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REFRACTORY-ALLOY COMPATIBILITY WITH PLUTONIA-238 AT 1800° AND 2000°C

J. D. WATROUS
W. E. FERGUSON

PREPARED FOR THE ATOMIC ENERGY COMMISSION
DIVISION OF SPACE NUCLEAR SYSTEMS
UNDER CONTRACT NO. AT(45-1)-2138
DATE PUBLISHED — AUGUST 1973

Donald W. Douglas Laboratories
Richland, Washington

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ABSTRACT

Investigation of refractory alloy compatibility with plutonia-238 at 1800° and 2000°C indicated that rhenium exhibited the least attack from plutonia. Variables included in the study were refractory alloy composition (W, W-25Re, Re, Mo, Mo-50Re, and W-30Mo-30Re), plutonia purity (~1 w/o and 0.23 w/o cationic impurities), plutonia stoichiometry (PuO_2 and $\text{PuO}_{1.8}$), temperature, and time (2000°C for 1000 hr, 1800°C for 2000 hr, and 1800°C for 18,000 and 15,000 hr). The test specimens consisted of 0.25-g plutonia pellets in contact with two polished metal discs, all in a thick wall pressure-vessel type container of the same alloy. General solution, intergranular precipitation, oxide precipitation, void formation, and intermetallic compound formation were observed in the different test specimens primarily to depths of less than 10 mils but much deeper for tungsten. Both the alloys and plutonia mass transported within the capsules. Rapid oxygen permeability through the molybdenum alloy containers reduced the capacity of the test to provide information on stoichiometric PuO_2 compatibility but remains valid for substoichiometric PuO_{2-x} . The $\text{PuO}_{1.8}$ was less aggressive chemically than PuO_2 . The relatively small plutonia volume resulted in minimal effect of plutonia purity. Several effects of test variables prevented development of mathematical expressions for alloy penetration as functions of temperature and time. Although rhenium exhibited the least attack, molybdenum, Mo-50Re, W-30Mo-30Re and W-25Re also appeared to offer adequate containment capabilities to 1800°C particularly for substoichiometric purer plutonia.

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Section 1

INTRODUCTION

Plutonia-238 has been, and continues to be, the only radioisotope launched into space in the United States program to produce long-term electrical energy to meet various mission requirements. Absolute containment of the isotope throughout the life cycle of the electrical generator is now considered essential although burn-up systems were permitted some years ago. Reliability guarantees to users require that potential detrimental reactions to the containers and degradation of the fuel be determined in detail.

Principal goals of the DWDL compatibility testing program were to determine the best container materials for plutonia-238 at high temperature and long times, define kinetics and mechanisms of fuel/container reactions, and determine relative reactivities of various plutonia fuel compositions. Test temperatures of 1800° and 2000°C were selected to provide high temperature compatibility data for thermionic energy conversion systems and to provide accelerated reactions between fuel and the container materials for thermoelectric and Brayton-cycle systems with proposed maximum operating temperatures of about 1500°C. Test durations of 1000 hours and longer were chosen to produce information useful for long-lived systems and to complement the work already underway at Mound Laboratory (Reference 1) at shorter times.

Container materials were selected primarily on the basis of prior DWDL work on compatibility with lanthanide oxides (Reference 2). Commercial availability was also required because system applicability was a primary consideration. Major effort involved determination of potential degradation of container materials caused by the presence of plutonia. Control specimens were included with the test specimens to separate thermal effects from fuel reactions.

At the start of the program, the effect of two levels of oxygen stoichiometry on the compatibility of production-grade plutonia used in the SNAP-27 program was the only fuel parameter to be studied. Calculations showed that thermodynamic

stability of oxygen in the plutonia increased with decreasing oxygen content. It was believed that an oxygen-to-plutonium ratio of approximately 1.80 would provide a good comparison to the stoichiometric composition $\text{PuO}_{2.00}$. Shortly after testing had begun, experimental evidence obtained at Mound Laboratory indicated that impurities in the plutonia had significant effect in reactions with refractory metals. This effect was believed to be important enough to compromise system integrity. Therefore, a second series of tests identical to the first was initiated with a purer form of plutonia.

Eighteen test specimens containing the "original" plutonia were assembled, exposed, and evaluated. Six specimens were exposed at 2000°C for 1000 hr (W, W-25Re, and Re in contact with both $\text{PuO}_{1.8}$ and $\text{PuO}_{2.0}$), six at 1800°C for 2000 hr (W, W-25Re, Re, Mo-50Re, Mo, and WMoRe in contact with PuO_2), and six at 1800°C for 18,000 hr (identical to the 1800°C, 2000 hr specimens). The "original" plutonia containing 0.95% to 1.22% metallic impurities was production grade material used in the SNAP-27 program.

A second set of eighteen test specimens containing "purer" plutonia was assembled, exposed, and evaluated in a similar manner to the "original" plutonia set. A minor difference was the length of the long-term 1800°C exposure being 15,000 hr instead of 18,000 hr. The purer plutonia contained 0.23% metallic impurities. The nomenclature "original" and "purer" will be used throughout this report to denote the two purity levels used in the test program.

Results of the short-term testing were reported in an interim report (Reference 3) which is incorporated into this final report. The long-term test information in Quarterly Reports No. 14, 15, and 16 has also been incorporated. In the interim report the "purer" plutonia was labeled "pure", which was true of the product at that time but, because of rapid technological change, that purity level is now considerably inferior to the current product and is therefore labeled "purer" to distinguish it from the current plutonia.

Section 2 EXPERIMENTAL

2.1 MATERIALS

2.1.1 Fuel

Two batches of plutonia-238 powder (50- to 250- μ particle size) were received from Mound Laboratory for fabrication into 0.25-g PuO_2 pellets. Both batches had approximately the same isotopic content: 80% Pu-238, 16% Pu-239, 2.5% Pu-240, 1% Pu-241, and 0.2% Pu-242 according to Mound analysis. Non-actinide cationic impurities are listed in Table 2-1 also based on Mound analysis. The first or original plutonia received was typical of 1969 production-grade material which normally ranged from 1% to 2% total metallic impurities. The purer

Table 2-1
IMPURITY ANALYSES OF PLUTONIA
(Impurities Expressed as Weight-Percent Based on PuO_2)

Element	Original Plutonia		Purer Plutonia
	PuO_2 2.00 $\pm$ 0.04 Powder	PuO_2 1.79 $\pm$ 0.02 Pellets	PuO_2 2.00 $\pm$ 0.04 Powder and PuO_2 1.8 Pellets
Aluminum	0.09	0.09	<0.01
Boron	<0.02	0.03	ND*
Calcium	0.12	0.08	0.03
Chromium	0.13	0.08	0.01
Copper	0.08	<0.03	ND*
Iron	0.47	0.47	0.15
Magnesium	0.04	0.04	ND*
Manganese	<0.02	<0.01	0.01
Nickel	0.08	0.04	<0.01
Silicon	0.09	Trace	ND*
Sodium	Trace	Trace	ND*
Zinc	0.08	0.08	0.01
Total Metallic	1.22	0.95	0.23

*ND - Not Determined

plutonia with approximately 0.23% non-actinide impurities was received after the first tests were underway with the original plutonia. The purer plutonia was part of a special shipment Mound Laboratory received from Savannah River Laboratory and was to be used in the Mound compatibility program as well as to obtain a direct correlation of data under the two programs.

The low oxygen content plutonia ($\text{PuO}_{1.80 \pm 0.04}$) at both purity levels was received in pellet form from Mound Laboratory. The original plutonia had slightly less metallic impurities (0.95%, Table 2-1) than the material pressed into pellets at DWDL. Further discussion on fabrication of the $\text{PuO}_{1.8}$ pellets is presented in Section 2.3.

2.1.2 Refractory Alloys

At and above 1800°C, only refractory alloy systems based on molybdenum, tantalum, rhenium, and tungsten appeared to fulfill container material requirements. Of these, tantalum had shown the greatest reactivity with either lanthanide or actinide oxides; this is predicted by the thermodynamic properties of the tantalum-oxygen-plutonium system (Section 3.1) and had also been experimentally verified in a comprehensive test program conducted at DWDL on lanthanide oxides (Reference 2). For these reasons, tantalum-base alloys were not included in this high-temperature testing program. Of the remaining three elements, molybdenum has the lowest melting point, lowest high-temperature strength, and highest vapor pressure. However, molybdenum and two of its alloys, molybdenum-50 w/o rhenium (Mo-50Re) and tungsten-30% molybdenum-30% rhenium (W-30Mo-30Re, actually W-18 w/o Mo-35 w/o Re) had shown good potential as container materials for lanthanide oxides in DWDL testing, and were, therefore, included for testing up to approximately 1800°C.

Although molybdenum could conceivably be used in closed systems at somewhat higher temperatures (to 2000°C), this appears to be technologically unfeasible because of rapid permeation of oxygen through container walls. The addition of rhenium and tungsten to the molybdenum reduces oxygen permeation but does not reduce vaporization of the molybdenum sufficiently for extended use at those temperatures. For 2000°C testing, tungsten, rhenium,

and tungsten-25% rhenium (W-25Re) were the remaining alloys commercially advanced enough for use in testing or subsequent application in the near future.

All materials were procured from commercial vendors using standard rod manufacturing techniques starting from powders. An attempt had been made to procure the W-25Re as arc-cast stock, but fabrication difficulties resulted in excessive delays to the program causing cancellation of the order. Pre-test chemical analyses of five of the six alloys are listed in Table 2-2. No analysis was obtained on the W-25Re.

Chemical analyses indicated that all alloys were typical of current commercial product, including the somewhat high oxygen content of the molybdenum.

Metallographic examination and microhardness measurements indicated that the as-received material was generally in an as-worked or stress-relieved condition. Figure 2-1 shows photomicrographs of each alloy. Both the Re (C, Figure 2-1) and the W-30Mo-30Re (F, Figure 2-1) have some form of inclusions present in the structure. Those in the Re are in the grain boundaries; those in the W-30Mo-30Re appear as stringers in the body of the material. The remaining alloys appeared to be devoid of any second phase. Microhardness measurements listed in Figure 2-1 are indicative of typical refractory metals.

2.2 CONFIGURATION

The test specimen configuration is shown in Figure 2-2. The 0.18-in. diameter by approximately 0.06-in. tall cylindrical plutonia pellet was in contact with two test alloy discs. The lower disc, polished with 600-grit silicon carbide, was placed in intimate contact with the plutonia, and was the primary source of penetration data. The upper disc was used as a weight and as an additional test sample.

The primary container was very conservatively designed as a pressure vessel for the helium released by the alpha decay process.

Table 2-2
CHEMICAL ANALYSES FOR PRIMARY CAPSULE MATERIALS
(Impurities Expressed in Parts Per Million)

Impurity*	Tungsten	Molybdenum		Rhenium		Mo-50Re		W-30Mo-30Re	
	Ledoux	Vendor (Certified)	Ledoux	Vendor (Typical)	Ledoux	Vendor (Typical)	Ledoux	Vendor (Typical)	Ledoux
Aluminum	ND**	18	10	<1	ND	20	ND	<10	ND
Chromium	ND	15	10	<1	30	<5	ND	<5	ND
Iron	ND	20	30	57	100	5	40	30	10
Nickel	ND	8	ND	1	20	<1	ND	10	ND
Silicon	ND	26	70	<1	40	5	10	20	ND
Titanium	ND	<10	ND	ND	ND	ND	10	ND	ND
Hydrogen	0.9	2 ±2	1.2	NS***	0.3	NS	0.2	NS	0.2
Carbon	25	<10	10	NS	27	NS	14	NS	8
Nitrogen	19	4 ±4	24	NS	18	NS	17	NS	58
Oxygen	13	11 ±5	127	NS	24	NS	32	NS	22
Molybdenum	10	Bal	High	5	50	53%	High	18%	High
Rhenium	ND	NS	ND	Bal	High	Bal	High	35%	High
Tungsten	High	125	ND	ND	ND	<50	ND	Bal	High

*Other Elements Not Detected

**ND - Not Detected

***NS - Not Stated

69-137

(A) TUNGSTEN
DPH = 462

69-126

(B) TUNGSTEN-25% RHENIUM
DPH = 600

69-138

(C) RHENIUM
DPH = 723

69-139

(D) MOLYBDENUM-50 W/O RHENIUM
DPH = 434

69-136

(E) MOLYBDENUM

69-140

(F) TUNGSTEN-30 A/O MOLYBDENUM-
30 A/O RHENIUM
DPH = 488

Figure 2-1. Photomicrographs of Six Refractory Alloys as Etched in Sodium Hydroxide-Potassium Ferricyanide-Water Solution; Hardness Measured using 500-g Load (500X)

Figure 2-2. Triply Encapsulated Compatibility Specimen (SNS/DWDL Configuration 1)

Each test specimen is monometallic from the primary capsule inward to eliminate dissimilar metals effects within the system.

