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PLUTONIA/CURIA COMPATIBILITY TESTING

OCTOBER - DECEMBER 1969

QUARTERLY REPORT NO. 5

DR. R. L. ANDELIN AND J. D. WATROUS

MASTER

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

DATE PUBLISHED - JANUARY 1970

Donald W. Douglas Laboratories
Richland, Washington

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ABSTRACT

Compatibility testing of relatively impure plutonia-238 in contact with six molybdenum, tungsten, and rhenium containing alloys at 1800° and 2000°C has shown that oxygen content of the plutonia affects reaction rates, and that significant amounts of oxygen are lost through the molybdenum alloy container walls. Further testing is currently underway with a higher purity plutonia representative of current production-grade material.

Curia-244 has been encapsulated in primary containers with contamination free external surfaces for exposure at 2000°C. This approach, also used in the plutonia effort, provides a significant improvement in the determination of damage to the primary capsule.

Plutonia-molybdenum cermet exposed for 1000 hours at 1800° and 2000°C in closed containers released approximately 40% of the stored helium. Longer duration exposure continues.

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Section 1 INTRODUCTION

Utilization of radioisotopes as high temperature heat sources for electrical power generation or space propulsion requires positive containment under all potential conditions. Plutonium-238 is currently being used at moderate temperatures in space, but further knowledge concerning its containment is essential for more advanced applications at higher temperatures. Similarly, curium-244 has been proposed as the fuel for advanced non-manned inter-planetary missions requiring long duration use at high temperatures.

The purpose of this program is to define the best radioisotope fuel-refractory alloy combinations under accelerated testing conditions and to determine the rates at which they interact. Exposure of test combinations is being performed at 1800° and 2000°C for times up to 10,000 hours. Both plutonia and curia are being exposed, initially in contact with six alloys of tungsten, rhenium, and molybdenum. Selection of long-term test combinations depends on results of the short-term tests. Final test results will provide reaction rate data above normal use conditions which can be used to calculate reaction rates for longer times at operating temperatures.

Original plans to test plutonia-refractory metal combinations included 24 specimens, 12 at 1800°C and 12 at 2000°C. Eighteen specimens were fabricated; 12 have completed exposure and evaluation. After exposure was underway, it was determined from tests at Mound Laboratory that major interactions between plutonia and the refractory metals at lower temperature were attributable to impurities in the plutonia and not intrinsic to the plutonia itself. The plutonia being tested (supplied by Mound Laboratory) contained 12,200 ppm metallic impurities. At this point, plans to encapsulate the last 6 specimens containing the original or "impure" plutonia were dropped. The program was then extended to add 18 capsules containing purer current production-grade plutonia containing approximately 2800 ppm metallic impurities. Fifteen capsules have been fabricated; 6 have completed exposure.

Original plans also included 12 curia-refractory metal test specimens. Six were to have been fabricated for evaluation after exposure for 1000 hours at 2000°C. Three metals would have been selected for further exposure at 1800° and 2000°C. Minor modifications have been made to the original plans to facilitate laboratory operations. The first 6 capsules have been fabricated. However, instead of waiting for evaluation, fabrication is proceeding on 12 additional capsules, 2 of each type for immediate exposure at 1800° and 2000°C. This will permit longer exposures of more materials at negligible additional cost to the program and also permit earlier removal of fabrication equipment.

Testing of plutonia-molybdenum cermets has also been added to the program. Eight cermets provided by Battelle-Columbus Laboratories are undergoing testing. Six were encapsulated for exposure at 1800° and 2000°C for times to 10,000 hours. Two have completed exposure and are being evaluated.

Revision 3 to the Classification Guide CG-IHS-1 has resulted in declassification of this program. This and subsequent documents will be issued as unclassified reports.

Section 2

RESULTS

Major accomplishments to date include (1) determination that $\text{PuO}_{1.8}$ is less reactive than $\text{PuO}_{2.0}$ in contact with W, W-25Re, and Re; (2) discovery that significant amounts of oxygen are lost through Mo base alloys at 1800°C; (3) successful encapsulation of curia in clean refractory metal capsules; and (4) determination that approximately 40% of stored helium is released from plutonia-molybdenum after 1000 hours at 1800° and 2000°C.

2.1 ORIGINAL PLUTONIA

Metal penetration amounts were discussed in the fourth Quarterly Report (Reference 1) for specimens exposed at 2000°C for 1000 hours and at 1800°C for 2000 hours. These data are listed in Table 2-1 together with additional information recently obtained on plutonia in contact with the metals.

