was crumbling as received. It remains uncertain whether the thermal stress caused by the curium-242 heat generation, high initial helium generation from the curium-242, or inadequate material availability and process development resulted in the poor quality fuel. The most likely is the latter.

Further process development work appears necessary to produce either PPO+Cm or PMC+Cm shapes with current production-grade quality. When curium-242 spiked plutonia-238 fuel forms can be produced with quality comparable to the standard products, a rerun of a fuel aging effort would be beneficial.

Tantalum-10% tungsten, which was selected to conform to the container material for space thermoelectric heat sources exhibited extensive reactions with the various fuel forms studied in the fuel aging task. Liquid phases were definitely formed between the PPO and Ta-10W during 1850°C thermal pulses. PMC and PMC+Cm fuel forms all stuck after 1200°C exposure because of fuel swelling. Only PPO and PPO+Cm specimens were relatively easy to remove. Any rerun of this effort should make use of advanced container materials such as Mo or Mo-46 Re for PMC and Mo-46 Re or Ir for PPO.

Metallographic examination was impossible on a number of samples because of fuel crumbling and a subsequent inability to obtain a polished surface. Several of the most important specimens could not be examined metallographically. This was expected on specimens if they had been impacted. However, it was planned to use scanning electron microscopic (SEM) techniques on badly fractured specimens to determine the mode of fracture. This technique was not applied to this effort because of the questionable nature of the original structure. SEM remains a useful technique for future work.

Examination of the PMC and PMC+Cm fuel forms permits limited conclusions about helium release, dimensional stability, and structural degradation of those materials studied in the program. Helium release of PMC and PMC+Cm were comparable after 850°C aging with differences attributable only to pseudo-chronological aging. Total release of helium into a sealed system occurs in PMC+Cm if 1200°C aged material is given an 1850°C thermal pulse. Approximately half of the helium generated in PMC+Cm is released into a sealed system at 850°C with a significant almost instantaneous increase, if thermally pulsed at 1425°C. Storage of helium is affected by overpressure but is overridden by higher temperature thermal pulses. A PMC specimen aged at 850°C and given a 1425°C thermal pulse swelled about 11% in volume but no comparable data are available for PMC+Cm fuel forms because they crumbled or stuck in the container. Ambient-aged and 850°C-aged PMC specimens were comparable after a 1425°C thermal pulse, with the probability that damage to the structure was caused by the rapid release of stored helium. Aging at 1200°C causes partial spheroidization of the molybdenum network in PMC, which tends to negate the usefulness of molybdenum in the cermet structure. The only PMC+Cm specimen to remain intact was the ambient aged plus 1425°C thermal pulse specimen. All others disintegrated, probably because of damage to the poor structure of the initial material.

Examination of the PPO(HP), PPO(CPS), and PPO+Cm fuel forms permits limited conclusions about helium release, dimensional stability, and structural degradation of the materials available to the program. Aging of PPO+Cm at 850°C results in almost complete helium release into a sealed system, as expected, thereby minimizing any pressure pulse during reentry. The PPO(HP) specimen retained its as-fabricated integrity after 850°C aging; however, the PPO+Cm specimen crumbled into powder, the difference being more attributable to poor initial structure than to aging. Aging of PPO and PPO+Cm fuels at 1200°C resulted in almost total helium release with limited helium storage attributable to helium overpressure. The low density PPO(HP) fuel aged at 850°C exhibited a volumetric shrinkage of 3% without a thermal pulse and 3.9% with a 1425°C thermal pulse. Diametral data on the lower density PPO+Cm fuel aged at 1200°C indicate a somewhat higher shrinkage. These values would be expected because of the low density of the starting material. Ambient storage plus an 1850°C thermal pulse resulted in comparably bad structures

in both PPO(HP) and PPO+Cm, probably caused more by reaction with the container than any intrinsic damage from the thermal treatments. Less internal porosity is visible in a PPO+Cm specimen comparably aged at 1200°C and given an 1850°C thermal pulse probably because the Cm-containing specimen was highly fractured. The plutonia structures are very different in appearance but comparable in apparent structural integrity. This may be a faulty evaluation because of the fuel interaction with the Ta-10W which may have masked or changed the aging mechanisms.

It is probable that performing a fuel-aging program would result in information useful to advanced technology programs, if good quality fuel forms can be produced with curia, carefully selected container materials and test configurations are used, pre-test evaluation is made on all materials prior to aging, and SEM is added as a supplement to metallography as an evaluation technique.

Accelerating plutonia fuel aging by the addition of curia-242 appears technically sound. The high initial thermal stress and perhaps the helium generation/transport phenomena apparently cause significant difficulty in producing sound fuel forms. The additional effort required to produce adequate-quality fuel forms, however, may preclude further effort because of economic considerations. Direct aging of standard fuel forms is currently underway but will not provide data on five-year aged material for several years. Repeating the fuel aging effort could still provide more timely data and prove the accelerated aging technique for current and future fuel forms. A cost/benefit analysis would be beneficial in reaching a decision to redo the fuel aging effort.

The MHW mockup test effort has produced a series of test capsules which provide substantially accurate representation of materials, volumes, and temperatures which are relevant to the engineering behavior of materials in the MHW heat source. These test capsules are now being exposed at specified temperature levels and are expected to provide significant confirmation of the high strain rate behavior of iridium after exposure to a realistic simulation of the MHW operating environment.

Section 4
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