COMPATIBILITY AND STABILITY OF PLUTONIA-238 BASE CERMET FUEL FORMS IN REFRACTORY ALLOY CONTAINERS AT 1500° TO 2000°C

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PREPARED FOR THE ATOMIC ENERGY COMMISSION,
DIVISION OF SPACE NUCLEAR SYSTEMS,
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ABSTRACT

The compatibility of two and stability of three plutonia-238 base cermet fuels were investigated at 1500° to 2000°C from July 1969 through November 1971, while these fuel forms were being developed for use in Radioisotope Thermoelectric Generators (RTG). Adequate containment, independent of fuel form, was achievable even at these very high temperatures. Fuel stability varied, but all three forms developed plutonia porosity and agglomeration of the metal network at the lowest test temperatures, which were well in excess of current RTGs.

A Battelle-Columbus Laboratories plutonia-molybdenum cermet (BCL-PMC) developed as a precursor of the current PMC fuel form was investigated for stability at 1800° to 2000°C for times to 10,000 hours. The thoria and molybdenum overcoated test specimens encapsulated in single W-25Re containers degraded with increasing time and temperature. The 1000-hour specimens remained relatively intact; the 10,000-hour specimens transported almost entirely to the container walls.

The interim plutonia-thoria-molybdenum solid-solution cermet (SSC) fuel form lost from most to all of the molybdenum network in exposure at 1800°C for 5000 hours. This behavior was inferior to the two PMC fuel forms. Comparative compatibility of the SSC was the same as the PMC.

Behavior of the current reference PMC fuel form was equivalent to the BCL-PMC, with enhanced stability exhibited when exposed in TZM or Ta-10W inner containers. Exposures at 1500°C for 500 and 5000 hours, 1800°C for 1000 and 5000 hours, and 2000°C for 1000 hours in double container semi-system test configurations resulted in increased fuel form degradation with increasing temperature and time. However, TZM liners with TZM, Mo-46Re, and W-25Re structural members provided excellent containment at all temperatures.

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Section 1

INTRODUCTION

Plutonia-238 base cermet fuel forms have been developed for use in thermoelectric and Isotope Brayton space electrical generators in which the heat source operates at temperatures to 1500°C. Compatibility between the radioisotope fuel form and container material is one criterion which must be established for safe use of radioisotope heat sources. Fuel form stability is a safety requirement both during operation and subsequent reentry from space.

In fiscal 1968, a program was initiated at Battelle Memorial Institute Columbus Laboratories (BCL) to develop a composite plutonia-238 fuel form capable of operating for 5 years at 1500°C. It was expected that the composite would provide higher thermal conductivity, higher mechanical strength, enhanced fuel retention and stability, and increased possibilities for control of helium release over bulk plutonia or plutonia microspheres. From this two-year developmental program came the basic plutonia-238 containing 20 volume-percent molybdenum cermet fuel form currently utilized in Transit and Pioneer radioisotope thermoelectric generator (RTG) space missions. The fuel form as developed at BCL utilized plasma-torch plutonia microspheres, coated with chemically vapor deposited (CVD) molybdenum, hot pressed into cylindrical or torodial shapes, and overcoated with molybdenum and thoria for protection against external environmental conditions. Chronological summaries of the BCL program are provided in References 1 through 4. As part of the overall program, cermet bodies were sent to the Donald W. Douglas Laboratories (DWDL) for thermal stability evaluation at temperatures above the expected maximum operating temperature of 1500°C. The accelerated test conditions at 1800° and 2000°C were to provide early information on stability at operating temperatures. Testing was also being performed at Mound Laboratory at about 1100°C for the Large Radioisotope Heat Source (LRHS) program (Reference 5). No attempt was to be made to determine compatibility with container materials. A tungsten-25% rhenium (W-25Re) alloy was selected for containment based on prior experience at DWDL (Reference 6). This fuel form has been designated BCL-PMC.

Technology on cermet fuel form fabrication was transferred from BCL to Mound Laboratories operated by Monsanto Research Corporation and eventually to Los Alamos Scientific Laboratory (LASL). The latter two organizations have been developing comparable fabrication techniques. Composition of the fuel form has remained at approximately 80 volume percent plutonia. However, the starting plutonia material changed from plasma-torch microspheres to shards having controlled particle size. Molybdenum coatings are applied to the particles utilizing chemical vapor deposition techniques before hot pressing into cylindrical discs. Initial plans were to coat each disc with molybdenum, but the technique was never developed for full-size hardware. However, the DWDL pellets did have a molybdenum overcoating. This fuel form has been designated as PMC (Reference 7). The Transit and Pioneer heat sources were designed to operate at temperatures around 850°C (Reference 8). During early stages of developing the Multi-Hundred Watt Radioisotope Thermoelectric Generator (MHW-RTG), a spherical PMC fuel form was a candidate for operation at or about 1500°C fuel-container temperature.

In the Transit and Pioneer heat sources, the compatibility liner is tantalum-10% tungsten (Ta-10W) and the structural member is a tantalum-8% tungsten-2% hafnium alloy (T-111). For operation at 1500°C, a better barrier than Ta-10W was needed to prevent oxygen diffusion from the fuel form into the T-111 structural member. Additionally, alternate structural member materials required investigation if T-111 was determined to be unsuitable. An accelerated approach appeared desirable to provide information on a timely basis. A basic test temperature of 1800°C was selected for 7 of the 16 test specimens with others at 1500°C for several T-111 combinations, and 2000°C for several W-25Re combinations.

By the time information was obtained from the DWDL test effort, PMC was no longer considered a viable option for the MHW-RTG program. However, test results provide a potentially valuable basis for future space system development if PMC or an equivalent fuel form is used.

For several months, another fuel form (designated SSC for plutonic solid-solution cermet) was the AEC/SNS reference fuel form. SSC was a compromise between PMC and a plutonia-thoria solid solution. Addition of a sufficient quantity of thoria was believed to reduce chemical activity and improve thermal

stability of plutonia. Fabrication difficulties resulted in SSC being replaced by PMC as the reference fuel. However, there was support for the better stability of the SSC fuel form resulting in inclusion of a limited number of comparative test specimens in the DWDL test matrix. Subsequently, no further work has been performed on the SSC fuel form.

Both the PMC and SSC test effort was engineering oriented with a semi-system type of configuration. A liner was included to provide compatibility with the fuel and minimize degradation to the strength member which is used in flight systems to provide structural integrity during operation and potential accident conditions. Compatibility liner materials were selected on the basis of preliminary tests with plutonia. Structural and bulk dimensional stability of the fuel forms were evaluated as well as the efficacy of the various liner materials for use with potential structural container alloys.

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Section 2

EXPERIMENTAL APPROACH

2.1 TEST MATRIX

Three plutonia-238 base cermet fuel forms were evaluated for high temperature stability. For the BCL-PMC precursor fuel form, DWDL was assigned the responsibility to determine thermal stability only, with no attempt being made to evaluate containment approaches. However, the PMC and SSC effort was directed primarily at determining potentially suitable containers for use at or about 1500°C. The overall test matrix is listed in Table 2-1.

Initially, the BCL-PMC effort was to determine stability of that fuel form at 1800° and 2000°C for 1,000, 5,000 and 10,000 hours. Two extra fuel specimens were included by BCL for use as pre-test specimens or spare fuel. Both were stored for possible future evaluation. After 2.5 years storage, the two fuel forms were sectioned with one examined in the ambient-aged condition, the other heated to 1500°C to determine short-term helium release and stability after long-term storage.

Sixteen PMC fuel specimens in double-layer containers comprised most of the test matrix. Almost half of the test specimens were exposed at 1800°C for either 1,000 or 5,000 hours. Structural alloys were primarily T-111 with both TZM (molybdenum-0.5% titanium-0.08% zirconium) and Mo-46Re (molybdenum-46% rhenium) as alternates. Liner materials listed according to decreasing permeability to oxygen were TZM, Mo-46Re, WMoRe (tungsten-18% molybdenum-35% rhenium, also known as W-30Mo-30Re from atomic-percent relationships), and W-25Re. Combinations were selected to maximize the potential range of response characteristics in the structural member. Five test combinations were exposed at 1500°C, primarily for 5,000 hours, but including one for only 500 hours to provide some preliminary information. All 1500°C specimens had T-111 structural members with Ta-10W, TZM, Mo-46Re, and W-25Re liners to provide varying protective capabilities. Four test specimens were exposed at 2000°C for 1000 hours. All had W-25Re structural members, the most refractory reasonably ductile alloy. Protective liners ranged from TZM through Mo-46Re and WMoRe to W-25Re.

Table 2-1
TEST MATRIX

Fuel Form	Exposure Temperature (°C)	Exposure Duration (hr)							
		— — — 500	1,000		5,000		10,000		
		Capsule Designation	Container Materials	Capsule Designation	Container Materials	Capsule Designation	Container Materials	Capsule Designation	Container Materials
BC L-PMC ^d	Ambient							AA-59B ^a	Ta-10W
BC L-PMC ^d	1500	AA-58A ^b	Ta-10W						
BC L-PMC	1800			AA-55	W-25Re	AA-54	W-25Re	AA-53	W-25Re
BC L-PMC	2000			AA-52	W-25Re	AA-56	W-25Re	AA-57	W-25Re
PMC	1500	PU266	Ta-10W/T-111			PU267	Ta-10W/T-111		
						PU268	T/M/T-111		
						PU276	Mo-46Re/T-111		
						PU272	W-25Re/T-111		
PMC	1800			PU273		PU280	W-MoRe/T-111		
				PU269	Mo-46Re/T/M	PU278	Mo-46Re/T/M		
				PU277	W-25Re/T-111	PU274	W-25Re/T/M		
					T/M/T/M	PU270	T/M/Mo-46Re		
PMC	2000			PU271	T/M/W-25Re				
				PU279	Mo-46Re/W-25Re				
				PU281	W-MoRe/W-25Re				
				PU275	W-25Re/W-25Re				
SSC	1500					PU262	Ta-10W/T-111		
	1800					PU263	T/M/T-111		
						PU264	W-25Re/T-111		
						PU265	W-MoRe/W-25Re		

a. Fuel stored 2.5 yr before examination

b. Fuel stored 2.5 yr before helium release thermal treatment of 120 hr at 1500°C

c. Container material combinations for PMC and SSC Fuels are listed as liner/structural alloy.

d. Fuel stored 2.5 yr before examination or test.

Four SSC test specimens were included in the program for comparison with the PMC fueled specimens. One Ta-10W liner/T-111 structural member, designated PU262, exposed at 1500°C for 5000 hours was a direct counterpart of PMC specimen PU267. At 1800°C for 5000 hours, only PU265 (SSC/WMoRe/T-111) had a direct PMC counterpart (PU280). The other two specimens matched equivalent PMC 1500°C specimens. It was originally believed that the SSC might provide a 200 to 300°C thermal gain in stability and chemical compatibility over the PMC fuel form.

2.2 CONFIGURATION

Two basic configurations were used in the test program. Figure 2-1 shows the BCL-PMC stability container configuration designated within the DWDL overall compatibility program is SNS/DWDL Configuration 2. The innermost container was W-25Re; the secondary container was tungsten; the tertiary container was Ta-10W. Solid-state bonding was minimized by W-25Re coiled wire standoffs. The long-term ambient aged BCL-PMC specimen heated at 1500°C for helium release determination was encapsulated in a 0.540 in. interior length by 0.510 inside diameter Ta-10W container which was spare from another DWDL task (Reference 9).

All PMC and SSC specimens were exposed in the triple containment system shown in Figure 2-2 and designated SNS/DWDL Configuration 3. The innermost (primary) container and discs were made from the same liner material for each test specimen. The discs were expected to provide a quantitative measurement of attack and had carefully polished surfaces. The primary container fit closely into the secondary (structural member) container as is typical in radioisotope heat sources. A Ta-10W tertiary guard container provided an additional level of containment in case the inner containers breached from excessive helium pressure.