Comparative data for $\text{PuO}_{1.8}$ and $\text{PuO}_{2.0}$ in contact with W, W-25Re and Re at 2000°C for 1000 hours conclusively show that the $\text{PuO}_{1.8}$ is less reactive. Gross reaction occurred between tungsten and PuO_2 with 10-mil intergranular penetration and an unknown amount of general solution attack (unknown because the surface grains fell out during metallography). Tungsten in contact with $\text{PuO}_{1.8}$ exhibited a 1-mil general solution attack and a single isolated case of intergranular penetration through the 30-mil disc. Tungsten-25% rhenium exhibited three forms of attack with penetration to 9 mils in contact with PuO_2 , but only a total attack of less than one mil in contact with $\text{PuO}_{1.8}$. Rhenium showed not only a 2-mil attack in contact with PuO_2 but also a massive amount of vapor-phase transport from the metal disc to the capsule wall. No transport was observed in the rhenium capsule containing $\text{PuO}_{1.8}$ combined with less than a 1-mil attack.

Appearance of the oxides indicate that the $\text{PuO}_{2.0}$ was somewhat reduced (to ~1.94 O/Pu) and that the $\text{PuO}_{1.8}$ was not reduced significantly. The loss of oxygen from the $\text{PuO}_{2.0}$ was expected on the basis of the high initial partial pressure

Table 2-1
METALLOGRAPHIC RESULTS

Exposure Temp (°C)	Time (hr)	Alloy	O/Pu Ratio	General Solution	Penetration (mils)			Oxide Appearance		
					Inter- granular pene- tration	Oxide Ppt	Inter- Metallic Ppt	Second Phase (%)	O/Pu Ratio	Metallic Ppt
2000	1000	W	2.0	Unknown	10	0	0	10	1.94	Yes (1 mil max)
2000	1000	W-25Re	2.0	8	4	9	0	Unknown	----	No
2000	1000	Re	2.0	2	2	0	0	15	1.93	No (Transport)
2000	1000	W	1.81	1	30 max	0	0	60	1.76	Yes
2000	1000	W-25Re	1.79	0.4	0	<1	0	50-60	1.79-1.76	No
2000	1000	Re	1.78	<1	0	0	0	Unknown	----	No
1800	2000	W	2.0	2	10	0	0	Some	>1.95	No
1800	2000	W-25Re	2.0	0.5	0	7	0	Some	>1.95	No
1800	2000	Re	2.0	5	3	0	0	10	1.94	No (Transport)
1800	2000	Mo-50Re	2.0	0	8	1	0	50	1.79	Yes (4 mil max)
1800	2000	Mo	2.0	0	6	0	0	70	1.72	Yes (6 mil max)
1800	2000	W-30- Mo-30Re	2.0	1.5	<2	4	2	<40	>1.83	Yes (1 mil max)

of oxygen which would permeate through the capsule wall until the driving force for permeation (oxygen partial pressure) is reduced to some lower level (apparently ~ 1.94 O/Pu ratio for tungsten or rhenium alloys). Examination of the oxide also showed that tungsten was apparently soluble at temperature and precipitated out upon cooling. No visible precipitates were observed in oxides in contact with either W-25Re or rhenium. There is almost no difference between the tungsten, W-25Re, and rhenium specimens exposed at 2000°C for 1000 hours and at 1800°C for 2000 hours in contact with $\text{PuO}_{2.0}$. The tungsten and W-25Re appear somewhat better after the 1800°C exposure; the rhenium appears better after the 2000°C exposure. Somewhat less oxygen may have been lost after the 1800°C exposure, and no tungsten precipitates were visible in the oxide.

Molybdenum exhibited the best compatibility in the 1800°C exposure group consisting of W, W-25Re, Re, Mo-50Re, Mo, and W-30Mo-30Re. This appears to be attributable to loss of oxygen from the plutonia within the capsule. Metallographic examination of the plutonia in contact with the molybdenum alloys clearly shows two facts, (1) a significant loss of oxygen from the plutonia approximately in proportion to the molybdenum content, and (2) solubility at 1800°C and subsequent precipitation of a metallic phase directly proportional to the molybdenum content. Potter's Pu-O phase diagram (Reference 2) and estimation of the amount of pro-monotectoid PuO_{2-x} provides an indication as to O/Pu ratios for the three molybdenum-base alloys which range from ~ 1.72 for Mo to ~ 1.79 for Mo-50Re and ~ 1.83 for W-30Mo-30Re. (In all cases the accuracy may be no better than ± 0.05). Figures 2-1, 2-2, and 2-3 show this and are to be compared with Figure 2-4 which is $\text{PuO}_{1.8}$ after contact with tungsten at 2000°C for 1000 hours. Calculation of oxygen permeation through molybdenum for a single capsule in a vacuum based on data in Reference 3 indicates a far greater loss than that shown in the test capsules which have a secondary tungsten capsule providing some degree of oxygen retention. These results demonstrate that, to investigate the reaction of $\text{PuO}_{2.0}$ with molybdenum-base alloys, more plutonia must be used, or a more completely sealed system must be obtained. Work at General Electric (Reference 4) has demonstrated the capability of sealed systems using rhenium as a secondary vessel to retain oxygen in urania testing. A finite loss of oxygen appears to be beneficial; however, the effect of continued loss of oxygen may prove to be detrimental.