A secondary tungsten capsule was also designed as a pressure vessel to contain any helium released if the primary capsule were to fail. Tungsten-25% rhenium wire coils kept the capsules from contacting each other. A tertiary tantalum capsule was designed to surround the first two capsules as an additional protection. From prior experimental work at DWDL, promethium-147 was safely contained by a tertiary capsule when a primary capsule was intentionally tested to failure. The triple capsule configuration provides the required protection both to and from the external environment.

2.3 FABRICATION

2.3.1 Capsules

All capsules were machined by Northwest Industries, Inc., Albany, Oregon, from bar stock supplied by three material vendors. General Electric supplied

the tungsten and molybdenum, Cleveland Refractory Metals supplied the rhenium containing materials, and Wah Chang supplied the tantalum for the tertiary capsules.

Each capsule was dimensionally inspected and visually examined upon receipt at DWDL. Machining defects and dimensional errors in capsule bottom thickness were detected. No material defects such as cracks or internal porosity were observed. Radiography and dye penetrant surface examination was performed on the first group of capsules, but discontinued later because these inspection techniques did not appear to reveal any defects which were not observable by magnified visual examination. Each capsule was helium leak checked for gas-tightness. One group of tungsten secondary capsules proved to be unweldable, and were replaced by another group machined from "weldable" tungsten. Magnified visual examination of all capsules after acid cleaning and prior to assembly was most definitive in determining defects and abnormal metallurgical structure.

2.3.2 Fuel Pellets

All plutonia fuel pellets prepared at both DWDL and Mound Laboratory were cold pressed in steel dies at approximately 100,000 psi using 0.25 g of oxide. Original $\text{PuO}_{2.0}$ pellets were prepared at DWDL utilizing vacuum sintering at 1200°C for five minutes to provide interparticle bonding and reduce surface activity. Two pellets were subsequently air-oxidized at 1150°C for 30 minutes to determine if any reduction in oxygen content had occurred during vacuum sintering. Comparison of weights indicated that no reduction in oxygen had occurred. Pellets were stored in a desiccator for up to three days prior to encapsulation.

Purer $\text{PuO}_{2.0}$ pellets prepared at DWDL were sintered in an argon atmosphere after cold pressing. The furnace cycle consisted of a 20- to 30-minute heatup to 1800°C, a 30-minute hold before cooling to 800°C in 5 to 10 minutes, another 10 minute hold, followed by furnace cooling to room temperature. Argon flow was maintained at 0.5 cfh during heatup, hold, and cooling to 800°C at which time the furnace was evacuated to 30 to 50 microns prior to cooling. This sintering cycle resulted in densification of approximately 75% to 85% of theoretical density and produced a surface with minimum airborne contamination while maintaining an oxygen content in the 1.98 to 2.00 O/Pu range. Metallography of a

typical fuel pellet is shown in Figure 2-3. The plutonia is single phase, indicating an oxygen content of 1.98 O/Pu or higher. The metallic appearing precipitates remain unidentified but are probably iron, nickel, chromium, and cobalt oxides reduced in fabrication from the oxides to the metallic state.

Substoichiometric $\text{PuO}_{1.8}$ pellets were prepared at Mound Laboratory. Quarter-gram pellets were cold pressed in steel dies furnished by DWDL. Sintering required approximately four hours at 1400°C in a 6% H_2 -94% Ar atmosphere. Considerable difficulty was encountered in maintaining control over the process. Small differences in furnace system, residual impurities, and the cycle used resulted in high variability in composition. Extremely rigid process control was required to produce pellets to the required 1.80 ± 0.04 O/Pu ratio. Figure 2-4 shows the structure of a purer plutonia substoichiometric pellet. The two-phase structure is evident, as is the presence of an unknown metallic precipitate, again probably related to the reduction of metallic oxide impurities originally present in the fuel.

2.3.3 Encapsulation

Primary capsules were individually assembled in a gloved box. Simple fixturing was devised to facilitate assembly operations. A disc, plutonia pellet, and top disc were loaded into the capsule after which the lid was positioned in place. The capsule weld joint and external surfaces were checked for smearable contamination prior to bagging-out the capsule to a chemical hood. Each capsule was then placed in a vacuum desiccator and pumped down twice before smear testing the surface. Any smearable contamination was cause for disassembly and starting through the assembly process again. Thirty-six capsules were assembled with no smearable or direct count contamination. Three capsules did show minor amounts of contamination somewhere in the assembly process; these were disassembled, and the fuel pellets salvaged.

The six $\text{PuO}_{1.8}$ capsules were assembled using somewhat different techniques for each group of three capsules. Three original $\text{PuO}_{1.8}$ pellets were removed from the Mound Laboratory shipping containers in the standard air

Figure 2-3. Microstructure of $\text{PuO}_{2.0}$

Figure 2-4. Microstructure of $\text{PuO}_{1.8}$

atmosphere gloved box. Pellets were weighed, measured, placed in a transfer container, bagged out of the first gloved box and into the assembly gloved box, taken out of the transfer container and put directly into the capsule; then operations continued as for the original plutonia. Elapsed time from opening the pellet container to pumpdown in the electron beam welding chamber was 75, 45, and 50 minutes, respectively, for the three capsules assembled. Discussions with Mound Laboratory personnel indicated that reoxidation of the pellets was extremely slow at room temperature, and therefore, this short exposure should not affect stoichiometry. This has also been verified by metallographic results in Figures 2-3 and 2-4. However, as an added precaution, the next three purer $\text{PuO}_{1.8}$ pellets were removed from the Mound Laboratory shipping container and all assembly operations performed in a gloved box with a flowing purified helium atmosphere.

All capsules were electron-beam welded at a vacuum of 1×10^{-4} torr or less in the 6-kw Hamilton Standard welder with no visual weld defects at 60x and no external contamination. After encapsulation, all capsules were then placed into a helium pressure chamber for pressurization at 70 to 100 psig for a minimum of two hours prior to bubble checking in water for leaks, and insertion into a helium leak detector capable of detecting leaks as small as 1×10^{-9} cc/sec. All capsules were leak tight.

Figures 2-5 through 2-10 show welds made on dummy capsules using the same weld parameters established for the fueled capsules. Limited porosity, somewhat characteristic of electron-beam welded powder metallurgy W and W-25Re, may be seen at the base of the 150% penetration weld in Figures 2-5 and 2-6. Figure 2-7 shows minor porosity in the Re capsule lid. Figures 2-8, 2-9, and 2-10 show 80% to 95% weld penetration for all molybdenum-base alloys with no porosity in the Mo and Mo-50Re and limited porosity in the base of the W-30Mo-30Re capsule weld.

Fueled capsules were further assembled into tungsten secondary capsules and tantalum tertiary capsules. A set of capsule components is shown in Figure 2-11. The square and spiral-shaped 0.020-in. diameter W-25Re wire spacers are placed on the ends and around the inner capsules to minimize diffusion bonding during long exposure at high temperatures. All 36 fueled capsules were assembled successfully into the secondary and tertiary containers,

69-430

Figure 2-5. Tungsten Primary Capsule Weld (20x)

69-431

Figure 2-6. Tungsten-25% Rhenium Primary Capsule Weld (20x)

69-432

Figure 2-7. Rhenium Primary Capsule Weld (20x)

69-433

Figure 2-8. Molybdenum-50% Rhenium Primary Capsule Weld (20x)

Figure 2-9. Molybdenum Primary Capsule Weld (20x)

Figure 2-10. Tungsten-30% Molybdenum-30% Rhenium Primary Capsule Weld (20x)

Figure 2-11. Capsule Components Including $\text{PuO}_{1.8}$ -Re Primary Capsule, W-25Re Wire Spacers, Tungsten Secondary Capsule, and Tantalum Tertiary Capsule

electron beam welded shut, visually examined, and helium leak tested.

Figures 2-12 and 2-13 show welds made to establish parameters on tungsten containers. For tungsten, approximately a 200% weld penetration was used to drive porosity deep into the capsule wall.

A set of three control specimens (W, W-25Re, and Re) was fabricated for exposure at 2000°C and six (W, W-25Re, Re, Mo, Mo-50Re, and W-30Mo-30Re) for exposure at 1800°C. Control specimens consisted of both discs and the primary capsule without further encapsulation.

2.4 EXPOSURE

Test temperatures of 1800° and 2000°C were selected as typical of the operating temperatures of interest in isotope-powered thermionic energy conversion systems and to provide accelerated test data for lower temperature thermoelectric or Brayton systems. Radioisotope-fueled thermionic generator fuel-container interface temperatures typically vary up to 1700°C maximum,

69-436

Figure 2-12. Tungsten Secondary Capsule Weld (20X)

69-437

Figure 2-13. Tantalum Tertiary Capsule Weld (20X)

with centerline fuel temperatures up to approximately 1900°C. The maximum test temperature of 2000°C was selected to provide some test acceleration and the 1800°C test temperature was selected to provide a positive correlation in observable reaction rates. For example, if a rate of 100% is observed at 2000°C, then the rate at 1800°C would be 65% as fast if the process thermal activation energy is 20,000 cal/mole (typical of interstitial diffusion) or 18% as fast with an 80,000 cal/mole activation energy (which is on the high side for substitutional diffusion) as shown in Figure 2-14. Determination of the temperature dependence of the controlling mechanism is essential to extrapolate to lower temperature regimes such as 1100° to 1500°C where current isotope systems are operating.

Exposure duration was selected originally as 1000 and 5000 hours at 2000°C along with 2000 and 10,000 hours at 1800°C to provide both time and temperature correlations. Subsequent program modification resulted in deletion of the 2000°C, 5000 hour tests and extension of the 1800°C, 10,000 hour tests to 15,000 hr for purer plutonia and 18,000 hr for the original plutonia. The long test durations were established to provide data useful for long-lived missions and to complement shorter duration tests in the Mound Laboratory compatibility program.

Long-duration exposure at high temperatures requires that impurities are not picked up by test specimens from the environment. Diffusion-pumped systems have not met these criteria in extended testing in several laboratories (References 4 and 5). Ion pumping is capable of maintaining surface cleanliness during long-term testing.

Two Varian Model VF-400 ultra-high-vacuum, cold-wall resistance-heated tungsten-mesh furnaces were used for exposing the specimens at 1800° and 2000°C. Each furnace has a 500 l/sec sputter-ion pump plus 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 by a thermal-watt converter. The furnaces were calibrated by observing the melting point (1960°C) of pure rhodium. Temperatures were monitored by optical pyrometry.

Figure 2-14. Relative Diffusion Rates

A Veeco residual gas analyzer, installed on one of the Varian furnaces as shown in Figure 2-15 was used to monitor gas species in the furnace. Predominant impurities in the 10^{-9} torr vacuum at 2000°C were hydrogen and water, with smaller amounts of carbon, CH₃, methane, OH, H₃O, and mass 28 (nitrogen or carbon monoxide).

All specimens exposed at 2000°C were wrapped in 1-mil tungsten foil to minimize sublimation of the tantalum tertiary container. The original plutonia specimens exposed at 1800°C were also wrapped in tungsten as shown in Figure 2-16 where the specimens are in place on the tungsten furnace rack. It was later determined that the 1800°C specimens did not require a protective foil, and therefore, it was eliminated on all subsequent tests.