2.3 MATERIALS

2.3.1 BCL-PMC Fuel Form

Eight plutonia-238 molybdenum cermet fuel forms were hot pressed at Battelle Memorial Institute Columbus Laboratories. Starting material was plasma-torch microspheres coated with molybdenum using chemical vapor deposition

Figure 2-1. BCL-PMC Stability Container Configuration (SNS/DWDL Configuration 2)

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techniques. Hot pressing was in graphite dies at 1550°C for 5 min under 12,000 psi. The dense bodies were then overcoated with 2 mils of molybdenum and about 4 mils of thoria. Fabrication technology is listed in Reference 4.

Cermet chemical composition is listed in Table 2-2. The reference fuel form designation for composition is given as Pu²³⁸O₂ - 19 v/o (volume percent) molybdenum; values in the first column of Table 2-2 were derived mathematically to correspond to the other fuel forms. Additionally, the O/Pu ratio, instead of the 2.0 regarded as typical was believed to be approximately 1.88 based on metallography at BCL (Reference 5). Reduction in oxygen content of the small size fuel pellets was believed to have occurred primarily during hot pressing.

Impurity level of the BCL-PMC cermets is listed in Table 2-3. The iron content of 2600 ppm was typical of plutonia microspheres produced at Mound Laboratory in 1969. Limitations of analytical techniques did not permit actual analyses of most of the elements listed.

Fuel form bulk data are listed in Table 2-4. The BCL-PMC was relatively large (double the weight) compared to the PMC and SSC fuel forms tested

Table 2-2
CERMET CHEMICAL COMPOSITION
(Weight Percent except as noted)

Element	BCL-PMC ^a	PMC ^c	SSC ^c
Pu	73.3	70.5	71.1 ± 0.7
U	NR ^b	0.7	NR
Th	NR	0.2	6.3 ± 0.3
O	9.1	9.9	10.48 ± 0.04
O/Pu Ratio	~1.88	1.97	2.01 ± 0.02
Mo	17.6	18.7 ± 0.5	12

- a. Calculated from the reference fuel form designation as Pu²³⁸O₂-19 v/o molybdenum. (Reference 4)
b. NR -- Not reported.
c. Calculated from partial analyses supplied by LASL at time of shipment and in their monthly report series to SNS.

Table 2-3
IMPURITY LEVELS OF CERMETS
(ppm in Pu)

Element	BCL-PMC ^c	PMC ^d
Be	NR ^a	<1
B	<600	<1
Na	Tr ^b	<100
Mg	<600	5
Al	<600	250
Si	<200	70
Ca	300	40
Cr	<600	40
Mn	NR	<5
Fe	2600	75
Co	NR	<5
Ni	<600	<25
Cu	<600	25
Zn	<600	25
Cd	NR	<10
Sn	NR	<5
Ta	NR	<150

a. NR -- Not Reported

b. Tr -- Trace

c. Analyzed at Mound Laboratory

d. Analyzed at LASL

later. The volume, average density, and power density are all based on geometric dimensions which prejudice somewhat against the BCL-PMC cermet because of rounded corners.

2.3.2 PMC Fuel Form

Eighteen plutonia-238 molybdenum cermet fuel forms were hot pressed at Los Alamos Scientific Laboratories. Starting material was carefully sized angular particles or shards, coated with molybdenum using chemical vapor deposition techniques. Hot pressing was performed in lined graphite dies at 1710°C for 10 min under 13,500 psi. A single disc approximately 2.14 in. diameter and 0.21 in. high was used for core drilling the individual pellets. Each pellet was overcoated at about 615°C for 4 hr using decomposition of molybdenum hexafluoride to deposit molybdenum over all surfaces to an average thickness of 3 mils. The pellets were baked out at 1200°C in an argon-6% hydrogen atmosphere for 24 hours.

Cermet chemical composition is listed in Table 2-2 as provided by LASL, partially at time of shipment and in their monthly report series to SNS. Extensive metallography and chemistry performed at LASL has shown the plutonia to be slightly substoichiometric, remaining typically from 1.96 to 1.98 O/Pu ratio. Impurity levels are listed in Table 2-3 showing the distinct improvement in both purity level and analytical capability that occurred between 1969 and 1971. Fuel form bulk data are listed in Table 2-4. Immersion density of the PMC was reported as 10.6 g/cm³ which is slightly higher than the bulk density calculated from geometric volumes. Similarly, the reported power density was 3.4 w/cm³ compared to the calculated bulk power density of 3.09 w/cm³.

2.3.3 SSC Fuel Form

Six plutonia-238 thorium molybdenum cermet fuel forms were hot pressed at Los Alamos Scientific Laboratories. Fabrication techniques were comparable to making the PMC fuel, except that the starting material was a plutonia-thorium solid solution. Hot pressing was in molybdenum- and tantalum-lined graphite dies at 1750°C for 15 min. under 13,500 psi. A single disc 2.137 in. diameter and 0.218 in. long with a 10.06 g/cm³ density and 3.16 w/cm³ power density was core drilled to produce pellets. These pellets were then overcoated with molybdenum. The pellets were baked out at 1200°C in an argon-6% hydrogen atmosphere for 24 hours.

The cermet chemical composition listed in Table 2-2 was estimated at LASL. The major difference between SSC and PMC is the replacement of about 6% molybdenum with thoria resulting in a slightly higher total oxygen content. Additionally, the apparent final oxygen content in SSC is stoichiometric (Pu, Th) $O_{2.0}$ within experimental error. Impurity levels in the SSC are believed to be approximately the same as for PMC although a direct analysis was not obtained. Fuel form bulk data are listed in Table 2-4 showing a comparison between PMC and SSC used in this experimental effort.

2.3.4 Inner or Liner Material Containers

Inner containers for the BCL-PMC fuel were made from powder metallurgy W-25Re produced by Cleveland Refractory Metals. The material was certified as 25% $\pm 0.5\%$ rhenium with a guaranteed purity of 99.98% tungsten plus rhenium. Because the BCL-PMC effort was fuel stability oriented and not directed toward compatibility of the inner container no chemical analyses were obtained on the W-25Re containers.

Inner containers of the liner materials for the PMC and SSC effort included Ta-10W, TZM, Mo-46Re, W-Mo-Re, and W-25Re alloys. Vendor analyses of Ta-10W and TZM are listed in Table 2-5. Both conform to typical commercial products. The Ta-10W was produced by Wah Chang Albany Company, Oregon. The TZM was produced by Climax Molybdenum Company, Michigan. The three rhenium containing alloys were produced by Cleveland Refractory Metals from powder metallurgy starting material. A certification was obtained for the W-25Re alloy comparable to that for the BCL-PMC containers. No certifications were ever received for the other two alloys. Metallographic examination of the five container materials disclosed that only Ta-10W was in the fully recrystallized condition. All other alloys had a level of cold work retention. All five alloys appeared single phase and relatively clean from inclusions. Hardness values using a 100-g load were: 237 DPH for Ta-10W, 266 DPH for TZM, 409 DPH for Mo-46Re, 512 DPH for WMoRe, and 676 DPH for W-25Re. Again, results were indicative of residual work hardening.

Containers were machined at Northwest Industries, Albany, Oregon to DWDL requirements. The compatibility discs were carefully machined at the same time to produce flat surfaces with an 8 rms or better surface finish.

Table 2-4
FUEL FORM BULK DATA

	BCL-PMC	PMC	SSC
Number of Pellets	8	18	6
Average Diameter (in.)	0.301	0.262	0.242
Range in Diameter (in.)	0.296-0.304	0.260-0.265	0.241-0.242
Average Length (in.)	0.389	0.223	0.221
Range in Length (in.)	0.382-0.403	0.216-0.228	0.205-0.225
Average Weight (g)	4.456	2.064	1.615
Range in Weight (g)	4.273-4.691	1.964-2.130	1.591-1.633
Inner Coating			
Material	Molybdenum	Molybdenum	Molybdenum
Thickness (in.)	0.002	0.002-0.004	0.002-0.003
Outer Coating			
Material	Thoria	--	--
Thickness (in.)	0.004	--	--
Volume (cc)	0.454	0.197	0.167
Average Density (g/cm ³)	9.82	10.48	9.70
Power Density (w/cm ³)	2.62	3.09	2.99

Table 2-5
CHEMICAL ANALYSES OF CONTAINER MATERIALS
(Impurities Expressed in Parts per Million)

Elements	Ta-10W Liner	T-111 Structural	Ta-10W Guard	TZM Liner	TZM Structural
Alloying					
Tungsten	9.6-9.7%	9.6-9.7%	9.4-9.6%	--	--
Hafnium	--	2.1%	--	--	--
Titanium	--	--	--	0.46%	0.48%
Zirconium	--	--	--	0.087%	0.087%
Impurity					
Cb	660	580-590	620-690	NA	NA
Mo	<20	<20	<20	--	--
Ni	<20	<20	<20	<10	<10
Fe	<40	<40	<40	<40	<30
Zr	--	740-920	--	--	--
H	1.5-2.0	<1	1.7-2.7	<1	<1
C	<30	30	<30	220	180
N	28-34	12	27-35	<1	<1
O	70-80	<50	50-100	<7	<6

2.3.5 Structural Alloy Containers

Four alloys were obtained for the PMC and SSC effort including T-111, TZM, Mo-46Re, and W-25Re. Chemical analysis of the T-111 produced by Wah Chang Albany Corporation is listed in Table 2-5. Microhardness was reported as 221 to 249 DPH average, with the structure fully recrystallized.

Chemical analysis of the TZM produced by Climax Molybdenum Company of America is listed in Table 2-5. Microhardness was reported as 297 to 309 DPH. Structural condition was stress relieved. The Mo-46Re and W-25Re was produced by Cleveland Refractory Metals with no chemical analysis submitted. Post-test chemical analyses reported in Section 3 indicate that the rhenium containing alloys had excellent purity levels as produced. Containers were machined at Northwest Industries to DWDL requirements.

2.3.6 Guard Capsules

Inner guard capsules for the BCL-PMC specimens were made from powder metallurgy tungsten produced by General Electric Co. An earlier attempt to use arc-cast tungsten resulted in badly cracked welds and major surface defects.

Outer guard capsules for the BCL-PMC specimens were made from Ta-10W produced by Wah Chang. Chemical analysis of the material used in the PMC-SSC effort is listed in Table 2-5. The analysis for the BCL-PMC material was directly comparable. All material was fully recrystallized. Hardnesses were 202 to 206 DPH for BCL-PMC containers and 200 to 208 DPH for PMC and SSC containers. All guard capsules were machined at Northwest Industries to DWDL drawing requirements.

2.4 ASSEMBLY

All vendor hardware was inspected for quality and conformance to drawing requirements. Dimensional measurements were made on all parts. Helium leak checking was performed on all containers.

Components were prepared for assembly primarily by acid cleaning and organic cleaning followed by water rinses. Dimensions and weight were

taken on selected fuel pellets to verify LASL values. Correlation was very close, in all cases checked, such that the remainder were assembled without further measurement.

Pellets were loaded into individual containers, lids were placed into position, smear checks were made to ensure that the welder would not be contaminated, and the capsules were electron-beam welded.

Each weld was made in a 6-kw Hamilton Standard electron beam welded at a 1×10^{-4} torr vacuum or better. Visual examination at 30x was used to determine defects; none were observed. Helium leak tightness of each container was checked by overnight pressurization in 150 psig helium, followed by measurement in a mass spectrometer. None leaked above the instrument detection limit which is 1×10^{-9} std cc/sec.

2.5 EXPOSURE

Planned exposure of the BCL-SSC cermet was 1800° and 2000°C for 1, 000, 5, 000, and 10, 000 hours. An additional capsule was exposed at 1500°C for 120 hours for helium release measurement. Planned exposure of the PMC and SSC specimens included 1500°C for 500 and 5, 000 hours, 1800°C for 1, 000 and 5, 000 hours, and 2000°C for 1, 000 hours.

Three Varian Model VF-400 ultra-high vacuum, cold-wall resistance-heated tungsten-mesh furnaces were used for exposure. The vacuum system for each unit consists of three cryopumps used to evacuate down to the ion pumping range, a 500 l/sec sputter-ion pump, and additional titanium sublimation pumping capacity. Furnace hot zones are 4-in. in diameter and 8-in. high with both axial and radial tungsten heat shields. Temperature was maintained within 10°C of the control point over extended times by a thermal-watt converter. The furnace systems were calibrated by observing the melting point of pure rhodium (1960°C). Temperatures were monitored by optical pyrometry.