2.5 EVALUATION TECHNIQUES

The primary basis for evaluation was metallography including light microscopy, microhardness, and electron-beam microprobe analysis. Originally, almost all the effort was to be devoted to evaluating the refractory metal discs in contact with the fuel to determine reaction depths and mechanisms. However, changes in fuel composition and the presence of vapor transport phenomena increased the emphasis on examining the entire capsule contents, including the walls, welds, and fuel.

Four somewhat different techniques have been used to prepare specimens for metallographic examination. The first technique used was to cut off the end of the capsule, drop out the fuel and the two discs, and place the fuel in one metallographic mount and the two discs in a separate mount. The capsule walls were examined visually for possible reactions but were not mounted. A second technique used for capsules where the fuel and discs were stuck in the capsule was to longitudinally section the capsule and contents using a wire saw followed by mounting and polishing. This provided most of the capsule and contents for investigation, all except the top weld area. The third technique evolved from a desire to observe all elements of the capsule. An upper corner was ground from the capsule, potting compound was poured in the hole, then the capsule was ground longitudinally down to approximately the centerline so that all the contents could be observed. This was time consuming even using a coarse diamond wheel but provided the most complete information.

Figure 2-15. Environmental Exposure Furnaces

Figure 2-16. Tungsten Furnace Rack Ready to Load into Furnace

The fourth technique used on all long-term specimens was to longitudinally section the entire capsule and contents using either a slow speed diamond saw or a high speed carbide saw; the wire saw previously used was disposed of for safety reasons.

Tertiary tantalum capsules were cut open after exposure using a tubing cutter while holding the capsule in an open-faced hood. Secondary tungsten capsules were removed by a gentle hammer blow. No contamination was ever detected in the deencapsulation operation. Primary capsule ends of short-term specimens were cut off by either a wire saw for the hard materials or a small jewelers' diamond-impregnated hack saw for the softer materials.

Early in the program, fuel pellets were mounted in copper-filled epoxy (Devcon) and the discs and capsules were mounted in plain epoxy. Later in the program, it was determined that Quickmount (Fulton Metallurgical Products Corp.) adequately resisted the heat and was used for the remaining short-term specimens. However, safety considerations in using flammable materials in gloved boxes resulted in a decision to stop use of Quickmount. Therefore, all long-term specimens were mounted in epoxy using individual packets of material.

Coarse grinding, on short-term specimens was performed with a metal-bonded diamond wheel (100 mesh), followed by grinding on silicon carbide papers through 600 grit. Coarse and fine grinding of long-term specimens was performed on a Stellapol slow-speed grinder using multiple sample holders using silicon carbide papers through 600 grit. All polishing was performed in two stages: 1-micron alumina followed by 1-micron diamond both done on Syntron polishing machines using Nylon cloth. Lubrication for grinding and polishing of short-term specimens was a 50-50 mixture of Buehler lapping oil and kerosene. Water was used as the only lubricant for grinding and polishing long-term specimens to prevent formation of radiation produced organic artifacts. Where plutonia was the only material in a mount to be polished, the diamond polishing was omitted because the slight polishing relief which is obtained from alumina is desirable in resolving two-phase structures.

All interfaces were initially examined in an unetched condition using a Leitz Ortholux microscope. Refractory alloys were also etched in a sodium hydroxide-potassium ferricyanide-water solution for detailed examination of

the reactions and the general structure. Plutonia was examined in the as-polished condition. Photographic techniques included use of both a Polaroid attachment on the microscope and a 35-mm film attachment. Microhardness was measured using a Leitz Miniload microhardness tester normally using a 100-g load and a 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 and Dr. Y. B. Katayama, Battelle-Northwest. Dr. Clark analyzed all short-term specimens and two of the long-term specimens before a radiological contamination problem prevented further analyses. Dr. Katayama conducted the remaining long-term specimen analyses. Both used MAC400 machines located at the Hanford facilities. Area scans up to 1000x, continuous traverses, and step scans were made in specific areas on fifteen specimens selected to provide a maximum amount of information as to reaction mechanism and depth.

Chemical analyses were performed by Ledoux and Company, Teaneck, New Jersey, on both pre-test and post-test control specimens. Analytical limits are indicated in the post-test control specimen table.

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Section 3

DISCUSSION AND RESULTS

Results have disclosed that there are complex relationships among refractory alloy composition, plutonia purity, plutonia oxygen content, test configuration, and exposure conditions. These variables affect measured compatibility, some directly, others more indirectly. Based on test conditions used, higher purity fuel and lower oxygen content fuel resulted in reduced reactions with refractory metals. Some of the variation in reactions is explainable using thermodynamics. Others appear to have been a function of container permeability to oxygen. Both of these factors are discussed prior to discussing the results.

3.1 THERMODYNAMICS AND OXYGEN PERMEATION

Variations in oxygen content of plutonia affect vapor pressure and species at high temperature, partial molar free energy at all temperatures, and structure more particularly at low temperatures. Figure 3-1 shows the vapor pressure at 1800°C of various species over plutonia as a function of oxygen content (Reference 6). It is readily apparent that a very high oxygen partial pressure, both diatomic and monotomic, is present at the stoichiometric $\text{PuO}_{2.00}$ composition. Minimum pressure for the system occurs at approximately 1.85 O/Pu ratio. In an open, evacuated system, vaporization would cause the composition of the solid phase to move toward the congruent vaporization composition (1.85 O/Pu). In a closed metallic system, two competing factors cause oxygen loss from the fuel. The first is oxygen species transport to the container walls; the second is permeation through the container walls to the external vacuum.

Oxygen permeation is a function of both oxygen partial pressure and the intrinsic permeability of the container material. Tantalum- and molybdenum-base alloys have higher oxygen permeation rates than tungsten or rhenium alloys (Reference 7). Total oxygen loss by permeation is also dependent on temperature

Figure 3-1. Vapor Pressure of Various Species over PuO_x at 1800°C

and time, in addition to partial oxygen pressure over the plutonia, and permeation rate through the container material. Calculations made using the Ackerman plutonia vaporization data (Reference 6) as correlated at Los Alamos Scientific Laboratory (Reference 8) coupled with permeability data from General Electric Company (References 7 and 9) for molybdenum and tungsten have been used to calculate composition changes in the test specimen fuel. Calculated final O/Pu ratios for $\text{PuO}_{2.0}$ starting material were above 1.8 for tungsten containers (believed to be equivalent to W-25Re and W-30Mo-30Re) at 1800° and 2000°C and somewhat below 1.7 for molybdenum containers. The plutonia in the Mo-50Re container would be expected to result in an intermediate O/Pu ratio. The plutonia in the rhenium container would probably have a higher O/Pu ratio than the tungsten. Recent data by Riley (Reference 10) on oxygen pressures over plutonia were also used to estimate final O/Pu ratios which resulted in lower values than those obtained using the LASL correlation. The final values using the Riley data are somewhat uncertain because no oxygen partial pressures were obtained below 1.80/Pu at 1800°C. However, it is believed that the LASL correlation presents a reasonable expected upper limit for final O/Pu ratio and the Riley data a potential lower limit for final O/Pu ratio.

Two additional, undefinable factors intrude into the accuracy of the permeation predictions. The secondary tungsten container, in the case of the molybdenum inner capsule, represents an additional barrier to oxygen transport through the test system. Because the oxygen partial pressure in the interspace between capsules is undefinable other than being less than that in the inner capsule, it is unrealistic to attempt to calculate permeation inhibition except in general parametric terms. For example, if the interspace oxygen pressure is two decades lower than that over the plutonia then the "double container" values in Table 3-1 are obtained. It is obvious that some permeation inhibition will occur, but the amount is unknown and probably quite variable. A second factor in permeation uncertainty is the presence of vapor transported plutonia on the capsule walls. This presence could result in changes in the situational thermodynamics to a chemical activity/diffusion condition somewhat at variance with the techniques used to calculate permeation. Because of the uncertainty in the high-temperature thermodynamics, this situation could result in quite different permeation rates.

Table 3-1
CALCULATED PLUTONIA OXYGEN LOSS CAUSED BY PERMEATION
(Final O/Pu Ratios)

Container Material	Starting Exposure Conditions			LASL Correlation		Riley Data	
	O/Pu Ratio	Temp (°C)	Time (hr)	Single* Container	Double** Container	Single Container	Double Container
Tungsten	2.0	2000	1000	1.81	1.86	1.67	1.73
Tungsten	1.8	2000	1000	1.78	1.80	1.67	1.72
Tungsten	2.0	1800	15000	1.84	1.89	1.67	1.70
Tungsten	2.0	1800	18000	1.83	1.89	1.67	1.70
Molybdenum	2.0	1800	15000	1.69	1.79	1.66	1.67
Molybdenum	2.0	1800	18000	1.68	1.78	1.66	1.67

* Single container assumes no permeation inhibition by outer containment.

** Double container assumes a two decade difference in oxygen pressure between the plutonia and the interspace between the primary container and the tungsten secondary container.

Reactions between the plutonia and the container materials can occur at elevated temperatures depending on thermodynamics of the various components of the system. Figure 3-2 shows the partial molar free energy of oxygen in PuO_{2-x} , also called oxygen potential, for various O/Pu ratios as a function of temperature from References 6 and 8. Also plotted in Figure 3-2 is free energy of formation of various metal oxides from References 8, 11, and 12. Thermodynamic equilibrium for oxygen is attained when the free energy of formation of the refractory metal oxide is equal to the partial molar free energy of oxygen in the plutonia. Of the metal oxide systems shown, only tantalum would react extensively with O/Pu ratios less than about 1.92. The next most reactive oxides are solid WO_2 and MoO_2 which are reported as having the same free energies. The least reactive combination shown is iridium and its oxides. Although tantalum and iridium were not included in this particular effort, both materials are in at least one AEC/SNS space electrical generator program.

An additional feature of Figure 3-2 is that the oxygen partial pressures over the oxides, including plutonia, can be determined by using a straight edge from

Figure 3-2. Metal Oxides and PuO_{2-x} Free Energy

the intercept at zero free energy and absolute zero temperature (-273°C) through the temperature-oxide free energy intercept, to the P_{O_2} scale to the right and below the graph. For example, the oxygen partial pressure over $\text{PuO}_{1.9}$ at 1800°C is 10^{-8} atm.

Extension of the thermodynamics shown in Figure 3-3 provides a capability to predict both equilibrium conditions and the effects of off-equilibrium conditions for plutonia reactions with hydrogen, carbon monoxide, and carbon dioxide. For example, the hydrogen-water reaction is in equilibrium with $\text{PuO}_{1.93}$ at 1800°C . However, in a flowing hydrogen system containing 1000 ppm water, the plutonia would be reducible to $\text{PuO}_{1.77}$. Similarly, varying CO to CO_2 ratios can result in major changes in oxygen content in the plutonia either to produce stoichiometric PuO_2 or highly substoichiometric compositions as confirmed by recent Los Alamos Scientific Laboratory experiments. The presence of carbon reacting to form carbon monoxide (the 2CO line) results in the formation of very substoichiometric plutonia in an open system, but in a closed system the reductive driving force would be rapidly decreased to insignificance.

Thermodynamic properties of the refractory metal oxides and plutonia are subject to varying levels of error and no measurements have been made on several species known to exist. Accuracies are typically in the ± 1 kcal/mole region for the gaseous reactions but approach ± 3 to 10 kcal/mole for refractory metal oxides and perhaps as much as ± 30 kcal/mole for oxygen activity in the plutonia. Regardless of the possible errors, the limited data available do permit reasonable interpretation of observed phenomena.