All specimens, fueled and control, were placed on a four-level tungsten furnace rack for exposure. Removal was performed as planned exposures were reached.

During the latter stages of the BCL-PMC 10,000-hour exposure, but before initiation of the PMC and SSC exposure, two furnaces were moved from the original positions in the DWDL Hot Laboratory to a smaller room with controlled air, water, and access. A third furnace was installed for use in this program.

2.6 EVALUATION TECHNIQUES

Metallography was used as the primary basis for evaluation. Light microscopy, microhardness measurement, and electron-beam microprobe analysis provided complementary information. Helium-release measurements were made after exposure on selected specimens. Techniques are summarized in Section 3. Chemical analyses were performed on seven control specimens.

Exterior Ta-10W containers were cut open after exposure using a tubing cutter while holding the capsule in an open-faced hood. The BCL-PMC tungsten containers were shattered with a hammer. Inner containers were then put into the metallographic gloved-box line for further disassembly. The BCL-PMC W-25Re containers were sawed open just below the lid and attempts were made to remove the fuel pellets. Only the 1,000 hour specimens were removable intact.

The remainder were longitudinally sectioned through the fuel. Similar techniques were used on the PMC and SSC specimens with a similar lack of success in fuel removal, resulting in sectioning through the fuel.

Visual observations were made and macrographs taken. In some cases, the contents were all included in one mount; in others, the content were mounted separately.

Metallographic mounts were made using Quickmount (Fulton Metallurgical Products Corp.) for the BCL-PMC specimens and individual packets of epoxy mounting material for the PMC and SSC specimens. Automated grinding was performed on a Stellapol slow-speed wheel, using multiple sample holders through 600-grit silicon carbide papers. Polishing was performed in two stages: 1-micron alumina followed by 1-micron diamond, both on Syntron polishing machines using Nylon cloth. Water was used as the lubricant for grinding and polishing. Where fuel was the only material in a mount to be

polished, diamond was generally not used because the slight polishing relief obtained from alumina is desirable in resolving two-phase structures in the plutonia.

All surfaces were initially examined in an unetched condition using a Leitz Ortholux microscope. Tantalum-base alloys were etched in a sulfuric-nitric-hydrofluoric acid solution. Molybdenum- and tungsten-base alloys were etched in a Potassium ferricyanide-sodium hydroxide-water solution. Plutonia was examined in the as-polished condition only. Photographic techniques included both a Polaroid attachment on the microscope and a 35-mm film attachment.

Microhardness measurements were made using a Leitz Miniload microhardness tester with a 100-g load and Vickers pyramidal diamond indenter. In special cases, a 15-g load was used to minimize or eliminate cracking in brittle materials.

Electron-beam microprobe analyses were performed by Dr. W.I. Clark, Westinghouse-Hanford Company, on several short-term PMC and SSC specimens, and by Dr. Y.B. Katayama, Battelle-Northwest, on three 5000-hour PMC and SSC specimens. Both used MAC 400 machines. Area scans to 1000x continuous traverses and step scans were made in specific areas selected to provide maximum information as to reaction mechanisms.

Chemical analyses were performed by Ledoux and Company, Teaneck, New Jersey, on seven control capsules after exposure. Analytical limits are indicated in Table 3-12.

Section 3

RESULTS

Examination of 8 BCL-PMC, 16 PMC, and 4 SSC specimens after exposure at 1500° to 2000°C showed interrelationships between fuel and container materials as to stability and compatibility. Fuel form stability varied with exposure temperature, exposure duration, and container material. The basic plutonia-molybdenum cermet structure generally remained intact after exposure at 1500°C, but both the molybdenum network and plutonia particles degraded drastically with time at temperatures of 1800° and 2000°C. Helium release increased with temperature and time. Helium storage in the structure decreased with exposure at 1500°C and above with retention and inverse function of temperature.

Liner materials varied in the amount and type of attack from the fuel forms. The two molybdenum-rich alloys, TZM and Mo-46Re, appeared to be most compatible. The Ta-10W, WMoRe, and W-25Re were attacked in a variety of ways.

Structural alloys varied in integrity after exposure with significant dependence on behavior of the liner materials. In all cases, T-111 behavior was poor in that massive oxide precipitation occurred throughout. In about half the cases, both TZM and W-25Re performed well. In the remainder, reaction with or failure of the liner container resulted in degradation.

Helium release measurements on all samples followed by visual and metallographic results for BCL-PMC, PMC, and SSC specimens are discussed in the sections which follow.

3.1 HELIUM RELEASE CHARACTERISTICS

Helium release measurements were completed on the three fuel forms to provide information as to relative stability. Actual measurements were made on the sealed containers after completion of exposures. The six BCL-PMC specimens exposed at 1800° and 2000°C were drilled at Westinghouse-Hanford Company using laser techniques. The laser was able to penetrate the 0.060 in. thick W-25Re in several pulses. However, the same technique

was incapable of penetrating the 0.100-in. thick capsule walls or the 0.120-in. thick ends of any of the PMC and SSC container sets. Specimens PU275 and PU277 were returned after unsuccessful attempts had been made. A rotary-sealed drilling technique was devised at DWDL that was capable of drilling Ta-10W, T-111 and TZM but not the harder alloys. This technique was incapable of drilling through the WMoRe liner in PU280. The BCL-PMC room temperature aged plus short time at 1500°C specimen, one PMC specimen, and two SSC specimens were drilled in this manner. In all cases, mass spectrometry at Westinghouse Hanford Company was used to determine species of the extracted gases.

Helium release information on the 10 specimens evaluated is listed in Table 3-1. During the BCL development program, it was estimated that approximately 0.1 cm³ of helium was retained for each gram of cermet. Helium retention in the as-fabricated PMC and SSC fuel forms were reduced by a 1200°C heat treatment subsequent to hot pressing. A value of slightly less than half that of the BCL-PMC, 0.04 g/cm³, was used, based on expected comparability of behavior of SSC and BCL-PMC when exposed at 1800°C for 5000 hours. Values for helium release are shown in Figure 3-1 indicating an upward release trend with time. An alternate way of showing helium release information is to determine residual helium stored in the cermet. These data are plotted in Figure 3-2 showing a decreased storage with time at 1500°, 1800°, and 2000°C with higher temperatures resulting in less stored helium for all three fuel forms. Storage, and release, are undoubtedly affected by helium overpressure in the sealed containers listed in Table 3-1. Based on the information determined for this series of specimens, there were no significant differences in helium release characteristics among the three fuel forms evaluated.

Evaluation of the 2.5-yr ambient aged plus 120 hr at 1500°C BCL-PMC fuel form is somewhat difficult because of the uncertainty as to helium released during the long-term storage. In Table 3-1, two rows of values are presented for helium release for specimen AA-58A. The first is based on no release during storage, which would be a lower limit. The second is based on a 10% release during storage, which was observed in the BCL effort (Reference 4, p 80). In either case, the release was 81% to 89% which is much higher than an expected release of about 20% for fresh fuel. Comparability with other fuel

Table 3-1

HELIUM RELEASE INFORMATION

Capsule Designation	Fuel Form	Exposure/Storage Conditions		Time from Fuel Fab To End of Exposure (yr)	Estimated Helium Storage As-Fabricated (cm ³ /g) ^b	Helium Generation from Fabrication To Exposure Completion (cm ³ /g)	Total Helium Storage (cm ³ /g)	Post-Test Helium Release		Container Helium Pressure At Temp. (psi)	Estimated Residual Helium Storage (cm ³ /g)
		Temperature (°C)	Time (hr)					(cm ³ /g)	(%)		
AA-55	BCL-PMC	1800	1,000	0.34	0.10	0.13	0.23	0.12	52	65	0.11
AA-54	BCL-PMC	1800	5,000	1.05	0.10	0.40	0.50	0.48	96	250	0.02
AA-53	BCL-PMC	1800	10,000	1.77	0.10	0.67	0.77	0.76	99	389	0.01
AA-52	BCL-PMC	2000	1,000	0.34	0.10	0.13	0.23	0.13	55	73	0.10
AA-56	BCL-PMC	2000	5,000	1.12	0.10	0.42	0.52	0.51	98	285	0.01
AA-57	BCL-PMC	2000	10,000	1.87	0.10	0.71	0.81	a	a	a	a
AA-58A	BCL-PMC	Ambient	21,800	2.49	0.10	0.93	1.03	0.83	81	112	0.20
		Plus 1500	Plus 120					0.83	89	102	0.10
PL 268	PMC	1500	5,000	1.16	0.04	0.45	0.49	0.45	92	267	0.04
PL 262	SSC	1500	5,000	1.33	0.04	0.52	0.56	0.49	87	211	0.07
PL 263	SSC	1800	5,000	1.19	0.04	0.46	0.50	0.48	96	200	0.02

a. Container leaked during exposure.

b. All cm³/g values based on STP and weight of cermet.

c. Upper row of values based on no helium release during storage, lower row based on 10% helium release during storage.

Figure 3-1. Helium Release for Cermet Fuel Forms

Figure 3-2. Helium Storage for Cermet Fuel Forms

data is best shown in residual helium storage which, with 10% release during aging, is calculated to be $0.10 \text{ cm}^3/\text{g}$ and is slightly higher than that observed in the PMC and SSC exposed at 1500°C for 5,000 hr.

3.2 BATTELLE COLUMBUS LABORATORIES PLUTONIA-MOLYBDENUM CERMETS

Six BCL-PMC fuel bodies were visually and metallographically examined after exposure at 1800° and 2000°C for 1,000, 5,000, and 10,000 hours. Two additional fuel pieces were examined after ageing at room temperature for 2.5 years with one having been heated at 1500°C for 120 hours to evolve helium from the structure.

Detailed results of the 1800°C exposures are shown in Table 3-2 and Figures 3-3, 3-4, and 3-5. It is apparent that 1800°C is above a temperature which the BCL-PMC fuel form is stable for long-term operation. The 1000-hour exposure showed only limited degradation. However, the 5000- and 10,000-hour specimens showed much more massive degradation. There is a distinct possibility that the 5000- and 10,000-hour specimens were interchanged after helium release based on external surface appearance and results of the internal examination. Generally, plutonia and thoria were predominantly deposited over the capsule walls to just above the top of fuel pellet. The cermet structure in the core of the fuel body remained intact after 1000 hours, was discontinuous after 5000 hours, and was unavailable for examination after 10,000 hours. The W-25Re container remained intact although precipitation of oxides occurred to a depth of 20 mils or more. In other efforts at DWDL, these precipitates in W-25Re have been identified as plutonium- and rhenium-rich, probably as oxides. Fine grain structure accompanied the precipitates. Coarse grain structure was prevalent throughout the remainder of the capsule walls.