The structure of plutonia remains single phase from $\text{PuO}_{1.61}$ to $\text{PuO}_{2.00}$ at temperatures over 700°C according to the most current phase diagram (Figure 3-4) from Reference 10, 13, and 14. The major difference between $\text{PuO}_{1.8}$ and $\text{PuO}_{2.0}$ at operating temperatures is the number of oxygen defects in the fluorite lattice. However, upon cooling to room temperature, the $\text{PuO}_{1.8}$ becomes a two-phase material consisting of pro-monotectoid PuO_y (which is approximately $\text{PuO}_{1.98}$) and the monotectoid mixture of $\text{PuO}_{1.52}$ and $\text{PuO}_{1.98}$. The appearance of the structure and the exact oxygen content of the PuO_{2-y} are dependent upon cooling rate through the critical temperature range of 700° to 300°C . Slow cooling produces a structure close to equilibrium, but rapid quenching inhibits partitioning of the promonotectoid reaction thereby producing a structure somewhat more difficult to evaluate on a quantitative basis.

Figure 3-3. Gaseous Oxides and PuO_{2-x} Free Energy

Figure 3-4. Partial Pu-O Phase Diagram

3.2 GENERAL OBSERVATIONS

Observations on all of the 36 capsules included in this effort differ somewhat from those listed in the interim report which contained results only on the short-term specimens. Long-term specimens showed no difference in appearance attributable to initial purity level. Short-term specimens had exhibited greater attack from the original plutonia compared to the purer plutonia. Metal transport has been observed in all six alloys instead of only two for the short-term tests. Tungsten and rhenium continued to show the largest amount of metal transport within the capsules.

There were few differences in behavior in the 1800°C specimens attributable to exposure duration. All observable forms of reaction occurred in both the short- and long-term specimens. Oxygen loss in the plutonia, however, was considerably more in the long-term specimens. This loss was exaggerated by the small plutonia volume in a relatively large capsule. In short-term testing, PuO_{1.8} was less reactive toward refractory metals than PuO₂, thereby contributing to the minimal effect of exposure time on refractory alloy attack.

The most compatible combination tested at 2000°C was rhenium and $\text{PuO}_{1.8}$. Behavior of the W-25Re- $\text{PuO}_{1.8}$ combination was only slightly inferior. Tungsten was inadequate at 2000°C.

Rhenium was the most compatible container for plutonia at 1800°C with metal transport being the only problem encountered. Molybdenum and Mo-50Re were also adequate containers with minimal damage and relatively less metal transport than in the rhenium container. Only tungsten is to be avoided as a container material, having shown severe attack in one or more cases.

Capsule integrity at test temperature was maintained in all cases. No radioactive contamination was ever detected on an external surface after exposure. The comparative appearance of capsule external surfaces after exposure at 1800°C for 2000 hours is shown in Figure 3-5. The W-25Re wire wrap often remained in place, being diffusion bonded to the capsule. The pure metal capsule surfaces were generally smoother after exposure than the alloy capsule surfaces. Pure molybdenum had the shiniest surface and the W-30Mo-30Re ternary alloy the roughest.

Appearance of sectioned capsules varied from complete retention of the plutonia pellet in its original location (Figure 3-6) to transport of the plutonia to the walls leaving no pellet in the original location (Figure 3-7). Most of the short-term fuel pellets remained intact. Only the one pellet shown in Figure 3-6 remained intact of the 12 long-term specimens.

3.2.1 Metallographic Examination

Table 3-2 lists metallographic results for each test specimen examined. Estimated penetration into the metal is given for four different attack mechanisms as determined by metallography. These are general solution, intergranular penetration, oxide precipitation, and intermetallic precipitation. Penetration values must be considered as approximate because the location of the original metal interface is unknown and probably a function of time, temperature, plutonia presence, and type. All penetration depths are referenced to the final surface. General solution is the most subject to measurement error because of changes in the interface. Surface roughness is the manifestation of solution attack that is typically measured. Intergranular penetration (IGP)

Figure 3-5. Purer Plutonia-Refractory Metal Capsules After Exposure at 1800°C for 2000 Hours
(Left to right: W-30Mo-30Re, Mo, W, Mo-50Re, Re, and W-25Re)

Figure 3-6. Macrograph of Original $\text{PuO}_2/\text{W-30Mo-30Re}$, 1800°C , 18,000 hr

Figure 3-7. Macrograph of Original PuO_2/Mo , 1800°C , 18,000 hr

Table 3-2
METALLOGRAPHIC RESULTS

Alloy	Starting O/Pu Ratio	Exposure		Penetration into Metal (mils)								Metal				Oxide Appearance			
		Temp (°C)	Time (hr)	General		IGP ^a		Oxide/ Voids		Intermetallic		Transport		Monotectoid		Est O/Pu		Metallic	
				Solution		O	P	O	P	O	P	O	P	O	P	Ratio	Precipitation		
				O ^b	P ^b												O	P	O
W	2.0	2000	1000	e	e	10 ^e	e	0	0	0	0	?	?	70	65	1.72	1.74	Few 1 ^d	Few 0.1 ^d
	1.8	2000	1000	1	0	<1 ^h	3 ^e	1	0	0	0	No	No	60	g	1.76	g	Few 0.6 ^d	g
	2.0	1800	2000	2	1	10 ^e	0	0	2	0	0	?	20	<10	10	1.95	1.94	No	Few 1.5 ^d
	2.0	1800	18/15K ^c	10	?	0	0	10	?	0	0	20	13	90	90	1.64	1.64	Few 0.2	Few 0.2
W-25Re	2.0	2000	1000	1	1	4	0	9	3 ^f	0	0	?	?	g	55-60	g	~1.77	g	Few 2.0
	1.8	2000	1000	0.4	0.6	0	0	1	0	0	0	No	No	50-60	75	~1.78	1.70	No	No
	2.0	1800	2000	0.5	1	0	0	7	3.5 ^f	0	0	No	No	5	10	1.96	1.94	No	No
	2.0	1800	18/15K ^c	5	2.5	0	1.2	12	4	0	0	Yes	No	g	80	g	1.68		Many 0.2
Re	2.0	2000	1000	2	2	2	0	0	0	0	0	20	15	15	10	1.93	1.94	No	No
	1.8	2000	1000	1	0.2	0	0	0	0	0	0	No	No	g	75	g	1.70	No	No
	2.0	1800	2000	5	0.5	3	0	0	0	0	0	10	No	10	5	1.94	1.96	No	Few 0.5
	2.0	1800	18/15K ^c	0	?	0	0	0	0	0	0	3.5	10	g	g	g	g	g	g
Mo-50Re	2.0	1800	2000	0.4	0.2	8	0	1	2.5	0	0	No	No	50	65	1.79	1.74	Few 4	Few 0.7
	2.0	1800	18/15K ^c	1	?	0	0	1.5	7	0	0	Yes	Yes	85	85	1.66	1.66	No	No
Mo	2.0	1800	2000	0	1.0	6	2	4	1.5	0	0	No	No	70	75	1.72	1.70	Few 6	Few 1.4
	2.0	1800	18/15K ^c	0	3	0	0	1	2	0	0	5	?	85	90	1.66	1.64	Many 0.2	Few 0.1
WMoRe	2.0	1800	2000	1.5	0.4	2	1	4	0	2	0	No	No	40	35	1.83	1.85	Many 1.0	No
	2.0	1800	18/15K ^c	2	2	0	1.5	6	10	0.8	2	No	2	80	85	1.68	1.66	Many 0.2	Many 0.3

- a. IGP - Intergranular Penetration
b. O - Original Plutonia, P - Purer plutonia
c. 18/15K - 18,000 hr for original plutonia, 15,000 hr for purer plutonia
d. Maximum size in mils
e. Very severe attack of capsule walls
f. Deeper precipitation away from plutonia
g. Fuel lost, transported, or not possible to evaluate
h. Plus one crack through small disc

is a serious attack mechanism along grain boundaries. Oxide precipitation as defined in Table 3-2 may be associated with intergranular penetration or may be independent of the grain boundaries. Intermetallic precipitation was present in only W-Mo-Re and was accompanied by other forms of attack.

It has been impossible to determine either a time or a temperature dependency of the reactions as listed in Table 3-2. For example, in comparing long-term to short-term results at 1800°C for all four types of penetration there are 48 possible short y long pairings; of these, 17 showed no penetration, 4 could not be compared because of questionable penetration measurements, 7 went from a measurable depth (short-term) to zero (long-term), 2 decreased in depth, 14 increased in depth, and 4 went from zero to a measurable depth. Only by eliminating all of the outliers can a reasonable number be obtained which is in the approximate range of 1.6 to 1.8 increase in penetration depths with increased time. Statistically, there is no way to place any limits on the probable range of this estimate. Similarly, comparison of PuO₂ data for 2000°C, 1000 hour with 1800°C, 2000 hr results in the largest probability that the two exposure conditions were comparable with a very small probability that the 1800°C, 2000 hr exposure might have produced somewhat more attack.

Metal transport was observed in all container materials with metal moving from relatively hot areas to cooler capsule walls. In some cases, the amount of wall build-up could be estimated relatively well; in others, it was impossible to determine amounts. Examination of long-term capsules indicated more transport occurred than in the short-term capsules. No transport was observed in the PuO_{1.8} specimens.

Oxide appearance is divided into two observations: oxygen content and metallic precipitates. Oxygen content was estimated by area analysis of the promonotectoid constituent. An assumption was made that cooling rate from approximately 1000° to 300°C was slow enough to result in an equilibrium structure. This may or may not be valid, but all specimens were cooled in approximately the same manner so that specimen to specimen comparisons should be valid. Application of the phase rule to Figure 3-4 and the monotectoid areas in the specimens resulted in the O/Pu ratio estimates listed in Table 3-2. It is

apparent that the 1800°C, 2000 hr plutonia oxygen content varied according to container permeability ranging from ~1.95 O/Pu ratio for rhenium containers to ~1.71 O/Pu ratio for molybdenum. The 1800°C, long-term plutonia oxygen content appeared to be independent of container material remaining in the range of 1.64 to 1.68 O/Pu ratio for all materials. The PuO₂ 2000°C, 1000 hr fuel oxygen content varied according to permeability. The comparable PuO_{1.8} specimens showed no relationship with permeability. Analysis of post-test oxygen contents tends to indicate that the reported oxygen pressures above plutonia reported by Riley (Reference 10) may be somewhat more accurate than the thermodynamic estimates by Ackermann (Reference 6).

Metallic precipitates were observed in several plutonia specimens and are listed along with the maximum size observable in the polished plane. These precipitates were determined to be either intermetallic compounds of tungsten and plutonium or molybdenum. No iron, chromium, nickel or cobalt were found in the precipitates.

3.2.2 Microhardness

Microhardness measurements are listed in Table 3-3. A Leitz Miniload tester was used with a Vickers pyramid diamond indenter. Values are reported as DPH (or Vhn) with kg/mm² as the units. The standard load for most of the measurements was 100 g; 15 g was used for most of the oxide measurements to prevent cracking. Concurrently exposed non-fueled control specimen hardness values are given for comparison. Comparative pretest plutonia hardnesses measured using a 15-g load are 919 for PuO_{2.0} and 1113 for purer PuO_{1.8}. A reported standard value is 740 kg/mm². The reason for the difference is probably related to technique. Post-test plutonia hardness values were too badly scattered for any definitive statement to be made.

Primary hardness measurements were made on the small discs for the short-term specimens and on the walls of the long-term specimens. Prior to testing it was believed that the disc would receive the highest level of attack. By the time metallography and microhardness were complete on the short-term specimens, it was found that more attack occurred in the walls and therefore, measurements were concentrated there for the long-term specimens. Several measurements indicated that transported metal was essentially the same purity as the bulk alloy.