Detailed results of the 2000°C exposures are shown in Table 3-3, Figures 3-6, 3-7, and 3-8. The BCL-PMC fuel form is obviously not stable for long-term operation at 2000°C . The core of the fuel remained intact after the 1000-hour exposure, but not for longer times. Fuel deposits built up on capsule walls were totally devoid of a metal network. Considerable loss of oxygen occurred in the plutonia, probably caused by diffusion through the capsule walls. Precipitation and grain structures occurred in the W-25Re walls comparable

Table 3-2
BCL-PMC RESULTS, 1800°C EXPOSURES

Exposure Time (hr)	Fuel Behavior		Container
	Bulk	Structural	
1000	Removed intact. Thoria coating turned black and shiny. Some surface spilling. Length increased 6.5%. Diameter increased 0 to 1.0% (A, B, Figure 3-3).	Metal network good in center, partially degraded at surface. Some oxygen loss in plutonia (>1.8 O/Pu). Some voids in both plutonia and metal. Thoria and molybdenum coatings retained intact (C & D, Figure 3-3).	Not examined
5000	Fuel deposited all over walls. Remainder of fuel pellet lost in sectioning (A, Figure 3-4)	Molybdenum partially spheroidized, not retained as network. No molybdenum near capsule surfaces. Plutonia very cracked and lowered oxygen (B, Figure 3-4)	Capsule bulged during exposure. Oxides to depths greater than 20 mils. Small grain size retained with precipitation; coarse grains beyond precipitation. Deeper oxides above fuel. (Figure 3-4)
10,000	Fuel remained reasonably intact and remained in place during sectioning. Surfaces had spongy appearance. Core remained intact. (A, Figure 3-4)	Both molybdenum and thoria coatings gone. Plutonia on walls is substoichiometric and has no metal network. Core retains metal network with considerable degradation. Plutonia very substoichiometric (~1.72 O/Pu). Molybdenum has voids, and/or precipitates. (B, C, Figure 3-5).	Capsule bulged during exposure. Very limited oxide precipitation in either walls or bottom. Fine grained at surface. Coarse grained through rest of wall. (B, Figure 3-5)

A. MACROGRAPH (~7x)

B. CROSS SECTION (~6x)

MOUNTING MATERIAL

C. CENTER 10 MILS (100x)

D. SURFACE 20 MILS (50x)

Figure 3-3. BCL-PMC, 1800°C, 1000 hr

A. AS SECTIONED

B. FUEL AND BOTTOM

10 MILS (100x)

Figure 3-4. BCL-PMC, 1800°C, 5000 hr

A. AS SECTIONED

10 MILS (100x)

B. CAPSULE WALL AND FUEL

10 MILS (100x)

C. CERMET CENTER

Figure 3-5. BCL-PMC, 1800°C, 10,000 hr

Table 3-3
BCL-PMC RESULTS, 2000°C EXPOSURES

Exposure Time (hr)	Fuel Behavior		
	Bulk	Structural	Container
1000	Removed intact. Major spalling. Length increased 10.2%. Diameter increased 0 to 3.6% (A, B, Figure 3-6).	Metal network good in center, degraded at surface. Considerable oxygen loss in plutonia (~1.80 O/Pu) Both thoria and molybdenum coatings cracked & degraded (C, D, Figure 3-6).	Not examined.
5000	Most of fuel lost during sectioning. Plutonia coated over walls and capsule bottom (A, Figure 3-7).	Plutonia along walls had no metal network. Material immediately adjacent to wall had lighter color appearance, probably high thoria. Molybdenum present not as network and had voids and precipitates (~1.76 O/Pu) (B, Figure 3-7).	Capsule bulged during exposure. Oxide precipitation to depths of 10 mils. Fine grained to depth of precipitation. Coarse grained through remainder of wall. No major attack (B, Figure 3-7).
10,000	Plutonia deposited on walls and bottom. Little remaining bulk material (A, Figure 3-8).	Oxide layer ~20 mils thick next to walls, irregular massive metal layer of ~20 mils, then more porous oxide. No cermet structure. Metal areas have subsurface voids. Plutonia very sub-stoichiometric (~1.70 O/Pu).	Leaked helium prior to end of exposure. No capsule bulging. Wall thinning of ~12 mils near bottom of capsule. Surface porosity & oxide precipitation (B, Figure 3-8). Pock-marks in capsule wall were from laser drilling for helium release measurement.

A. MACROGRAPH ($\sim 7\times$)

B. CROSS SECTION ($\sim 6\times$)

MOUNTING MATERIAL

C. CENTER | 10 MILS (100 $\times$)

D. SURFACE | 10 MILS (100 $\times$)

Figure 3-6. BCL-PMC, 2000 $^{\circ}$ C, 1000 hr

A. AS SECTIONED

B. FUEL AND CAPSULE BOTTOM

Figure 3-7. BCL-PMC, 2000°C, 5000 hr

A. AS SECTIONED

B. FUEL AND CAPSULE BOTTOM

Figure 3-8. BLC-PMC, 2000°C, 10,000 hr

to that observed at 1800°C. However, in the 2000°C, 10,000 hour specimen, the only wall thinning which occurred was about 12 mils. It is undeterminable as to whether metal was moved by vaporization of a solution-precipitation mechanism.

Dimensional measurement of two cermet specimens stored under ambient conditions for 2.5 years indicated a 1% diametral growth with no axial increase. Each specimen was sectioned into two half-length cylinders. Figure 3-9 shows the edge of the specimen examined in the as-aged condition. The plutonia spheres appear cracked but are generally intact and slightly substoichiometric. The molybdenum network surrounding the plutonia remains completely intact. The molybdenum (white) and thoria (multi-layer gray) coatings over the cylindrical surface also remained intact. Figure 3-10 shows the edge of the second specimen after heating to 1500°C for 120 hours. Heating damaged the cermet structure near the molybdenum coating. The plutonia fragmented and was lost near the surface. The molybdenum network became porous. The surface molybdenum coating reacted to form a nonmetallic appearing layer. The thoria coating was fractured and developed a completely different appearance.

Total degradation of the aged and thermally treated material was considerably more severe than for a comparably heated new cermet. The structure, particularly at the specimen periphery, was far more porous than that exhibited in a specimen heated by BCL for 1000 hours at 1500°C (Reference 4).

Fragmentation of the microspheres also occurred throughout the bulk of the specimen which did not occur in fresh material. Helium release measurement of the aged material indicated at least 81% of the stored helium was released by the thermal treatment. An expected value for a relatively fresh cermet heated for comparable conditions would be less than 20% release. This indicates that a cermet stored at or near room temperature for a long time will release the large majority of the stored helium in one burst during a reentry pulse resulting in major structural degradation.

3.3 PLUTONIA-MOLYBDENUM CERMETS

Sixteen PMC fuel bodies and containers were visually and metallographically examined after exposure. Detailed results are listed in Tables 3-4 to 3-11

100x (10 MILS)

Figure 3-9. Room-Temperature Aged BCL-PMC

100x (10 MILS)

Figure 3-10. Room-Temperature Aged and Heated BCL-PMC

Table 3-4
PMC RESULTS -- 1500°C, 500, AND 5000 HR

Capsule Designation and Exposure Time	Fuel Observations	Liner Material and Observations	Structural Alloy and Observations
PU266 (500 hr)	Fuel intact with minor spalling of the Mo coating. Mo network recrystallized. Many fine voids in plutonia and some in Mo. Plutonia about 50% monotectoid (~1.80 O/Pu). (A, B, C, D, Figure 3-11).	<u>Ta-10W</u> Intergranular attack to disc and wall ~1 to 2 mils. Some oxide precipitation. Minor attack on outside (C, D, Figure 3-11). Little hardening (Table 3-5).	<u>T-111</u> Halo of oxide precipitation shown in A, Figure 3-11. Heavy precipitation to ~30 mils. Precipitation at both grain boundaries and in the matrix. (C, Figure 3-11) inside of wall hardened (Table 3-5). Oxygen content: above fuel 230-240 ppm; capsule bottom 450-1590 ppm.
PU267 (5000 hr)	Fuel intact except for minor internal cracks and spalling of 15% of Mo coating. Mo network comparable to 500-hr specimen except in fuel corners. Somewhat coarser voids in plutonia, not in Mo. Substoichiometric, but unable to determine amount (A, Figure 3-12).	<u>Ta-10W</u> Intergranular attack to 8 mils on discs and 2 mils on walls. Precipitates in wall. Areas of wall bonded to T-111 with voids and oxides at interface (B, Figure 3-12). Hardening of the wall (Table 3-5).	<u>T-111</u> Heavy precipitation throughout wall. (B, Figure 3-12). Indeterminate as to hardness effects (Table 3-5).
PU268 (5000 hr)	Fuel intact except for one major crack near top center. Mo coating intact over most of surface. Mo network less continuous than PU267. Plutonia considerable porous with greater than 50% monotectoid (<1.80 O/Pu) (A, Figure 3-13).	<u>TZM</u> Very fine precipitates decreasing from inside to outside. Very fine grain structure on inside becoming coarser on outside. Bonded to T-111 with apparent diffusion of Mo into T-111. Large intergranular precipitates adjacent to boundary (A, B, Figure 3-13). Hardening occurred (Table 3-5).	<u>T-111</u> Heavy oxide precipitation throughout wall with stringers aligned in rolling direction (A, B, Figure 3-13). Inconclusive hardness (Table 3-5).

Table 3-4
PMC RESULTS -- 1500°C, 500, AND 5000 HR (Continued)

Capsule Designation and Exposure Time	Fuel Observations	Liner Material and Observations	Structural Alloy and Observations
PU276 (5000 hr)	Fuel body totally intact except for complete loss of Mo coating and plutonia near surface Mo network comparable to PU267. Higher plutonia porosity than PU267. Considerably less substoichiometry than PU266 (A, Figure 3-14).	Mo-46Re Plutonia and molybdenum buildup on surface. Otherwise no reaction from contact with PMC (Apparent precipitation in A, Figure 3-14 is an artifact). Intermetal-reaction layer with T-111 is Ta+Re according to microprobe (B, Figure 3-14). Inner surface softened from molybdenum deposition of PMC coating (Table 3-5). Control capsule chemical analyses showed no transport between alloys (Table 3-12).	T-111 Oxide precipitation throughout wall; somewhat less than in PU267 and PU268. Intermetallic compound at interface with Mo-46Re is Ta+Re. Oxide precipitates at interface and in T-111 are Hf + Ta rich (B, Figure 3-14). Inside may be hardened somewhat (Table 3-5). Control capsule chemical analyses showed no transport between alloys (Table 3-12).
PU272 (5000 hr)	Fuel lost corners and had large diagonal crack. Mo coating gone over entire surface. Mo network comparable to PU267. Larger plutonia porosity than PU267. Plutonia appeared almost stoichiometric (>1.94 O/Pu) (A, B, Figure 3-15).	W-25Re Plutonia and Mo buildup on surface. Voids and precipitates throughout discs and walls. Control specimen exhibited similar precipitation, probably a sigma phase formation from structural instability. No reaction with T-111 (B, Figure 3-15). Hardness is indeterminate (Table 3-5).	T-111 Precipitation throughout the wall. No reaction with W-25Re (B, Figure 3-15). Highest hardness of any 1500°C T-111 wall (Table 3-5).

Table 3-5

PMC CONTAINER MICROHARDNESS
 AFTER EXPOSURE AT 1500°C FOR 500 AND 5000 HOURS
 (Diamond Pyramid Hardness, 100-g load; values in kg/mm²)

Capsule Designation and Exposure Time	Capsule		Location in Capsule	Location in Specimen		
	Layer	Alloy		Adjacent to Fuel	In Center	Away from Fuel
PU266 (500 hr)	Primary	Ta-10W	Adjacent to PMC	228	219	224
	Primary	Ta-10W	Above PMC	240	236	241
	Secondary	T-111	Adjacent to PMC	241	257	236
8-9A Control (500 hr)	Secondary	T-111	Above PMC	257	259	259
	Primary	Ta-10W	Wall	224	219	216
	Secondary	T-111	Wall	222	240	245
PU267 (5000 hr)	Primary	Ta-10W	Top disc	243	233	230
	Primary	Ta-10W	Bottom disc	233	202	216
	Primary	Ta-10W	Wall	314	225	227
	Secondary	T-111	Wall	233	256	227
8-9B Control (5000 hr)	Primary	Ta-10W	Wall	210	212	207
	Secondary	T-111	Wall	233	228	262
PU268 (5000 hr)	Primary	TZM	Wall	212	205	195
	Secondary	T-111	Wall	233	253	225
7-9 Control (5000 hr)	Primary	TZM	Wall	177	182	178
	Secondary	T-111	Wall	227	224	227
PU276 (5000 hr)	Primary	Mo-46Re	Bottom disc	319	336	342
	Primary	Mo-46Re	Wall	262	333	373
	Secondary	T-111	Wall	247	235	228
4-9 Control (5000 hr)	Primary	Mo-46Re	Wall	339	325	339
	Secondary	T-111	Wall	213	237	221
PU272 (5000 hr)	Primary	W-25Re	Wall	498	560	548
	Primary	W-25Re	Bottom disc	517	511	517
	Secondary	T-111	Wall	258	256	258
2-9A Control (5000 hr)	Primary	W-25Re	Wall	425	429	459
	Secondary	T-111	Wall	180	202	189

Table 3-6
PMC RESULTS - 1800°C, 1000 hr

Capsule Designation	Fuel Observations	Liner Material and Observations	Structural Alloy and Observations
PU273	Fuel intact except that no coating remains and corners were lost. Mo network intact with a recrystallized structure. Voids in both Mo and plutonia. Plutonia has ~10% monotectoid (~1.94 O/Pu) present (A, Figure 3-16).	W-25Re	T-111
		Deposit of Mo coating with areas of plutonia. Voids and precipitation very deep. Capsule interior has intermittent dark deposits. Appeared bonded to T-111 (B, Figure 3-16). Hardness higher in wall adjacent to PMC (Table 3-7).	Intermetallic appearance of bond with W-25Re ~0.5 mil. Precipitation throughout. Significant hardening in wall (Table 3-7).
PU269	Fuel intact including total coating adherence. Two diagonal cracks in PMC. Large and fine voids in plutonia. Fine voids in Mo. Mo network excellent. More monotectoid than PU273 (<1.94 O/Pu) (A, B, Figure 3-17)	TZM	TZM
		Bright, shiny interior surface above fuel. Fine grained structure on inside caused by a fine intergranular precipitate to a depth ~2 mils. Grains remained reasonably fine throughout wall. Bonded to TZM outer container (A, B, Figure 3-17). Hardened compared to control specimen (Table 3-7). Chemical analysis of control specimen showed no change caused by exposure (Table 3-12).	Bonded to inner TZM liner. Coarser grained than liner. No apparent precipitation. Hardened throughout wall adjacent to PMC but hardened only at inner surface above PMC (Table 3-7). Chemical analysis of control specimen showed no change caused by exposure (Table 3-12).
PU277	Fuel intact except for total coating loss and diagonal crack in one corner. Metal network remained intact, recrystallized, and had fine voids. Plutonia had about same appearance as in PU273 except somewhat higher monotectoid, (<1.94 O/Pu) (Figure 3-18).	Mo-46Re	TZM
		Surface had deposited layer of Mo and plutonia. No attack to the liner except for the irregularity of the Mo deposit (Figure 3-18). No hardening (Table 3-7).	Bonded to Mo-46Re with layer of voids. No compounds or oxides at bond line. Major fine precipitation throughout wall (Figure 3-18). Slight hardening throughout wall (Table 3-7).

Table 3-7
 PMC CONTAINER MICROHARDNESS
 EXPOSED AT 1800°C FOR 1000 HOURS
 (Diamond Pyramid Hardness, 100-g load; values in kg/mm²)

Capsule Designation	Capsule		Location in Capsule	Location in Specimen		
	Layer	Alloy		Adjacent to Fuel	In Center	Away from Fuel
PU269	Primary	TZM	Adjacent to PMC	229	228	220
			Above PMC	226	224	219
	Secondary	TZM	Adjacent to PMC	216	215	220
			Above PMC	217	197	196
7-7 Control	Primary	TZM	Wall	193	201	203
	Secondary	TZM	Wall	187	186	190
PU273	Primary	W-25Re	Adjacent to PMC	546	610	590
			Above PMC	495	546	546
	Secondary	T-111	Adjacent to PMC	272	282	300
			Above PMC	266	297	297
2-9B ^a Control	Primary	W-25Re	Wall	498	496	514
			Disc	500	498	498
	Secondary	T-111	Wall	225	232	233
PU277	Primary	Mo-46Re	Wall	351	351	317
	Primary	Mo-46Re	Bottom disc	325	357	360
	Secondary	TZM	Wall	212	206	206
4-7A Control	Primary	Mo-46Re	Wall	354	351	357
	Secondary	TZM	Wall	198	184	186

a. Control Specimen 2-9B exposed at 1800°C for 5000 hours.

Table 3-8
PMC RESULTS - 1800°C, 5000 hr

Capsule Designation	Fuel Observations	Liner Material and Observations	Structural Alloy and Observations
PU280	Fuel corners lost, coating gone, much porosity in core. Mo network was degraded considerably. Unknown stoichiometry. (A, B, Figure 3-19).	W-MoRe	T-111
		Thick plutonia coating along walls resulting in a roughened dark surface. Porosity to 10 mils. Oxide in walls inter-metallic at interface with T-111 (A, B, Figure 3-19). Hardness indeterminate (Table 3-9).	Some diffusion at interface into T-111. Heavy precipitation both very fine throughout and large oxides in stringers along rolling direction (B, Figure 3-19). No hardness effect (Table 3-9).
PU278	Massive fuel with minor cracking and no coating remaining. Mo network intact, recrystallized, and had voids. Plutonia had both small and large voids and much micro-cracking. Large amount of monotectoid (~60 - 70%) (~1.75 O/Pu) (A, B, Figure 3-20).	Mo-46Re	TZM
		Coating of Mo and plutonia on surface resulted in roughened appearing surface. No attack in the wall. Large grain clean structure (A, B, Figure 3-20). Hardest in center because of Mo diffusion into both surfaces. (Table 3-9). Chemical analyses of control specimen shows that titanium and zirconium transferred from TZM to Mo-46Re but rhenium did not transfer from Mo-46Re to TZM (Table 3-12).	Well bonded to Mo-46Re. No attack in any form (A, Figure 3-20). No hardness change (Table 3-9). Chemical analyses of control specimen shows that titanium and zirconium transferred from TZM to Mo-46Re but rhenium did not transfer from Mo-46Re to TZM (Table 3-12).
PU274	Fuel lost large amount of corners. Many small cracks. No coating remaining. Mo network intact, recrystallized, large voids. Plutonia has fewer large voids than PU270 below. Less monotectoid (~30%) than either PU278 or PU270 because W-25Re is least permeable to oxygen (~1.87 O/Pu).	W-25Re	TZM
		Layer of Mo and plutonia on surface presenting darkened, roughened surface. Voids and oxide precipitates to depth of 20 mils or more. Partially bonded to TZM. (Figure 3-21). Inside and outside of wall softened by presence of Mo from PMC coating or from TZM (Table 3-9).	Bonded to primary. Precipitation in walls. No major damage (Figure 3-21). No hardness change (Table 3-9).

Table 3-8

PMC RESULTS - 1800°C, 5000 HR (Continued)

Capsule Designation	Fuel Observations	Liner Material and Observations	Structural Alloy and Observations
PU270	Massive crack (~0.2 in. long by 0.02 in. wide) in fuel body. Coating intact over all surfaces. Mo network in excellent condition with voids present. Plutonia had large voids. Approximately 50% monotectoid (~1.80 O/Pu) (A, Figure 3-22).	TZM	Mo-46Re
		Shiny surface without Mo or plutonia deposits. Subsurface oxide precipitates to depth of 6 to 7 mils. Very fine precipitates throughout wall identified by microprobe as Ti rich. Large precipitates near Mo-46Re interface are Ti+2Re in proportion of about 3:1, probably as oxides (B, Figure 3-22). Wall was definitely hardened by precipitation. (Table 3-9). Microprobe examination on fueled specimen shows detectable interdiffusion of over 40 mils for Re and 25 mils for Mo. Chemical analyses of control specimen indicate that titanium diffused from TZM into Mo-46Re (Table 3-12).	Bonded completely to TZM. Some voids near the outer surface associated with Ta from transport from Ta-10W guard capsule (B, Figure 3-22). Inside wall softened by Mo diffusion from TZM. Outside hardened by Ta (Table 3-9). Microprobe examination on fueled specimen shows detectable interdiffusion of over 40 mils for Re and 25 mils for Mo. Chemical analyses of control specimen indicate that titanium diffused from TZM into Mo-46Re. (Table 3-12).

Table 3-9
 PMC CONTAINER MICROHARDNESS
 EXPOSED AT 1800°C FOR 5000 HOURS
 (Diamond Pyramid Hardness, 100-g load; values in kg/mm²)

Capsule Designation	Capsule		Location in Capsule	Location in Specimen		
	Layer	Alloy		Adjacent to Fuel	In Center	Away from Fuel
PU280	Primary	W-30Mo-30Re	Wall	429	409	493
	Secondary	T-111	Wall	225	210	215
6-9 Control	Primary	W-30Mo-30Re	Wall	446	459	463
	Primary	W-30Mo-30Re	Disc	446	450	450
	Secondary	T-111	Wall	205	222	221
PU278	Primary	Mo-46Re	Wall	314	327	274
	Secondary	TZM	Wall	185	180	186
4-7B Control	Primary	Mo-46Re	Wall	340	345	351
	Primary	Mo-46Re	Disc	317	192	314
	Secondary	TZM	Wall			
PU274	Primary	W-25Re	Wall	420	493	394
	Primary	W-25Re	Bottom disc	446	508	488
	Secondary	TZM	Wall	183	192	201
2-7 Control	Primary	W-25Re	Wall	514	508	488
	Primary	W-25Re	Disc	464	192	473
	Secondary	TZM	Wall			
PU270	Primary	TZM	Wall	230	230	242
	Primary	TZM	Bottom disc	188	198	217
	Secondary	Mo-46Re	Wall	272	330	405
7-4 Control	Primary	TZM	Wall	189	182	187
	Primary	TZM	Disc	193	345	201
	Secondary	Mo-46Re	Wall			

Table 3-10
PMC RESULTS - 2000°C, 1000 hr

Capsule Designation	Fuel Observations	Liner Material and Observations	Structural Alloy and Observations
PU271	Intact with one horizontal crack. Coating gone except for most of ends. Porosity present. Mo network reasonably intact. Unknown stoichiometry (A, Figure 3-23).	TZM	W-25Re
		Layer of Mo and plutonia on walls. Precipitation throughout wall, finer grained at surface than interior. Layer of Kirkendall type voids below interface with W-25Re. Ruptured with little ductility (A, B, Figure 3-23). Hardened throughout wall (Table 3-11). Chemical analyses of control specimen showed only very limited transfer of Mo and Ti from TZM to the W-25Re (Table 3-12).	Bonded to TZM along areas of wall. Diametral and end cap creep. Plutonia was metallographically observed in weld area. No oxides or other attack in areas other than weld (A, B, Figure 3-23). Softening occurred at TZM interface; hardening adjacent to PMC (Table 3-11). Chemical analyses of control specimen showed only very limited transfer of Mo and Ti from TZM to the W-25Re (Table 3-12).
PU279	Fuel swelled to fill cavity. Many large voids but no cracking. Did not polish sufficiently to determine Mo network condition or plutonia stoichiometry.	Mo-46Re	W-25Re
		Mo and plutonia in contact with surface from fuel swelling and transfer. Brittle weld failure. Fine precipitates in disc and wall (A, Figure 3-24). Hardened (Table 3-11).	Weld rupture from plutonia attack resulted in loss of helium and external contamination. Precipitates voids near surface and along grain boundaries (B, Figure 3-24). No hardening or softening (Table 3-11).
PU281	Fuel corners gone. Swelling occurred with void formation. Fuel very friable (unpolishable).	W-Mo-Re	W-25Re
		Much transfer of Mo and plutonia to walls. Intergranular oxide precipitation and voids throughout walls. Weld area attacked. (A, B, Figure 3-25). Hardened adjacent to PMC, softened above PMC (Table 3-11).	Extensive precipitation/void formation along walls (B, Figure 3-25). Softened next to WMoRe and above PMC. Hardness of Ta-10W guard capsule indicates oxygen content of 200 ppm or less showing that WMoRe/W-25Re are effective barriers to oxygen diffusion from fuel (Table 3-11).
PU275	Corners and coating gone. Porous appearance with small horizontal cracks. Mo network intact with odd angular appearance. Plutonia has much porosity and >50% monotectoid (<1.80° O/Pu) (A, B, Figure 3-26).	W-25Re	W-25Re
		Mo and plutonia transported to walls. Massive oxides and voids in discs and walls (worse than Figure 3-21). Softening at PMC interface from Mo diffusion (Table 3-11). Chemical analyses of control specimens showed no changes caused by exposure (Table 3-12).	Some penetration at weld. Bonded along walls with no signs of attack or damage. No hardening or softening (Table 3-11). Chemical analyses of control specimens showed no changes caused by exposure (Table 3-12).