Table 3-3
MICROHARDNESS VALUES

(Diamond Pyramid Hardness, 100-g Load Values in kg/mm²)

Alloy	Plutonia	Starting O/Pu Ratio	Exposure Temp (°C)	Time (hr)	Metal				
					Capsule Component	Near Fuel	Center	Outside	Oxide
W	Original Purer	2.0	2000	1000	Disc	464	514	514	1069 ^a
		2.0	2000	1000	Disc	514		464	
	Original Purer	1.8	2000	1000	Wall	464		488	
		1.8	2000	1000	Disc	464	464	401	
	Original Purer	1.8	2000	1000	Disc	420		420	
		2.0	1800	2000	Disc	450	450	514	
	Original Purer	2.0	1800	2000	Disc	401		420	
					Wall	373		420	
	Original Purer	2.0	1800	18,000	b	387			
					Lge Disc	433	405	454	
	Original Purer	2.0	1800	18,000	Wall	380	387	389	
		2.0	1800	15,000	Wall	420	493	514	
	Original Control	None	1800	18,000	Sm Disc	409	403		
					Lge Disc	397	397		
W-25Re	Original Purer	2.0	2000	1000	Wall	370	382	409	1113 ^a 522 ^a
		2.0	2000	1000	Disc	464	464	464	
	Original Purer	1.8	2000	1000	Disc	542		542	
		1.8	2000	1000	Disc	514	514	464	
	Original Purer	1.8	2000	1000	Disc	441		464	
		2.0	1800	2000	Disc	542	542	542	
	Original Purer	2.0	1800	2000	c				
		2.0	1800	2000	Disc	488		464	
	Original Purer	2.0	1800	18,000	Sm Disc	536	493	511	
					Wall	525	530	548	
	Original Purer	2.0	1800	15,000	Sm Disc		542		
					Wall	554	606	566	
	Original Control	None	1800	18,000	Sm Disc	514	519		
					Lge Disc	493	503		
Re	Original Purer	2.0	2000	1000	Wall	500	508	503	1720 1113 ^a 1208 ^a
		2.0	2000	1000	Disc	642	665	540 ^d , 503 ^e	
	Original Purer	1.8	2000	1000	b	274			
		1.8	2000	1000	Disc	464		401	
	Original Purer	1.8	2000	1000	b	413			
		1.8	2000	1000	Disc-c	464	383	381	
	Original Control	None	2000	1000	Disc-d	606	681	681	
		None	2000	1000	Disc	464 ^d		383	
	Original Purer	2.0	1800	2000	Disc	317 ^d , 572 ^e			
		2.0	1800	2000	Disc	1018	946	813	
	Original Purer	2.0	1800	2000	b	433			
		2.0	1800	2000	Disc	383		383	
	Original Purer	2.0	1800	18,000	Wall	357	348	413	
		2.0	1800	15,000	Sm Disc	566	585	473	
Mo-50Re	Original Purer	2.0	1800	2000	Wall	530	681	554	1374 ^a
		2.0	1800	18,000	Sm Disc	330	281		
	Original Purer	2.0	1800	2000	Lge Disc-c	268	264		
		2.0	1800	2000	Lge Disc-d	464	394		
	Original Purer	2.0	1800	18,000	Wall-c	309	322	357	
		2.0	1800	18,000	Wall-d	425	550	554	
	Original Purer	2.0	1800	2000	Disc	401	383	351	
		2.0	1800	2000	Disc	401		401	
	Original Purer	2.0	1800	18,000	Sm Disc	363	370	359	
		2.0	1800	15,000	Wall	363	360	405	
	Original Control	2.0	1800	15,000	Lge Disc	356	380	366	
		2.0	1800	15,000	Wall	330	354	394	
	Original Control	None	1800	18,000	Sm Disc	351	329		
		None	1800	18,000	Lge Disc	373	372		
Mo	Original Purer	2.0	1800	2000	Wall	342	345	352	1530 ^a
		2.0	1800	2000	Disc	181	181	170	
	Original Purer	2.0	1800	2000	Disc	237		221	
		2.0	1800	18,000	Lge Disc	182	166	165	
	Original Purer	2.0	1800	18,000	Wall	182	185	186	
		2.0	1800	15,000	Sm Disc	176	177	182	
	Original Control	2.0	1800	15,000	Wall	174	177	206	
		2.0	1800	15,000	Sm Disc	193	183		
	Original Control	None	1800	18,000	Lge Disc	182	181		
		None	1800	18,000	Wall	187	182	189	
	Original Purer	2.0	1800	2000	Disc	508	566	642	1530 ^a
		2.0	1800	2000	Disc	548		493	
	Original Purer	2.0	1800	18,000	Sm Disc	450	443	464	
		2.0	1800	18,000	Wall	473	483	501	
	Original Purer	2.0	1800	15,000	Sm Disc	488	464	483	
		2.0	1800	15,000	Wall	464	459	464	
	Original Control	2.0	1800	15,000	Sm Disc	459	417		
		2.0	1800	18,000	Lge Disc	459	473		
	Original Control	None	1800	18,000	Wall	483	454	493	
		None	1800	18,000	Wall	483	454	493	

Note a 15-g load
b Vapor transported metal
c Metal precipitate in oxide
d Dark appearing grains
e Light appearing grains

Refractory alloy hardness values appear to be influenced by five variables affected by the test environment. Annealing by exposure at the temperatures used caused softening from the as-received material condition. Higher temperature appeared to permit dissolution of more solute elements in the alloy, resulting in a higher hardness for specimens heated at 2000° than at 1800°C. Higher oxygen content in the plutonia also appeared to cause higher hardness because of the increased availability of oxygen for transfer and diffusion. The presence of impurities in the fuel which could be transferred to the refractory metal would be expected to result in higher hardness for specimens in contact with the original plutonia than the pure plutonia. This was true the majority of the time for short-term tests but not in the long-term tests. Exposure at 1800°C resulted in relatively softer materials after the longer time. In each of these generalizations, there was at least one exception, apparently independent of the other variables. Therefore, statements based on hardness variations must be considered as somewhat tenuous.

3.2.3 Electron-Beam Microprobe Analyses

The electron-beam microprobe analyses tend to confirm metallographic results. Analysis was completed on 15 selected specimens. Fourteen test combinations were examined. One test combination had plutonia and discs in separate mounts. An additional specimen remained too contaminated to examine even after extensive cleaning. Two further specimens had been selected for examination but were deleted to minimize costs. Results are listed in Table 3-4 for correlation with the metallographic results listed in Table 3-2. Bulk diffusion of plutonium into the refractory alloys was not extensive. The interdiffusion of metal and PuO_x was measured as less than 1.5 micron for W-25Re and less than 1 micron for Re (2000°C, 1000 hr). Diffusion of plutonium into Mo was about 1 micron (1800°C, 2000 hr). Plutonia precipitates were found several mils deep in W-25Re and short-term Mo-50Re capsule walls. Plutonia was also found in vapor transported rhenium but not in the base material.

Table 3-4

ELECTRON BEAM MICROPROBE RESULTS OF SELECTED PLUTONIA SPECIMENS

Alloy	Plutonia	O/Pu Ratio	Exposure		Observations in Metal			
			Temp (°C)	Time (hr)	Cr, Fe, Ni, Co in Precipitate or Solution	Pu in Precipitate or Solution	Other	Observations in Plutonia
W	Purer	1.8	2000	1000	No	No (only in crack in capsule)		*
W-25Re	Purer	2.0	2000	1000	No	Inclusions (no W or Re in inclusions)		*
W-25Re	Purer	1.8	2000	1000	No	No	<1.5- μ interdiffusion of metal and PuO _x	No inclusion; no Fe, Cr, or Ni
W-25Re	Purer	2.0	1800	2000	No	Precipitates		*
W-25Re	Purer	2.0	1800	15000	No	Put Re in precipitates		Pu plus trace of W in precipitates
Re	Purer	1.8	2000	1000	Possibly 0.1% Fe and Cr in solution	Small precipitates near interface	<1- μ interdiffusion of metal and PuO _x	No inclusions
Re	Original	2.0	1800	2000	Fe and Cr in inclusions in vapor deposited Re	Inclusions in vapor deposited Re		Not looked at
Re	Original	2.0	1800	18000	No	PuO ₂ in vapor deposited Re		*
Re	Purer	2.0	1800	15000	No	PuO ₂ in vapor deposited Re		*
Mo-50Re	Purer	2.0	1800	2000	No	Precipitates		Mo inclusions
Mo-50Re	Purer	2.0	1800	15000	No	No	Precipitates were Re + Mo	Not looked at
Mo	Purer	2.0	1800	2000	No	No	<1- μ diffusion of Pu into metal	Inclusions of Mo with 5% Pt; 2%-3% Mo in solution; no Fe, Cr, Ni, or Co in inclusions or matrix
Mo	Original	2.0	1800	2000	Not detected	Pu in interface between two discs	<1- μ diffusion of Pu into metal	*
WMoRe	Purer	2.0	1800	2000	No	No		Not looked at

*Oxide area not available in specimen for examination

Attempts were made to determine the location of the Fe, Ni, Cr, and Co originally present in the fuel, but this was generally unsuccessful because of the relatively high refractory-metal-to-plutonia ratios. Metallic appearing precipitates in the plutonia contained both tungsten and plutonium in the W-25Re specimen and molybdenum and platinum in the molybdenum specimen. Source of platinum is undetermined. Results were based on the use of back-scattered electron photomicrographs, area scans for individual elements, rapid traverses across interfaces, and step scans across selected interfaces.

3.2.4 Chemistry

Semiquantitative emission spectrochemical analyses were completed by Ledoux and Company, Teaneck, New Jersey, on control capsule materials which had been exposed 18,000 hours at 1800°C at the same time as the fueled specimens. These chemical analyses (Table 3-5) indicate a reduction in the amount of volatile species such as chromium, iron, nickel, silicon, and possibly aluminum and titanium to a nondetectable level. This is in agreement with Bourgette's work on superalloys (Reference 15). There was an increase in molybdenum content in the three nonmolybdenum-containing alloys because of the high (4×10^{-7} torr) vapor pressure of molybdenum at 1800°C. Fueled specimens would not have been affected because two guard capsules surrounded each specimen, thereby protecting the inner container from molybdenum transport. The control specimens were exposed without external guard capsules to minimize cost and to provide maximum interaction with the external vacuum.

Table 3-5

ORIGINAL PLUTONIA CONTROL CAPSULE CHEMICAL ANALYSES
(Impurities Expressed in Parts Per Million)

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

NOTE:

High - 10% to 100%

ND - Not detected (no detection limit stated)

Detection limits for other elements analyzed for but not detected:

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

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

<50 ppm - Sb

<100 ppm - Bi

<300 ppm - As, Zn

<500 ppm - Hf, Ta

3.3 INDIVIDUAL ALLOY RESULTS

In this section, results are presented alloy by alloy using the purer plutonia 1800° - 2000 hr test as the reference test condition and comparing all other results to that test condition. Reactions in the metal are described followed by descriptions of oxide appearances.

3.3.1 Tungsten

Tungsten appeared to be the least reliable container material for plutonia. Severe intergranular attack was observed on the tungsten capsules, particularly the capsule walls. This degradation is believed to be caused by oxygen from the plutonia in the grain boundaries. Both tungsten and plutonia vapor transported from hot to cold surfaces which would tend toward unstable equilibrium during heat source operations.

Figure 3-8 shows the appearance of the tungsten/purer PuO_2 specimen exposed at 1800°C for 2000 hours. Vapor deposited tungsten located between the large disc and the capsule wall shown in A, Figure 3-8 had a microhardness (387 DPH) equivalent to the control specimen. Voids were present in grain boundaries of the vapor-deposited material, but the structure appeared remarkably clean otherwise. This was the only short-term tungsten specimen to display tungsten vapor transport, however, both long-term specimens exhibited vapor transport. The surface of the tungsten discs was roughened by vaporization losses, but oxide precipitates were present below the surface as shown in C, Figure 3-8. The single white spot is an unidentified metallic precipitate, probably containing tungsten and plutonium based on comparable precipitates in W-25Re containers.

Precipitates similar to these were also visible at the same magnification for the original plutonia exposed at 1800°C for 2000 hours. However, significant intergranular attack was also visible as shown in Figure 3-9. The plutonia structure was almost identical in the two specimens.