Table 3-11
 PMC CONTAINER MICROHARDNESS
 EXPOSED AT 2000°C FOR 1000 HOURS
 (Diamond Pyramid Hardness; 100-g load; values in kg/mm²)

Capsule Designation	Layer	Alloy	Location in Capsule	Location in Specimen		
				Adjacent to Fuel	In Center	Away from Fuel
PU271	Primary	TZM	Adjacent to PMC	207	211	211
	Secondary	W-25Re	Above PMC	226	207	207
			Adjacent to PMC	243	590	600
			Above PMC	330	546	546
7-2 Control	Primary	TZM	Wall	188	181	180
	Secondary	W-25Re	Wall	435	451	519
PU279	Primary	Mo-46Re	Adjacent to PMC	365	412	495
	Secondary	W-25Re	Above PMC	445	463	515
			Adjacent to PMC	531	546	543
			Above PMC	500	565	510
4-2 Control	Primary	Mo-46Re	Wall	366	370	380
	Secondary	W-25Re	Wall	454	514	536
PU281	Primary	WMoRe	Adjacent to PMC	490	477	546
	Secondary	W-25Re	Above PMC	421	390	358
			Adjacent to PMC	390	541	481
			Above PMC	411	391	343
	Tertiary	Ta-10W	Adjacent to PMC	209	208	211
			Above PMC	208	187	152
6-2B Control	Primary	WMoRe	Wall	437	446	464
	Secondary	W-25Re	Wall	468	498	473
PU275	Primary	W-25Re	Wall	464	514	519
	Primary	W-25Re	Disc	420	493	483
	Secondary	W-25Re	Wall	516	516	514
2-2 Control	Primary	W-25Re	Wall	530	508	503
	Secondary	W-25Re	Wall	468	493	493

and shown in Figures 3-11 to 3-26 starting with 1500°C exposures and moving through the 1800° to 2000°C exposures. Table 3-12 presents the chemical analyses performed on the accompanying control specimens.

Behavior of the PMC fuel forms was dependent on both exposure temperature and container materials. The basic cermet structure remained intact after 1500°C exposures but was badly degraded after 2000°C exposures. Porosity within the plutonia and in the molybdenum network appeared to be a directly increasing function of temperature and exposure time. In general, the molybdenum network was recrystallized and tended somewhat to agglomerate, but remained intact in all PMC specimens. Molybdenum coating retention was a direct function of container material. The best behavior was in either Ta-10W or TZM containers. For example, the molybdenum coating was intact on PMC specimens with TZM liners exposed at 1800°C for both 1000 and 5000 hours while the coating was completely gone from specimens exposed in Mo-46Re, WMoRe, and W-25Re containers. Similarly, corners of the fuel bodies were lost first in W-25Re containers then at higher temperatures in the WMoRe and Mo-46Re containers. Only minor cracking was observed in PMC bodies exposed in TZM containers even at 2000°C.

Oxygen content in the plutonia varied with both temperature and the double container materials used. Ta-10W and T-111 have the highest permeability to oxygen of the alloys in the program. Permeability to oxygen increases with additions of tungsten and rhenium to molybdenum. TZM has the highest permeability to oxygen while W-25Re has the lowest. Mo-46Re would be expected to be somewhat more permeable than WMoRe, and both would be intermediate to TZM and W-25Re. Under each exposure condition, the variation in oxygen content followed the expected pattern. For example, at 1500°C and 5000 hours the TZM container PMC specimen had greater than 50% monotectoid decomposition product present, the Mo-46Re less than 50% and the W-25Re was almost stoichiometric where all had T-111 secondary containers. At 1800°C and 5000 hours, the W-25Re/TZM combination had only 30% monotectoid, the TZM/Mo-Re had 50%, and the Mo-46Re/TZM had 60% to 70% monotectoid showing a decreasing oxygen content with decreasing permeability to oxygen, as expected. Because of the difficulty in polishing the porous, swelled PMC after exposure at 2000°C, only the W-25Re/W-25Re PMC specimen was interpretable as to oxygen content.

APPROX 4.3x

A. CROSS SECTION

5 MILS (200x)

B. PMC

20 MILS (50x)

C. PMC WITH Mo COATING/Ta-10W CAPSULE/T-111 CAPSULE

5 MILS (200x)

D. PMC WITH Mo COATING/Ta-10W CAPSULE

Figure 3-11. PU266 (PMC/Ta-10W/T-111, 1500°C, 500 hr)

Figure 3-12. PU267 (PMC/Ta-10W/T-111, 1500°C, 5000 hr)

Figure 3-13. PU268 (PMC/TZM/T-111, 1500°C, 5000 hr)

A. PMC/Mo-46Re CAPSULE WALL

B. Mo-46Re/T-111 WALLS

Figure 3-14. PU276 (PMC/Mo-46Re/T-111, 1500°C, 5000 hr)

A. CROSS SECTION

B. PMC/W-25Re/T-111

Figure 3-15. PU272 (PMC/W-25Re/T-111, 1500°C, 5000 hr)

A. PMC

5 MILS (200x)

B. W-25Re WALL

10 MILS (100x)

Figure 3-16. PU273 (PMC/W-25Re/T-111, 1800°C, 1000 hr)

A. CROSS SECTION

B. TZM WALL, PMC, TZM DISC

Figure 3-17. PU269 (PMC/TZM/TZM, 1800°C, 1000 hr)

Figure 3-18. PMc/Mo-46Re/TZM in PU277, 1800°C, 1000 hr

A. CROSS SECTION

B. PMC/W-30Mo-30Re/T-111

Figure 3-19. PU280 (PMC/WMoRe/T-111, 1800°C, 5000 hr)

A. CROSS SECTION

B. PMC/Mo-46Re/TZM

Figure 3-20. PU278 (PMC/Mo-46Re/TZM, 1800°C, 5000 hr)

Figure 3-21. W-25Re/TZM from PU274, 1800°C, 5000 hr

Figure 3-22. PU270 (PMC/TZM/Mo-46Re, 1800°C, 5000 hr)

A. CROSS SECTION

ORIGINAL ↑ INTERFACE
B. TZM/W-25Re 20 MILS (50x)

Figure 3-23. PU271 (PMC/TZM/W-25Re, 2000°C, 1000 hr)

A. PMC/Mo-Re WALL 20 MILS (50x)

B. W-25Re WALL 10 MILS (100x)

Figure 3-24. PU279 (PMC/Mo-46Re/W-25Re, 2000°C, 1000 hr)

A. W-Mo-Re WALL AND DISC

20 MILS (50x)

B. W-25Re CAPSULE/W-Mo-Re WELD AREA

20 MILS (50x)

Figure 3-25. PU281 (PMC/WMoRe/W-25Re, 2000°C, 1000 hr)

A. CROSS SECTION

B. PMC

10 MILS (100x)

Figure 3-26. PU275 (PMC/W-25Re/W-25Re, 2000°C, 1000 hr)

Table 3-12

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	Outer	Inner	Outer	Inner	Outer	Inner	Outer	Inner	Outer	Inner	Outer	Inner	Outer
	Mo46Re	T111	TZM	TZM	TZM	Mo46Re	Mo46Re	TZM	W25Re	T111	W25Re	W25Re	TZM	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

Attack to the primary or liner capsule varied as expected with material, temperature, and time all affecting the results. The Ta-10W was the worst material with intergranular attack of 1 to 2 mils after only 500 hours at 1500°C and increasing to 2 to 8 mils after 5000 hours at 1500°C. The W-25Re was actually the next worst with subsurface voids and precipitates present after exposure at all temperatures. No actual attack to the surface occurred other than diffusion of the former PMC molybdenum coating into the surface. Similar behavior was exhibited by the WMoRe. The TZM liner showed no attack at 1500°C, precipitation of oxides near the surface at 1800°C, and complete precipitation at 2000°C. The Mo-46Re showed no attack at either 1500°C or 1800°C, and exhibited fine precipitates at 2000°.

Liner materials exhibited different levels of damage to the entire structure, some being related to this type of attack. The Ta-10W had oxide precipitates throughout after 1500°C exposure. The W-25Re had voids and precipitates at all exposure temperature. The 1500°C precipitation had the appearance of a sigma phase, in that, the control specimen also exhibited a comparable precipitation. However, at 1800° and 2000°C, voids appeared to be the dominant form of degradation. Comparable structures were observed in the WMoRe. The TZM liners had fine precipitation at all temperatures with amount and size increasing with temperature. The Mo-46Re was totally unaffected, except at 2000°C where a fine precipitate was present.

T-111 was convincingly an inadequate structural member for use at 1500°C or above. Both fine and coarse precipitation occurred throughout the wall regardless of liner material used. Additionally, reactions occurred at the interface with most of the liner materials. Reactions were either intermetallic compounds or large oxides, both being detrimental to structural integrity.

TZM appeared to be promising as a structural alloy. In four specimens, two exhibited precipitation in the structure, the other two showed no damage. No structural damage occurred in the 1800°C, 1000 hour specimen with TZM liner. Similarly, no damage occurred in the 1800°C, 5000 hour specimen with a Mo-46Re liner. However, the matched Mo-46Re 1800°C, 1000 hour specimen had a void layer at the interface and precipitation throughout. The 1800°C, 5000 hour specimen with W-25Re liner also had precipitation throughout. It is probably that precipitation was the result of liner capsule rupture with subsequent free access of oxygen vapor species. Further testing is necessary to establish the utility of TZM as a structural alloy for RTG's.

W-25Re was tested only at 2000°C as a structural alloy with two successes and two failures. Combinations with TZM and W-25Re liners appeared in excellent condition after the 1000 hour exposure. However, combinations with Mo-46Re and WMoRe resulted in voids and precipitates probably because of early inner capsule rupture. If integrity of an inner liner could be assured, W-25Re would very likely retain structural integrity to temperatures approaching 2000°C for extended operation.

In the one test with Mo-46Re as a structural member and TZM as a liner exposed at 1800°C for 5000 hours, the Mo-46Re remained totally undamaged.

In the 16 PMC tests, there was no single best combination. In the one totally undamaged liner/structural member tested at 1800°C with Mo-46Re/TZM, the PMC lost its molybdenum coating and considerable oxygen. Where the PMC looked best at 1800°C in a TZM/Mo-46Re combination, the TZM had precipitation, but the Mo-46Re was undamaged.

3.4 SOLID SOLUTION CERMETS

Four plutonia-thoria-molybdenum SSC fuel bodies and their containers were examined for comparison with the PMC fuel form. Detailed results are listed in Tables 3-13 and 3-14 and shown in Figures 3-27 through 3-30.

Behavior of the SSC fuel form is unknown after the single 1500°C exposure because the fuel was lost during sectioning. Behavior during the 1800°C, 5000 hour exposure was dependent upon liner material composition. SSC exposed in a TZM container remained intact, lost a small amount of molybdenum coating, and had a partially degraded molybdenum network. Structurally, the SSC was only slightly poorer than the comparably exposed PMC, and the bulk appearance was better. However, SSC exposed in W-25Re and WMoRe containers lost all the molybdenum coatings, the same as comparable PMC specimens, and the molybdenum network disappeared, not comparable to PMC. It appears that the lower molybdenum content, together with the addition of thorium, either resulted in dissolution of molybdenum or enforced migration from the structure. In microprobe studies of the oxide structure in PU263, only plutonium and thorium were present. The appearance of the oxide structure in PU264 and PU265 seems to indicate only a modification in the substoichiometric plutonia structure. The answer as to the location of the former molybdenum network is unknown.

Table 3-13
SSC RESULTS - 1500°C AND 1800°C, 5000 hr

Capsule Designation and Expo- sure Temp.	Fuel Observations	Liner Material and Observations	Structural Alloy and Observations
PU262 (1500°C)	Fuel was lost during sectioning.	<u>Ta-10W</u> Shiny surface with slight irregularities. Intergranular attack to ~3 mils and subsurface void formation. Precipitation throughout. Oxide interface between Ta-10W and T-111. (A, B, Figure 3-27). Slightly hardened (Table 3-14).	<u>T-111</u> Slight diffusion layer with Ta-10W; probably depletion of Hf. Much oxide precipitation throughout wall (B, Figure 3-27). No hardening (Table 3-14).
PU263 (1800°C)	Intact with almost entire coating present. Metal network degraded, partially spheroidized. Moderate porosity. Plutonia was single phase except for odd structure at grain boundaries (perhaps >1.80 O/Pu). Microprobe examination showed areas to contain only Pu+Th as oxides (A, Figure 3-28).	<u>TZM</u> Very slight Mo deposit on surface; no plutonia. Surface adjacent to SSC in excellent condition. No Pu diffusion into TZM. Interface with T-111 has intermetallic compounds and voids in TZM. Microprobe exam shows particles in TZM at interface to be Hf+Ti oxides (B, Figure 3-28). Hardness somewhat higher (Table 3-16).	<u>T-111</u> Intermetallic compounds in interface with TZM. Massive oxide precipitation throughout. Microprobe exam shows inclusions to be Hf oxide. (B, Figure 3-28). Hardening occurred at interface, but not deeper (Table 3-16).
PU264 (1800°C)	Cracked in two during sectioning. Corners gone. Coating gone. Much large porosity. No metallic network--unusual structure with extra gray phase, probably Mo in solution (perhaps ~1.83 O/Pu) (A, Figure 3-29).	<u>W-25Re</u> Mo and some plutonia on walls. Oxides and other precipitates throughout walls in some areas. Bonded with intermetallic appearing layer to T-111 (B, Figure 3-29). Slight softening from interior Mo diffusion (Table 3-16). Chemical analyses of control specimen shows transfer of Hf and Zr from T-111 to W-25Re (Table 3-12).	<u>T-111</u> Intermetallic layer with W-25Re. Some diffusion into T-111. Both fine and large oxide precipitation throughout walls (B, Figure 3-29). Hardening at inner surface (Table 3-16). Chemical analyses of control specimen shows transfer of Hf and Zr from T-111 to W-25Re (Table 3-12).
PU265 (1800°C)	Cracked during sectioning. No cracking otherwise. Coating gone. No metallic network. Similar structure to PU264 except that caused by lower oxygen permeability (perhaps <1.87 O/Pu) (A, Figure 3-30).	<u>WMoRe</u> Transfer of Mo to walls but no plutonia. Oxide precipitation to 15 mils No bonding with W-25Re (B, Figure 3-30). Slight softening from Mo diffusion into inner surface (Table 3-16).	<u>W-25Re</u> Voids and oxide precipitates to 10 mils. No bonding with WMoRe (B, Figure 3-30). No hardening or softening (Table 3-16).

Table 3-14

SSC CONTAINER MICROHARDNESS
 EXPOSED AT 1500°C AND 1800°C FOR 5000 HOURS
 (Diamond Pyramid Hardness, 100-g load; Values in kg/mm²)

Capsule Designation	Exposure Temperature (°C)	Layer	Alloy	Capsule	Location on Specimen		
					Adjacent to Fuel	In Center	Away From Fuel
PU262	1500	Primary	Ta-10W	Wall	222	221	209
		Secondary	T-111	Wall	235	206	233
8-9B Control	1500	Primary	Ta-10W	Wall	210	212	207
		Secondary	T-111	Wall	233	228	262
PU263	1800	Primary	TZM	Wall	188	195	195
		Secondary	T-111	Wall	249	215	209
7-9 Control	1500	Primary	TZM	Wall	177	182	178
		Secondary	T-111	Wall	227	224	277
PU264	1800	Primary	W-25Re	Wall	468	464	483
				Bottom Disc	376	493	450
		Secondary	T-111	Wall	281	206	240
2-9B Control	1800	Primary	W-25Re	Wall	498	496	514
				Disc	500	498	498
		Secondary	T-111	Wall	225	232	233
PU265	1800	Primary	W-MoRe	Wall	454	464	514
				Bottom Disc	441	450	420
		Secondary	W-25Re	Wall	493	493	498
6-2A Control	1800	Primary	W-MoRe	Wall	473	483	468
				Disc	450	459	446
		Secondary	W-25Re	Wall	498	483	530

A. Ta-10W SURFACE

200x (5 MILS)

B. Ta-10W/T-111 INTERFACE

200x (5 MILS)

Figure 3-27. PU262 (SSC/Ta-10W/T-111, 1500°C, 5000 hr)

A. SSC

200x (5 MILS)

B. TZM/T-111 INTERFACE

100x (10 MILS)

Figure 3-28. PU263 (SSC/TZM/T-111, 1800°C, 5000 hr)

A. SSC

50x (20 MILS)

B. W-25Re/T-111

50x (20 MILS)

Figure 3-29. PU264 (SSC/W-25Re/T-111, 1800°C, 5000 hr)

A. CROSS SECTION

B. W-25Re WALL/WMoRe WALL AND DISC

50x (20 MILS)

Figure 3-30. PU265 (SSC/WMoRe/W-25Re, 1800°C, 5000 hr)

Attack to the liner materials by the SSC was somewhat less than that caused by PMC. Ta-10W at 1500°C was directly comparable. W-25Re at 1800°C was also comparable. However, both TZM and WMoRe exhibited either no or lessened precipitation in the SSC situation.

T-111 was also an inadequate structural container for SSC at both 1500° and 1800°C. Precipitation occurred throughout the walls. Intermetallic compounds were formed with both TZM and W-25Re liners.

Rupture of the WMoRe liner resulted in major degradation within the W-25Re structural member at 1800°C. Voids and oxides were found to depths of 10 mils. It remains indeterminate as to what the W-25Re behavior would be if the liner had retained its integrity.

3.5 COMPARATIVE RESULTS SUMMARY

Comparative results are summarized in Table 3-15 as extracted from previous tables in this section. The BCL-PMC and PMC fuel forms, compared under approximately the same exposure conditions, appear to perform the same. SSC shows definite signs of structural instability. Helium release and storage of the three fuel forms was the same within accuracy of the measurements.

Oxygen content of the plutonia was primarily affected by temperature and time, but a strong secondary factor was permeability of the containers to oxygen. W-25Re was the least permeable and resulted in the highest post-test oxygen contents in the fuel. Ta-10W had the highest permeability with TZM the second highest. Mo-46Re and WMoRe were intermediate in permeability. There was no apparent correlation between oxygen content and plutonia porosity.

Coating loss and subsequent transfer of plutonia to container surfaces were direct functions of liner material. TZM and Ta-10W liners resulted in the least transfer, Mo-46Re, and WMoRe, and W-25Re the most. Degradation of the cermet body, particularly the corners, was also affected by variations in liner material.

Table 3-15
COMPARATIVE RESULTS SUMMARY

Capsule Designation	Fuel Form	Exposure		Fuel Results							Liner				Interaction	Structural Member			
		Temp (°C)	Time (hr)	Bulk Appearance	Coating	Mo Network	Porosity	O/Pu Ratio	Helium Release (%)	Helium Storage (g/cm ²)	Material	Attack	Structure	Hardness		Material	Structure	Hardness	
AA-55	BCL-PMC	1,800	1,000	Ok	Ok	Ok	Fine	>1.80	52	0.11	W-25Re	?	?	?	-	-	-	-	
AA-54			5,000	Transferred	Lost	?	?	?	96	0.07		Ppt 20 mil	Oxides	?	-	-	-	-	
AA-53			10,000	Spongy	Lost	Degraded	Large	~1.72	99	0.01		Ppt	Less oxides	?	-	-	-	-	
AA-52			2,000	1,000	Spalling	Spalling	Ok-	Large	~1.80	55	0.10		?	?	?	-	-	-	-
AA-56				5,000	Transferred	Lost	Bad	Large	~1.76	98	0.01		Ppt 10 mils	Fine grains	?	-	-	-	-
AA-57				10,000	Transferred	Lost	None	Large	<1.70	?	?		Voids,thinning	Oxides	?	-	-	-	-
AA-59B			20	21,800	Ok	Ok	Ok	Cracks	?	-	-	Ta-10W	?	?	?	-	-	-	-
AA-58A		20	21,800	Ok	Reacted	Ok	More cracks	?	89	0.10	Ta-10W	?	?	?	-	-	-	-	
		+1,500	+120																
266	PMC	1,500	500	Ok	Minor spall	Ok	Fine	~1.80	-	-	Ta-10W	Inter 1-2 mil	Oxide ppt	↗	None	T-111	Ppt 30 mil	In↑	
267			5,000	Ok	Ok	Ok	Coarser	?	-	-	Ta-10W	Inter 2-8 mil	Oxide ppt	↑	Voids Oxides	T-111	Ppt Throughout	→	
268				1 crack	Ok	Ok-	Porous	<1.80	92	0.04	TZM	None	Fine ppt	↑	Ppt, Diffusion	T-111	Ppt Throughout	Center↗	
276				Surface PuO ₂ lost	Total loss	Ok-	>267	>1.80	-	-	Mo-46Re	None	Ok	In↓	Inter, Oxides	T-111	Ppt Throughout	In↑	
272				Corners lost	Total loss	Ok	>267	>1.94	-	-	W-25Re	Voids & ppt	Ppt	↑	None	T-111	Ppt Throughout	↑	
273			1,800	1,000	Corners lost	Lost	Ok	Fine	~1.94	-	-	W-25Re	Voids & ppt	Ppt	In↑	Intermetallic	T-111	Ppt Throughout	↑
269				2 cracks	Ok	Ok	Small & Large	<1.94	-	-	TZM	Ppt 2 mil	Fine Grains	↑	Bonded	TZM	Ok	↑	
277				Crack	Lost	Ok	273	<1.94	?	?	Mo-46Re	None	Ok	→	Void layer	TZM	Fine ppt throughout	↗	
280			1,800	5,000	Corners lost	Lost	Degraded	Much	?	?	?	WMoRe	Pores 10 mils	Oxides	→	Intermetallic	T-111	Ppt Throughout	→
278				Minor cracks	Lost	Ok	Small & Large	~1.75	-	-	-	Mo-46Re	None	Ok	Center↑	Bonded	TZM	Ok	→
274			Corners Lost; cracks	Lost	Ok	<270	~1.87	-	-	-	W-25Re	Voids & Ppt	Oxides	In, Out↓	Bonded	TZM	Ppt	→	
270			Massive crack	Ok	Ok+	Large	~1.80	-	-	-	TZM	Ppt 6-7 mil	Fine ppt	↑	Oxide ppt	Mo-46Re	Ok	In↓	
271	SSC	2,000	1,000	Crack	Sides lost	Ok-	?	?	-	-	TZM	Ppt	Ppt	↑	Bond w/voids	W-25Re	Ok	In↓	
279				Swelling	Lost	?	Very much	?	-	-	-	Mo-46Re	Ppt	Fine ppt	↑	None	W-25Re	Ppt, Voids	→
281				Corners lost; swelling	Lost	?	Very much	?	-	-	-	WMoRe	Voids & Ppt	Oxides, voids	↑	None	W-25Re	Ppt, Voids	↓
275				Corners lost; cracks	Lost	Ok	Much	<1.80	?	?	-	W-25Re	Voids & Ppt	Oxides, voids	In↓	Bonded	W-25Re	Ok	→
262			1,500	5,000	?	?	?	?	?	87	0.07	Ta-10W	Inter 3 mil	Ppt, voids	↗	Oxides	T-111	Ppt Throughout	→
263		1,800	5,000	Ok	Slight loss	Degraded	Moderate	>1.80 ?	96	0.02	TZM	None	Ppt	↗	Inter, Voids	T-111	Ppt Throughout	In↑	
264				Corners lost; crack	Lost	None	Mod large	~1.83 ?	-	-	W-25Re	Ppt	Oxides, ppt	In↘	Intermetallic	T-111	Ppt Throughout	In↑	
265				Cracks	Lost	None	Mod large	>1.87 ?	-	-	WMoRe	Ppt 15 mil	Oxides	In↘	None	W-25Re	Voids, Oxides 10 mil	→	

The molybdenum networks remained intact in all cases where the PMC or BCL-PMC body remained intact. The SSC molybdenum network degraded earlier and disappeared entirely in two specimens, entirely contrary to PMC behavior.