Tungsten in the original plutonia, 1800°C, 18,000 hr capsule was grossly damaged as shown in Figure 3-10. The small disc originally in contact with the plutonia pellet had a very irregular surface and large internal voids. Mass transport occurred to the colder surfaces such as the capsule corners. The attack to the walls was less than that observed for the short-term tests. The plutonia had

70-857

CAPSULE WALL | DEPOSITED TUNGSTEN | DISC (50X)

A. CAPSULE WALL - DEPOSITED W - W DISC INTERFACE
(SPHEROIDS AT TOP ARE MOUNTING MATERIAL)

70-858

(100X)

B. TUNGSTEN SURFACE
(SPHEROIDS AT TOP ARE MOUNTING MATERIAL)

70-859

C. TUNGSTEN SURFACE (500X)

70-1262

D. PLUTONIA (100X)

Figure 3-8. Tungsten/Purer Plutonia After Exposure at 1800°C for 2000 Hours

69-1484

20 MILS (50x)

69-1485

5 MILS (200x)

Figure 3-9. Tungsten/Original PuO_2 , 1800°C, 2000 hr

A. MACROGRAPH OF
SECTIONED CAPSULE

B. SMALL DISC, CAPSULE BOTTOM AND WALL, PLUTONIA

Figure 3-10. Tungsten/Original Plutonia, 1800°C, 18,000 hr

migrated from its original location and was present as a meniscus above the upper disc and co-deposited with tungsten along the walls. The plutonia was very substoichiometric and had fewer metallic precipitates than the short-term tests. There was no discernible difference between the two plutonia purity levels.

The appearance of the tungsten disc in contact with purer $\text{PuO}_{2.0}$ after exposure at 2000°C for 1000 hours was equivalent to that at 1800°C , 2000 hr. The capsule wall shown in an obliquely lighted photomicrograph in A, Figure 3-11 has voids caused by loss of grains during polishing and was obviously considerably degraded during exposure. Similar degradation was observed to a greater or lesser degree in a majority of the specimens. Plutonia structure is shown in B, Figure 3-11 where the lighter angular areas are the promonotectoid PuO_{2-y} (Figure 3-3); the darker appearing mixture is the monotectoid decomposition product. In this specimen, the monotectoid is estimated as being 65% of the total specimen area which represents a composition of 1.75 O/Pu ratio indicating a significant oxygen loss for this specimen.

The comparable tungsten/original $\text{PuO}_{2.0}$ specimen exposed at 2000°C for 1000 hours exhibited gross attack of the discs (Figure 3-12) as well as the capsule wall. This may have been influenced by plutonia purity. Plutonia appearance was similar for the two specimens.

Limited intergranular attack was observed on the tungsten disc after contact with purer $\text{PuO}_{1.8}$ at 2000°C for 1000 hours. The capsule wall was seriously degraded. This is shown in the secondary electron photomicrograph in Figure 3-13 where the fracture is shown along grain boundaries. The plutonia fuel pellet dropped from the capsule during sectioning and was not included in the mount. The comparable original $\text{PuO}_{1.8}$ disc specimen had one area of deep intergranular attack and limited oxide precipitation but no general intergranular attack.

Microhardness values generally followed the approximations made in Section 3.2.2. Tungsten in contact with the original PuO_2 exposed at 2000°C was perhaps harder than when exposed to the purer PuO_2 because of the presence of impurities, harder than when in contact with $\text{PuO}_{1.8}$ because of extra oxygen, and harder than the 1800°C test specimens because of higher solubility of elements in the tungsten.

71-387

70-1457

125 MILS (8x)

A. CAPSULE MACROGRAPH

5 MILS (200x)

B. PLUTONIA

Figure 3-11. Tungsten/Purer PuO_2 , 2000°C, 1000 Hours

71-388

20 MILS (50x)

Figure 3-12. Tungsten/Original PuO_2 , 2000°C, 1000 Hours

The long-term 1800°C specimens had higher hardness in the plutonia specimen than in the original plutonia. A hardness value of 1069 DPH for the purer PuO₂, 2000°C, 1000 hr specimen appears to be in the correct range for typical plutonia.

Structure of the tungsten control specimen exposed at 1800°C for 18,000 hr is shown in Figure 3-14 and exhibits intergranular degradation without contact with plutonia.

3.3.2 Tungsten-25% Rhenium

Tungsten-25% rhenium appears to offer better potential than tungsten as a high temperature container for plutonia, but appears to be inferior to rhenium and the molybdenum containing alloys. The major form of degradation was plutonia precipitation below the metallic surface which occurs in contact with PuO₂ but not in contact with purer PuO_{1.8}. Plutonia precipitation occurred both in direct contact with plutonia (B, Figure 3-15) and at some distance from the plutonia (A, Figure 3-15). Electron-beam microprobe analyses of these areas showed the presence of plutonium and absence of tungsten and rhenium in the precipitates as shown in Figure 3-16 for the purer PuO_{2.0} specimen exposed at 2000°C for 1000 hours. A somewhat larger amount and depth of precipitation was exhibited by the original PuO_{2.0} specimen exposed at 1800°C for 2000 hours. Precipitation occurred at grain boundaries which would be detrimental to mechanical properties. The structure of both pure and original PuO₂, 1800°C, 2000 hours is exemplified by C, Figure 3-15 showing approximately 10 area-percent monotectoid representing a 1.94 O/Pu ratio which is about the same as that in contact with tungsten or rhenium under the same exposure conditions.

Tungsten-25% rhenium exposed at 1800°C for 18,000 and 15,000 hours had a large number of subsurface oxide precipitates previously identified as plutonia. Precipitate depth ranged to 12 mils for the original plutonia as shown in Figure 3-17 but only to about 4 mils for the purer plutonia with somewhat fewer precipitates. Penetration into the metal was universally deeper in the long-term capsules than in the short-term specimens. Metal transport was observed in the long-term original plutonia specimen, the only W-25Re specimen to exhibit metal transport.

Figure 3-13. Secondary Electron Scan of W/Pure $\text{PuO}_{1.8}$ Capsule Wall, 2000°C , 1000 Hours (200x)

Figure 3-14. Tungsten Control Specimen, 1800°C , 18,000 hr

70-1069

5 MILS

70-1058

5 MILS

A. DISC CORNER NOT IN CONTACT WITH PLUTONIA (200X)

B. DISC SURFACE IN CONTACT WITH PLUTONIA (200X)

70-1065

10 MILS

C. PLUTONIA (100X)

Figure 3-15. Tungsten-25% Rhenium/Purer Plutonia, 1800°C, 2000 Hours

70-1812

A. SECONDARY ELECTRON SCAN OF W-25Re

70-1813

B. PLUTONIUM

2 MILS

70-1814

C. TUNGSTEN

70-1815

D. RHENIUM

2 MILS

Figure 3-16. Electron Beam Microprobe Area Scans of W-25Re/Purer PuO_2 Interface, 2000°C, 1000 Hours (500x)

The appearance of the metallic structures of the $\text{PuO}_{2.0}$ 2000°C, 1000 hour specimens was almost exactly the same as the 1800°C - 2000 hour specimens with similar depths of oxide precipitation. The one difference appeared to be a somewhat more complete precipitate layer with the original PuO_2 resulting in more continuous precipitation along grain boundaries which apparently caused sporadic loss of surface material during polishing.

Behavior of W-25Re in contact with pure $\text{PuO}_{1.8}$ at 2000°C for 1000 hours was excellent. Plutonia adhered to the surface, but the lack of interdiffusion of the metallic elements and plutonia shown by the electron-beam step scan in Figure 3-18. Less than a 2-micron penetration is shown in either direction using 0.5-micron steps. The comparable original $\text{PuO}_{1.8}$ specimen showed a similar appearance except for an extremely fine surface precipitation to a depth of approximately 1 micron.

Microhardness of the W-25Re generally followed the pattern described previously. Heat-treated hardness was consistently less than the as-received material but varied both above and below that measured in the control specimen. The most valid comparisons seem to be possible with the purer plutonia, in that the W-25Re was softer at 1800° than at 2000°C in contact with $\text{PuO}_{2.0}$ and softer at 2000°C in contact with $\text{PuO}_{1.8}$ than in contact with $\text{PuO}_{2.0}$. In the long-term tests at 1800°C the alloy adjacent to the purer plutonia was harder than that adjacent to the lower purity plutonia. Structure of the W-25Re control specimen exposed at 1800°C for 18,000 hr is shown in Figure 3-19 indicating grain growth but no other form of degradation.

The structure of the plutonia exposed at 2000°C appeared to be independent of starting composition. Figure 3-20 (A and B) shows purer $\text{PuO}_{2.0}$ and $\text{PuO}_{1.8}$, respectively, after exposure at 2000°C for 1000 hours. Both had approximately the same O/Pu ratio with the $\text{PuO}_{2.0}$ specimen containing a metallic precipitate, identified in the 1800°C specimen as containing plutonia and tungsten. The purer plutonia in the 1800°C long-term specimens had many small metallic precipitates, while none could be observed in the original plutonia. The plutonia appeared slightly less stoichiometric than in the comparable tungsten capsules, probably caused by a lower permeability to oxygen. Electron-beam microprobe analysis of the 2000°C, 1000 hr $\text{PuO}_{2.0}$ specimen showed no inclusions or

Figure 3-17. W-25Re/Original Plutonia, 1800°C, 18,000 hr

70-1818

Figure 3-18. Electron Beam Microprobe Step Scan Across W-25Re/Pure PuO_{1.8} Interface

Figure 3-19. W-25Re Control Specimen, 1800°C, 18,000 hr

70-1267

10 MILS

A. $\text{PuO}_{2.0}$ (100x)

70-1257

5 MILS

B. $\text{PuO}_{1.8}$ (200x)

Figure 3-20. Tungsten-25% Rhenium/Purer Plutonia, 2000°C, 1000 Hours

solution of iron, chromium, and nickel to the limit of detectability (0.1%). Plutonia microhardness was measured as 1113 DPH for the original plutonia, 1800°C, 2000 hr specimen which was comparable to pre-test values. Hardness of the metal inclusions in the same plutonia was 522 DPH, equivalent to W-25Re in hardness, thus inferring metallic character and not intermetallic compound formation.

3.3.3 RHENIUM

Rhenium displayed the best appearance of the six alloys investigated in this effort. In particular, the $\text{PuO}_{1.8}$, 2000°C, 1000 hr specimens were unattacked and exhibited no metallic mass transport. Similarly, the PuO_2 , 1800°C long-term rhenium specimens were unattacked but did exhibit significant rhenium mass transport. Even more mass transport occurred in the PuO_2 , 2000°C, 1000 hr specimens. Rhenium transport is related to temperature and internal thermal gradient, volatility of rhenium containing vapor species, presence of oxygen from the plutonia, and relatively low permeability of rhenium to oxygen.

The rhenium specimen in contact with purer $\text{PuO}_{2.0}$ at 1800°C for 2000 hours showed no apparent attack to the surface (A, Figure 3-21). Surface roughening occurred, resulting either from surface volatilization or solution in the plutonia. Rhenium vapor transport was not observed in this capsule, but no attempt was made to section the capsule wall which would have exhibited the deposition. The appearance of the plutonia is shown in B, Figure 3-21. This fuel specimen has the highest oxygen content and highest apparent densification of any specimen in the program. The oxygen-deficient areas (dark acicular monotectoid reaction product) are related to the major voids. The comparative rhenium specimen in contact with original plutonia at 1800°C for 2000 hours was a contrast, in that, the small (lower) disc bonded to the capsule bottom, and the upper disc was attached to the capsule wall on one side. Appearance of the disc surface indicated that metallic transport had occurred, causing surface roughening. Examination of the vapor deposited material on the capsule wall in the electron-beam microprobe disclosed the presence of iron and chromium in conjunction with plutonia as precipitates in the grain boundaries of the deposited rhenium. There was no detectable plutonium, chromium, iron, nickel or cobalt in the deposited rhenium matrix.

Rhenium in the 1800°C, long-term specimens appeared virtually unaffected except for mass transport to the colder surfaces. This is shown in Figure 3-22 where the small disc at the top of the photo has thinned considerably with material transported to the bottom of the capsule along with "fingers" of oxide. Otherwise there was no attack to rhenium surfaces. Microprobe examination of the deposited material showed plutonia in the "fingers" but nothing in solution in the deposited rhenium. Capsule walls had a small amount of what appeared to be oxides, but there was no plutonia body visible in the capsule either as the original pellet or as thick deposits along the walls. These were the only two capsules where this occurred.

The two PuO_2 , 2000°C, 1000 hr disc surfaces were extensively roughened and vapor deposition occurred along the capsule walls. Figure 3-23 shows the cross-section of the original PuO_2 /rhenium capsule and the various areas of interest. The upper pictures show the transported material and the adjacent eroded surface. The lower pictures show the small disc bonded to the capsule bottom and the erosion of the upper surface of the small disc. The purer plutonia exhibited comparable behavior.

No vapor transport was observed in either $\text{PuO}_{1.8}$ capsule exposed at 2000°C for 1000 hours. The surface of the rhenium discs in contact with the plutonia are shown in Figure 3-24 displayed no evidence of attack other than very minor surface roughening. The surface visually appeared no worse than that of a control specimen exposed under the same conditions (Figure 3-25). The purer $\text{PuO}_{1.8}$ specimen was examined in the electron-beam microprobe which provides some additional insight. Step scans were made across the rhenium-plutonia interface showing less than a one-micron interpenetration in both directions. Step scans, which were used for a higher level of precision than the usually used traverse technique, resulted in detection of approximately 0.1% iron and chromium uniformly distributed in the rhenium. There was no buildup of iron, chromium, or nickel at the interface. Small inclusions of plutonia were detected in the metal near the metal interface which were not seen under light microscopy. The purer plutonia structure, shown in Figure 3-26, had an apparent oxygen content of 1.70 O/Pu.

A RHENIUM DISC (200X)

MOUNTING
MATERIAL

5 MILS

B PLUTONIA (100X)

10 MILS

Figure 3-21. Rhenium/Purer $\text{PuO}_{2.0}$, 1800°C , 15,000 hr Figure 3-22. Rhenium/Purer Plutonia, 1800°C , 15,000 hr

Figure 3-23. Original $\text{PuO}_{2.0}/\text{Re}$, 2000°C , 1000 hr

10 MILS

Figure 3-24. Rhenium/Original $\text{PuO}_{1.8}$, 2000°C, 1000 Hours (100X)

69-1481

(100X)

10 MILS

Figure 3-25. Rhenium Control, 2000°C, 1000 Hours

Figure 3-26. Plutonia in Rhenium/Pure $\text{PuO}_{1.8}$, 2000°C, 1000 Hours

Microhardness measurements on rhenium were complicated by an apparent orientation phenomena. Dark appearing grains were softer than light appearing grains as measured in both a control specimen and rhenium specimens in contact with original plutonia. The 1800°C, 2000 hr rhenium specimen in contact with original plutonia was anomalously harder than that in contact with purer plutonia. The purer PuO_2 1800°C specimen was softer than the 2000°C specimen, as expected, but there was no difference between the $\text{PuO}_{2.0}$ and $\text{PuO}_{1.8}$ at 2000°C. The purity of the vapor-deposited rhenium was indicated by both the microprobe results and the low hardness values (274 to 433 DPH). One anomalously high plutonia hardness value is listed (1720 DPH for original PuO_2 , 2000°C, 1000 hours) and two normal values (1113 DPH for purer PuO_2 , 2000°C, 1000 hr and 1208 DPH for purer $\text{PuO}_{1.8}$, 2000°C, 1000 hr). The reason for the high hardness is unknown.

3.3.4 Molybdenum-50% Rhenium

Molybdenum-50% rhenium, molybdenum, and tungsten-30 molybdenum-30 rhenium were exposed only at 1800°C because it was believed that excessive

volatilization and potential reactions would occur at 2000°C. No vapor transport was observed in the molybdenum-base alloy short-term test specimens but was observed in four out of six long-term specimens. Oxygen loss in the short-term specimens was a function of molybdenum content with the Mo-50Re alloy being intermediate in loss rate. However, there was no apparent difference in oxygen loss behavior for the long-term specimens.

Oxide precipitation was the primary attack mechanism that occurred in the Mo-50Re in contact with plutonia. The surface appearance of the Mo-50Re/purer PuO_2 , 1800°C, 2000 hr specimen is shown in A, Figure 3-27. The same area examined in the microprobe showed the location of plutonium (presumably plutonia) both on the surface and in the subsurface precipitates. No plutonium was detected in solution in the metal (detection limit 0.8% Pu). No iron, chromium, nickel, or cobalt was detected in the alloy disc. However, electron-beam scans of the plutonia showed molybdenum inclusions (without rhenium) as shown in C and D, Figure 3-27.

Attack by the original plutonia in the 1800°C, 2000 hr specimens appeared to be worse than that of the pure plutonia as shown in A, Figure 3-28. Oxides were present along grain boundaries in areas both in direct contact with the fuel and away from the fuel. Behavior observed in this one short-term specimen may have been an anomaly based on examination of the long-term specimens.

The long-term Mo-50Re specimens exhibited minimal damage with primary attack limited to subsurface voids. One large agglomerated void approximately 7 mils deep was observed in the corner of one Mo-50Re disc in contact with purer plutonia, but otherwise, voids were limited to depths of 1.5 mils or less as shown in Figure 3-29. The two specimens appeared identical in behavior. Microprobe exam indicated that the subsurface precipitates contained molybdenum and rhenium without plutonium in contrast to short-term test results. Metal transport was observed, but the amount was not measurable.

There was no effect of plutonia impurity level on Mo-50Re hardness in either short- or long-term tests but fueled specimens were somewhat harder than comparable control specimens. However, long-term specimens were softer than the short-term specimens, being in the range of the control specimens.

Plutonia from the short-term purer PuO_2 capsule exhibited considerable monotectoid formation and lenticular promonotectoid $\text{PuO}_{1.98}$ areas (B, Figure 3-27).

70-660

70-671

A. Mo-50Re DISC

PLUTONIA

MOUNTING
MATERIAL

5 MILS (200x)

71-391

B. PLUTONIA

10 MILS (100x)

71-392

C. PLUTONIA

2 MILS (500x)

D. PLUTONIA MOLYBDENUM SCAN

2 MILS (500x)

Figure 3-27. Mo-50Re/Purer PuO_2 , 1800°C, 2000 Hours

69-1490

A. Mo 50Re

2 MILS (500x)

69-1655

B. PLUTONIA

10 MILS (100x)

Figure 3-28. Mo-50Re/Original PuO_2 , 1800°C, 2000 Hours

A. Mo-50Re DISC/ORIGINAL PLUTONIA/MO 50Re WALL

10 MILS (100x)

B. Mo-50Re DISC/PURER PLUTONIA/MO 50Re WALL

10 MILS (100x)

Figure 3-29 Mo-50Re/ PuO_2 , 1800°C, 18,000 or 15,000 hr

Equivalent behavior was also shown in the comparable original plutonia. The plutonia in both specimens exhibited metallic precipitates which were shown to be molybdenum. The long-term plutonia did not appear to have any metallic precipitates. Oxygen content of the long-term specimens was somewhat lower than the short-term plutonia specimens (1.64 to 1.66 O/Pu ratios y 1.70 to 1.72 O/Pu ratios).

3.3.5 Molybdenum

The resistance of pure molybdenum to attack may be related directly to the rapid loss of oxygen. Post-test examination of the plutonia exposed at 1800°C for 2000 hr indicated oxygen contents of 1.70 to 1.72 O/Pu ratio. Continued reduction to 1.64 to 1.66 O/Pu ratio occurred in long-term specimens. This rapid loss probably prevented any vapor transport of molybdenum within the capsule and major volatilization from the discs. It did not prevent dissolution of molybdenum in the plutonia which occurred in all four specimens.

Bulk oxide precipitation, intergranular oxide presence, and surface roughening all occurred to a limited extent at the molybdenum/plutonia interface as shown in A, Figure 3-30 for purer PuO_2 . An electron-beam step scan across the interface showed no plutonium, iron, chromium, nickel, or cobalt in the molybdenum. This was not surprising as the precipitation was both fine and randomly dispersed.

Comparable behavior of the short-term original plutonia specimen is shown in A, Figure 3-31, where minor areas of intergranular penetration occurred. Attack of the molybdenum surface was somewhat more severe than with purer plutonia, but not spectacularly so.

Long-term molybdenum specimens exhibited subsurface voids, limited precipitation, and minimal mass transport as shown in Figure 3-32 for the purer plutonia capsule. The upper corner of the disc (to the right in the photomicrograph) appears to have been eroded with transport to the wall (to the left). The original plutonia capsule wall exhibited comparable behavior as shown on the left side of Figure 3-33. The capsule cross-section had been shown previously in Figure 3-7 as an example of complete plutonia transport to locations away from the original pellet area.

A. Mo DISC

2 MILS (500x)

B. PLUTONIA

10 MILS (100x)

Figure 3-30. Molybdenum/Purer PuO_2 , 1800°C , 2000 Hours

A. MOLYBDENUM

5 MILS (200x)

B. PLUTONIA

10 MILS (100x)

Figure 3-31. Mo/Original PuO_2 , 1800°C , 2000 Hours

Figure 3-32. Mo/Purer Plutonia, 1800°C, 15,000 hr

Figure 3-33. Mo/Original Plutonia, 1800°C, 18,000 hr

Exposure softened the molybdenum from the as-fabricated hardness of 302 DPH to the final control specimen hardness of 181 to 193 DPH. The control specimen is shown in Figure 3-34. The fueled specimens softened comparably, except that the short-term purer plutonia remained somewhat hard.

Plutonia was highly substoichiometric in all four specimens with the long-term specimens somewhat lower in oxygen content. Structures are shown in B, Figure 3-30, B, Figure 3-31, Figure 3-32, and Figure 3-33. Some metallic precipitates occurred in all four specimens. In the short-term purer plutonia specimen, the precipitates were examined in the microprobe and found to contain approximately 95% Mo and 5% Pt. Cause for the platinum presence is unknown. Approximately 2% to 3% molybdenum was present in solution in the plutonia, indicating this level of solubility at 1800°C.

3.3.6 Tungsten -30% Molybdenum -30% Rhenium

The ternary W-30 Mo-30Re (actually W-18 w/o Mo-35 w/o Re) alloy exhibited the largest variety of attack mechanisms of any alloy. Total attack depths

71-269

Figure 3-34. Mo Control Specimen, 1800°C, 18,000 hr

were generally comparable to the Mo-50Re alloy. The plutonia retained the highest oxygen content and had the smallest amount of metallic precipitates of any of the three molybdenum alloys.

Appearance of the test disc after contact with the short-term purer plutonia specimen is shown in A, Figure 3-35. Only limited oxide penetration along grain boundaries was visible. Electron-beam microprobe analysis was unable to detect any plutonium, chromium, nickel, or cobalt in the metal.

The comparable short-term original plutonia W-Mo-Re specimen had an intermetallic precipitate at the surface along with solution attack, intergranular penetration, and some subsurface oxide formations. The surface is shown in A, Figure 3-36. The intermetallic precipitation was not observed in any other alloy.

A macrograph of the original plutonia specimen exposed 18,000 hr was shown in Figure 3-6 as the only long-term specimen which had retained the plutonia as an intact body. Appearance was very similar to both the comparable short-term specimen except that the intermetallic precipitation became a layer at the longer time. The comparable appearing purer plutonia specimen is shown in Figure 3-37. Only the long-term purer plutonia capsule exhibited metal mass transport of the four WMoRe specimens.

Microhardness of the short-term WMoRe specimens was high, compared to as-fabricated, control, and long-term specimens which were all about the same. This has remained unexplainable, particularly in the case of hardening which occurred in the short-term purer plutonia disc.