Attack to the liner materials was approximately the same for all three fuel forms. The Ta-10W and W-25Re liners behaved the worst, followed closely by WMoRe. TZM and Mo-46Re appeared to remain intact to 2000°C, except for the presence of internal fine precipitates. Hardness changes were related to precipitation (hardening), molybdenum diffusion from deposition of the PMC or SSC coating on the surface (softening), and interaction with the structural member (both hardening and softening). The liner is included to prevent degradation of the structural member by the fuel. The major attack observed on structural members occurred either because of oxygen permeation through the liner or direct contact with oxygen containing vapor species caused by liner rupture. Precipitation in W-25Re structural members only occurred when the inner liner ruptured. However, massive precipitation occurred in all T-111 structural members, even at the lowest test temperature of 1500°C, as a result of oxygen permeability through the liners. Liners appeared to offer significant protection to TZM and Mo-46Re structural members with only minor visible precipitation.

Interactions between liner and structural members were related to material differences or similarities. Bonding occurred between similar materials without formation of extraneous products. Dissimilar materials such as Mo-46Re and T-111 resulted in intermetallics and oxide precipitates at the interface. Alloys containing strong oxide formers such as T-111 and TZM typically had oxide precipitates in the interaction layer. A Kirkendall void layer was formed between TZM and Mo-46Re. Interdiffusion was significant when intermetallic layers were not formed. Hardness changes were related either to precipitation or diffusion, particularly near the interface with the liner.

Material transfer was shown in chemical analyses of control specimens (Table 3-12). The only elements that actually transferred in significant quantities at 1800°C and above were hafnium, titanium, and zirconium, the active oxide formers in T-111 and TZM. All other elements remained relatively in place during exposure.

Section 4

CONCLUSIONS

Fourteen conclusions have been reached, based on the various tests conducted with cermet fuels in refractory alloy containers. These conclusions have been grouped into four categories: fuel, liner, liner/structural member combinations, and total system. The last conclusion is also a recommendation as to optimal potential high-temperature systems configuration.

4.1 FUEL CONCLUSIONS

4.1.1 PMC and BCL-PMC Behaved Similarly with SSC Being Inferior

Bulk behavior such as cracking, swelling, coating loss, and helium release were comparable for PMC and BCL-PMC exposed under the same circumstances. Porosity and molybdenum network retention were also comparable. SSC bulk behavior was the same as for PMC and BCL-PMC, but degradation or total loss of the molybdenum network indicated inferior fuel stability.

4.1.2 PMC Structurally Degrades at 1500°C and Above

Some bulk degradation such as cracking, coating loss, and some subsurface plutonia loss occurred at 1500°C with major increases in degradation at 1800°C. Of more importance, the internal molybdenum network and the plutonia both become porous with concurrent loss of mechanical integrity. Plutonia porosity has also been observed in the 1100° to 1200°C range at Mound Laboratory (Reference 5), LASL (Reference 7), and DWDL (Reference 10), but the molybdenum network remains intact. Impact testing of the lower temperature aged fuel indicates retention of mechanical integrity. The effect of porosity on structural stability under higher temperature operating and impact situations should be determined before concluding that all porosity is categorically bad.

4.1.3 Helium Release is Not Likely to be an Engineering Problem with Cermets at 1500°C and Above

PMC and SSC exhibited comparable helium release and storage behavior which resulted in essentially 100% release of the helium generated subsequent to fabrication after 5000 hours at 1500°C. It appears that helium release starts slowly (only 52% to 55% reported as released after 1000 hours at 1800° and 2000°C), increases to a slightly higher than 100%, then decreases to an equilibrium 100% release value. Initial storage release is estimated to be as much as 0.10 cm³/g of cermet. Helium storage estimates made after helium release show that less than 0.04 to 0.07 cm³/g may be a stable storage condition for long-term 1500°C operation with less storage at longer times and higher temperatures. The only question arises as to the amount stored during earlier stages of operation. Excessive quantities could result in rapid release during a reentry thermal pulse similar to that exhibited in the long-term ambient aged BCL-PMC fuel form, which released essentially all the generated helium in the 120 hours at 1500°C.

4.1.4 Long-Term Ambient Storage Degrades the BCL-PMC Structure

In the BCL-PMC fuel form stored 2.5 years under ambient conditions, the plutonia was badly cracked and the molybdenum network was fractured in many areas. In the matched specimen heated to 1500°C for 120 hours, helium was released more readily from the structure than in freshly manufactured material, with the conclusion that the mechanical integrity of PMC was impaired by long-term room-temperature storage.

4.1.5 Molybdenum Overcoat Retention is Related to Liner Material Composition

The best molybdenum overcoat retention occurred in TZM and Ta-10W liners. There was apparently no driving force for transfer of the molybdenum from the cermet to the slightly lower temperature wall to at least 1800°C in the case of TZM. Only at 2000°C was the coating missing. Use of Mo-46Re, WMoRe, and W-25Re liners at 1500°C and above always resulted in total loss of the coatings. Generally accompanying this loss was subsequent transfer of plutonia to the walls. It appears necessary to use TZM or Ta-10W as a first liner material to minimize degradation of the cermet coatings.

4.1.6 Plutonia Oxygen Content is a Function of Container Permeability and Gettering Characteristics

At temperatures of 1500°C and above, it was readily possible to discriminate among the various levels of permeability and gettering caused by varying the container materials. The Ta-10W/T-111 container combination is both a window and a getter for oxygen, permitting oxygen loss and resulting in the lowest plutonia oxygen contents observed in this test series. Oxygen loss is not necessarily bad if the concurrent density decrease can be accommodated. Conversely, W-25Re provided the lowest level of oxygen permeability together with a small but finite gettering action in forming oxide precipitates. TZM, Mo-46Re, and WMoRe provided lessening permeabilities for oxygen than Ta-10W but higher than W-25Re. TZM did getter oxygen, having both titanium and zirconium present as alloying ingredients, but in lesser quantities than in T-111.

4.2 LINER CONCLUSIONS

4.2.1 TZM is the Best Liner for PMC at 1500° to 2000°C

A TZM liner results in the best retention of coating and bulk appearance of the PMC fuel form. No attack is observed on the TZM surface other than minor oxide precipitation to temperatures of 2000°C. Precipitation occurs throughout the wall at temperatures as low as 1500°C, caused by oxygen permeation and reaction with the titanium and zirconium in the TZM. However, the minor mechanical degradation occurring in the TZM does not affect behavior of whatever structural member is being used. The only disadvantage with TZM is its relatively high permeability to oxygen compared to the tungsten and rhenium containing alloys.

4.2.2 The Highest Melting Alloys Have the Worst Appearances

Both W-25Re and Ta-10W, the highest melting or most refractory alloys, display the poorest appearance in contact with cermet fuel forms. At 1500°C, the Ta-10W had intergranular attack and oxide precipitation throughout the wall. Similarly at 1500°C, W-25Re had voids and precipitation in the wall which worsened with increasing temperature. WMoRe behaved only slightly better than W-25Re. The least refractory alloys, TZM and Mo-46Re, behaved best in contact with cermet fuels.

4.2.3 Ta-10W May be Useful as a Sacrificial Liner

Although Ta-10W had intergranular penetration and oxide precipitation from contact with PMC, its presence resulted in minimal degradation to the PMC after exposure at 1500°C. The Ta-10W acts as both a window and getter for oxygen from the plutonia. The presence of Ta-10W and its intrinsic thermodynamic properties may prevent major vapor transport from the PMC with its concomitant degradation. Instead, the Ta-10W degrades, acting as a sacrificial liner. Use in this mode most likely requires an additional liner, thereby providing marginal utility for an engineering application.

4.3 LINER/STRUCTURAL MEMBER CONCLUSIONS

4.3.1 T-111 is Inadequate as a Structural Member at 1500°C with All Liner Materials

Massive oxide precipitation occurred within all T-111 structural members, regardless of what liner material was used. The amount appeared to be somewhat dependent on oxygen permeability of the liner material. Work at Oak Ridge National Laboratory (Reference 11) appears to indicate that this level of precipitation and oxygen content may be ductile in slow rate tensile tests. Behavior under impact conditions would, however, be more likely to be brittle at the high oxygen contents. The DWDL tests did not provide maximum safe usage temperatures for T-111 but did show that 1500°C is too hot for T-111.

4.3.2 Attack to Structural Members (Other than T-111) Appeared to be Caused by Liner Container Failure

Whenever the liner remained intact, the structural member containers, other than T-111, were undamaged by the test conditions except for minor precipitates from oxygen permeation through the liner. In the two cases where TZM structural members had precipitation, it appeared that the liner capsules had ruptured, causing direct vapor oxygen access to the TZM. Conversely in the remaining TZM structural members, it was apparent that liner capsule failure did not occur. This was particularly evident in the TZM/TZM combination where there was no precipitation in the structural member. Directly comparable behavior was exhibited by W-25Re. Massive precipitation and void formation appeared

to occur only when the liner capsule had ruptured. Whenever the liner remained intact, TZM at 2000°C for 1000 hours for example, the W-25Re remained totally intact even though oxygen permeability through the TZM was high.

4.3.3 Interactions were Functions of Alloy Dissimilarities and Oxygen Presence

Voids, oxide precipitation, and intermetallic compounds were present in various liner/structural member alloy combination. Voids occurred between Ta-10W and T-111, Mo-46Re and TZM, TZM and T-111, and TZM and W-25Re. In most cases, the voids appeared to be Kirkendall type caused by differential diffusion rates of constituents of one alloy into the other. These voids are intrinsic in nature and will occur whenever intimate contact between these dissimilar materials occurs. Internal helium pressurization caused the liner to creep, creating pressure contact and consequent diffusion. Comparable control capsules, without pressurization did not have comparable diffusion and void formation. Intermetallic compounds were observed only in combinations of T-111 with the molybdenum, tungsten, or rhenium containing alloys. Oxide precipitation occurred between T-111 and Ta-10W, T-111 and Mo-46Re, and TZM and Mo-46Re wherein both T-111 and TZM supplied an active oxide former which diffused to a site where oxide formation/precipitation occurred. In each case, the original source of oxygen was the PMC. Oxygen permeation through the liner resulted in the ultimate oxide formation at the interface. Chemical analysis of control specimens showed diffusion of active elements such as hafnium, titanium, and zirconium. Microprobe analysis also showed extensive diffusion between TZM and Mo-46Re with very small probable effect on properties.

4.3.4 The Best Liner/Structural Member Combinations at 1500°C and above were TZM Liners with TZM, Mo-46Re, or W-25Re Structural Members

In all cases where TZM was the liner and TZM, Mo-46Re, and W-25Re were the structural members, no attack was observed in the structural member. Interfaces exhibited varying minor oxide precipitation with Mo-46Re and voids with W-25Re, but no bulk degradation was observed. Other successful combinations were Mo-46Re/TZM at 1800°C for 5000 hours (however not at 1000 hours) and W-25Re/W-25Re at 2000°C for 1000 hours. A major factor probably contributing to the success of TZM as a liner is its creep ductility at operating temperature which permitted deformation to meet the structural member without rupture, thereby preventing vapor contact with oxygen species.

4.4 SYSTEM CONCLUSIONS AND RECOMMENDATION

4.4.1 PMC Fuel, TZM Liner, and TZM, Mo-46Re, or W-25Re Structural Members Comprise the Best Overall System, but Not for Long-Term Operation at 1500°C or Above

A TZM liner with a TZM, Mo-46Re, or W-25Re structural member resulted in no degradation to the structural member at 1500°C and above, thereby ensuring adequate long-term containment. TZM liners showed precipitation but not surface attack. Of more importance, TZM liners result in the molybdenum coatings on PMC fuel bodies remaining intact at 1500°C and above. Structurally, the PMC retains its best appearance in TZM liners. However, even at 1500°C, the overall molybdenum network and plutonia degrade with time, resulting in probable decreased mechanical performance in impact situations. Because no tests were conducted at lower temperatures in this task at DWDL, it is impossible to predict an upper temperature limit for PMC utilization even in the above combinations.

Section 5

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