Oxygen content of the short-term plutonia exposed for 2000 hr was considerably higher than the long-term plutonia exposed for 15000 to 18000 hr (1.83 to 1.85 O/Pu ratio v 1.66 to 1.68 O/Pu ratio). Permeability of the WMoRe to oxygen was the lowest of the three molybdenum containing alloys resulting in the highest short-term oxygen content. Plutonia structures are shown in B, Figure 3-35 and 1B, Figure 3-36. Metallic precipitates were observed in all except the short-term purer plutonia. The precipitates were relatively fine in all cases. Hardness of the short-term purer plutonia was measured as 1530 DPH, somewhat higher than most other values determined on plutonia. The reason is obscure.

70-676

70-673

A. W-30Mo-30Re DISC
(200x)

MOUNTING MATERIAL

MOUNTING MATERIAL

5 MILS (200x)

B. PLUTONIA

Figure 3-35. W-30Mo-30Re/Purer PuO_2 , 1800°C, 2000 Hours

69-1492

69-1656

5 MILS (200x)

A. W-30Mo-30Re

10 MILS (100x)

B. PLUTONIA

Figure 3-36. W-30Mo-30Re/Original PuO_2 , 1800°C, 2000 Hours

Figure 3-37. W-30Mo-30Re/Purer Plutonia, 1800°C, 15,000 hr

Section 4

CONCLUSIONS

Major factors influencing measured compatibility of refractory alloys with plutonia-238 at 1800° to 2000°C included refractory alloy composition, plutonia oxygen content, and test configuration. Less significant variables included temperature, test duration, and plutonia impurity content. A series of inter-related conclusions has been made within the context of this experimental effort and is presented in three arbitrary categories with the last conclusions being the basic recommendation regarding system modeling requirements for investigations of this kind.

4.1 CONTAINER CONCLUSIONS

4.1.1 Rhenium Was the Most Compatible Material with Plutonia at 2000°C

Of the three alloys tested at 2000°C, rhenium was the most compatible with plutonia. Minimal attack occurred with PuO_2 and essentially zero attack occurred with $\text{PuO}_{1.8}$. W-25Re exhibited excellent behavior with $\text{PuO}_{1.8}$ but not with PuO_2 . Tungsten was degraded badly, perhaps as much from the thermal treatment, which resulted in extensive grain boundary attack, as from the plutonia.

4.1.2 Rhenium Also Exhibited the Least Attack from Plutonia at 1800°C

Of the six alloys tested at 1800°C, rhenium was marginally superior in observed attack with a maximum of 5-mil attack and essentially no attack with purer plutonia. Both molybdenum and Mo-50Re exhibited less than 10-mil attack in all cases, and in contact with purer plutonia, the attack was 2.5 mils or less with one minor exception. The remaining alloys exhibited degradation to 10 mils or more.

4.1.3 Permeability of Refractory Alloys to Oxygen Probably Affected Observed Compatibility

All refractory alloys are permeable to oxygen with rhenium being least permeable, tungsten intermediate, and molybdenum the most. Alloy permeability is probably intermediate to the individual constituents. Short-term test plutonia

oxygen contents appeared to have varied according to expected permeability. The rapid loss of oxygen from the molybdenum specimens and perhaps Mo-50Re reduced the chemical activity for attack of these alloys by the plutonia. It has been shown thermodynamically that the oxygen activity in plutonia is a strong function of oxygen content as also exhibited in other oxide systems. Confirmation of this was obtained on the $\text{PuO}_2 \text{ v } \text{PuO}_{1.8}$ tests conducted at 2000°C . It is highly probable that, at least in the case of molybdenum and probably Mo-50Re, attack was inhibited by the rapid loss of oxygen through the containers. The other alloys probably also were affected, but to a lesser extent because of lower oxygen permeability.

4.1.4 All Alloys Mass Transported with Tungsten and Rhenium Exhibiting the Largest Effect

All alloys exhibited mass transport from relatively hotter to relatively cooler surfaces in the long-term tests at 1800°C . Transport varied from bare detectability to a 20-mil buildup under the same test conditions. The least transport was observed in the molybdenum-containing alloys probably because of their higher permeability to oxygen and thereby lessened source of oxygen. There was no transport observed when the starting plutonia was $\text{PuO}_{1.8}$. The largest amount of transport occurred in the tungsten and rhenium containers with five out of six rhenium specimens showing transport. Material movement depends on oxygen presence, a thermal gradient, and favorable refractory alloy-oxide system thermodynamics. Massive transport would weaken hot areas by removal of material. The amount of transport can be minimized by reduction in oxygen content in the plutonia and reduction of thermal gradients, partially by plutonia mass transport.

4.1.5 Purification of Refractory Alloys Occurred at 1800°C in Ultra-High Vacuum

Volatile impurities such as aluminum, iron, and silicon were lost from refractory alloy control specimens exposed in ultra-high vacuum at 1800°C for 18,000 hr. Removal of these specific constituents in all refractory alloys would not be detrimental and in fact, may be beneficial in producing enhanced ductility when cold. Molybdenum-containing alloys lose molybdenum from the surface at 1800°C in a vacuum, at a rate of 10 mils per year, but appear to retain bulk properties. However, exposure of a molybdenum-containing alloy at 2000°C

in a vacuum results in preferential volatilization of molybdenum leaving a porous degraded structure behind. A depth of over 0.1 in. became a spongy mass in a 10,000 hr exposure to vacuum. Other factors, such as strength, tend to eliminate the use of molybdenum-containing alloys at temperatures lower than that causing damage because of volatility of the molybdenum.

4.1.6 Hardness Changes are Caused by at Least Five Interactive Variables

Refractory alloy hardness is affected by: annealing of the as-fabricated structure resulting in softening; exposure temperature causing varying solubility of hardeners; plutonia oxygen content providing interstitial oxygen; fuel impurities as another source of hardeners; and exposure duration providing an opportunity for the other variables to interact. Annealing, oxygen content reduction, and impurity element diffusion all tended to cause softening with time. The interactive nature of the variables caused as many exceptions to the general trends as there were agreements within trends.

4.1.7 Plutonium Appears to be Virtually Insoluble in Refractory Alloys

Microprobe examination showed subsurface precipitates containing plutonium but no general solubility of plutonium in the alloys. The limit of detection was below 1% plutonium in all cases. There must be some solubility for diffusion from the surface to the precipitate locations, but it is below limits of detection in all refractory alloys examined. This behavior directly corresponds to that observed at Mound Laboratory (Reference 1).

4.2 PLUTONIA CONCLUSIONS

4.2.1 Substoichiometric Plutonia is More Compatible with Refractory Alloys than is PuO_2

In the three alloys tested at 2000°C for 1000 hr with both PuO_2 and $\text{PuO}_{1.8}$, the refractory alloys had uniformly better appearances after exposure with $\text{PuO}_{1.8}$. The oxygen activity in plutonia is a direct function of plutonia oxygen content from PuO_2 to $\text{PuO}_{1.61}$ according to the current literature. There is no reason to believe that $\text{PuO}_{1.8}$ is an optimum composition. From an oxygen activity viewpoint, the best oxygen content in a closed refractory alloy system is closer to 1.61 O/Pu ratio. However, due to possible formation of plutonium-refractory metal compounds with or without oxygen, the optimal oxygen content may be somewhat above 1.61 O/Pu ratio. In an open system the optimum composition would be at or near the congruent vaporization composition which is about $\text{PuO}_{1.85}$ at 1800°C.

4.2.2 Compatibility Differences Due to Plutonia Purity Levels Decreased with Exposure Time

Short-term test results at both 1800° and 2000°C indicated differences in refractory alloy attack attributed to plutonia purity. No differences were observable in the long-term 1800°C specimens. A combination of small plutonia fuel volume in a relatively large container and rapid diffusion rates of the iron, calcium, chromium, and other plutonia impurities in refractory alloys at 1800°C probably resulted in a brief wave of diluted impurities passing through the container walls.

It is probable that even the short-term test duration was on the upper fringe of detectability of differences between the purity levels utilized in the program.

4.2.3 Plutonia Transported to Cooler Capsule Locations

Vapor pressure of plutonium-containing species at 1800°C is such that about 10 mils of plutonia would be transported across a gradient of 5°C in 2000 hr. Massive movement of plutonia was not observed in the short-term tests, but in almost all of the long-term tests, the plutonia had transported up the walls or into the corners. Initially, the plutonia pellet was relatively hot compared to the capsule walls, resulting in transport to those surfaces. As plutonia built up on the walls, the thermal gradient decreased until eventually, a stable equilibrium is reached. Whether a stable equilibrium was reached in the 15,000 to 18,000 hr at 1800°C is uncertain, but movement had occurred extensively.

4.2.4 Refractory Alloy Solubility and Precipitation in Plutonia Depended on Alloy Composition

Microprobe examination of various specimens indicated that rhenium solubility in plutonia was below detection limits and that molybdenum solubility in plutonia appeared to be approximately 2% to 3%. No data were obtained for tungsten. Precipitates containing tungsten were observed in plutonia contained in W-25Re. Precipitates containing molybdenum were observed in plutonia contained in Mo and Mo-50Re. No precipitates were observed containing rhenium. Variation of precipitate amount depended primarily on alloy content and not the initial plutonia purity level.

4.3 TEST PROGRAM CONCLUSIONS

4.3.1 The Re/PuO_{1.8} Combination was the Most Compatible

There was essentially no interaction between rhenium and PuO_{1.8} at 2000°C for 1000 hr including attack to the rhenium, transport of rhenium, and oxygen loss in the plutonia. Rhenium is the least oxygen-permeable refractory alloy. The two materials appear to be mutually insoluble. Rhenium would provide an excellent liner for substoichiometric plutonia if a means could be developed to fabricate a sealed container.

4.3.2 The Test Configuration Resulted in Excessive Changes in Plutonia and Inhibited Effects in the Refractory Alloys

The test configuration of a small plutonia pellet in a relatively large container resulted in a swamping of the effects of any possible differences in plutonia purity and the relatively rapid reduction in plutonia oxygen content. Major changes occurred rapidly in the plutonia. The actual amount of plutonia impurities was very small relative to the container volume, particularly so when compared to volume relationships in actual radioisotope heat sources. The same small plutonia volume also resulted in rapid oxygen loss because of container permeability resulting in a lessened driving force for oxygen attack. Consequently, at longer times, there was a lower total driving force for interaction between the plutonia and its container.

4.3.3 Observed Penetration Data Do Not Appear to be Extrapolatable in Temperature and Time

Time dependency of observed penetration data at 1800°C was highly variable with only a tenuous statistical inference of a penetration increase by a factor of 1.6 to 1.8 for the time increase of a factor of 7.5 to 9. This variation indicates a fourth root time relationship ($t^{1/4}$), somewhat below that typically observed. The only temperature correlation also requires a time relationship (2000°C, 1000 hr y 1800°C, 2000 hr). Comparison of observed penetrations resulted in a very large probability that the results were the same and only a small probability that the lower temperature was a more rigorous condition. Because of limitations of the test program, there does not appear to be any suitable means to extrapolate downward in temperature and/or longer in time. Comparison with the data obtained at Mound Laboratory (Reference 1) does not increase the ability to extrapolate.

A major factor causing this was the changing oxygen potential of the plutonia with concurrent reduced driving force for refractory metal attack. A better ability to extrapolate was observed in some of the Mound Laboratory tests having larger fuel/container volume/surface area ratios.

4.3.4 Compatibility Tests Must be Close Approximations of Systems Configurations

Reaction mechanisms and amounts of materials migration are influenced by temperature, thermal gradients, accessibility, and relative area or volume ratios of various system components. Gross affects were found to be discernable in the simple low-cost test configuration utilized in this study. However, the relatively low fuel volume resulted in potentially erroneous results for at least the PuO_2 -molybdenum-containing alloys and possibly even the more refractory alloys at 1800°C for long times. Complex interactive mechanisms require that final compatibility testing be performed much closer to expected operating temperatures using a configuration closely approximating the relative volumes, accessibility, and thermal gradients occurring in the engineering system.

Section 5
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