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Figure 2-1. PuO_2 after Exposure at 1800°C for 2000 hr in Contact with Mo (100X)

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Figure 2-2. PuO_2 after Exposure at 1800°C for 2000 hr in Contact with Mo-50Re (100X)

69-1656

Figure 2-3. PuO_2 after Exposure at 1800°C for 2000 hr in Contact with W-30Mo-30Re (100X)

69-1657

Figure 2-4. $\text{PuO}_{1.8}$ after Exposure at 2000°C for 1000 hr in Contact with W (100X)

Microhardness values have been obtained on the refractory metal discs after exposure in contact with the plutonia. A Leitz microhardness tester with a Vickers diamond and a 25-gram load was used to obtain hardness values. Table 2-2 lists the values obtained. The very light load used to measure hardness results in considerable scatter which may or may not be a reason why hardness values seem to vary randomly from the surface in contact with the plutonia (which should be harder because of the presence of oxygen) to the center of the disc (which should be somewhat softer). However, it may be concluded that the hardness of the majority of the alloys was not drastically affected by contact with plutonia. Rhenium proves to be the exception where, at 1800°C, a drastic increase in hardness occurred. Rhenium also exhibits unusual behavior at 2000°C, in that light and dark appearing grains have dissimilar hardness values. This phenomena is probably the result of crystal orientation variations. Vapor-transported rhenium had hardness values of 274 kg/mm² at 2000°C and 433 kg/mm² at 1800°C which is indicative of relatively pure material. Plutonia (PuO_{2.0}) in contact with rhenium at 2000°C has a hardness of 1720 kg/mm² which is more than twice as hard as the reported values for plutonia. Six remaining capsules of original plutonia have attained 5000 hours at 1800°C.

2.2 PURE PLUTONIA

Fifteen refractory metal capsules containing a purer form of PuO_{2.0} have been fabricated. Twelve of the capsules have been exposed at 1800°C. Six of these capsules have been removed after 2000 hour exposure time and are ready for metallography; the remaining six will be exposed for 10,000 hours.

Three of the capsules (W, W-25Re, and Re) contain PuO_{2.0} for exposure in conjunction with three matched capsules containing PuO_{1.8}. However, Mound Laboratory has been unable to deliver pure PuO_{1.8} pellets for this program; this has resulted in a four-month delay for this exposure.

2.3 CURIA

Six leak-tight, smear-free curia capsules have been fabricated for exposure at 2000°C for 1000 hours. The 10-gram batch of curia-244 received from ORNL was broken down into multiple 2-gram batches for ease of handling and control of operator dose levels during capsule fabrication.

Table 2-2
MICROHARDNESS VALUES

Exposure Temp (°C)	Time (hr)	Alloy	O/Pu Ratio	Microhardness (kg/mm ²)			As Received
				Surface (contact with plutonia)	Half- Way	Center (of 30-mil disc)	
2000	1000	W	2.0	464	514	514	462
2000	1000	W-25Re	2.0	464	464	464	600
2000	1000	Re	2.0	642	665	420	723
2000	1000	W	1.8	464	464	401	462
2000	1000	W-25Re	1.8	514	514	464	600
2000	1000	Re	1.8	dark* 464 light* 606	383 681	383 681	723 •
2000	1000	Re	None	dark* light*		317 572	
1800	2000	W	2.0	450	450	514	462
1800	2000	W-25Re	2.0	542	542	542	600
1800	2000	Re	2.0	1018	946	813	723
1800	2000	Mo-50Re	2.0	401	383	351	434
1800	2000	Mo	2.0	181	181	170	302
1800	2000	W-30Mo- 30Re	2.0	508	566	642	488

*Dark appearing grains have a lower hardness than light appearing grains.

The original approach to curia handling had been to use a large stainless-steel gloved box with a recirculating purified-argon system for reduction and pellet making, and to transfer pellets into air for encapsulation. During visits to Savannah River Laboratory and Oak Ridge National Laboratory, the necessity to perform all operations in an inert atmosphere was determined. To perform all assembly operations in an inert atmosphere, 2 Lucite gloved boxes were fabricated, one for reduction from CmO_2 to Cm_2O_3 and pellet making, the other for pellet loading and capsule assembly. Both boxes were designed for use in chemical fume hoods with flow-through argon vented to the hot laboratory air exhaust system.

The pellet making box (Figure 2-5) contains a specially designed graphite element resistance tube furnace for reduction of CmO_2 to Cm_2O_3 at 1300°C and for sintering 0.25-gram pellets at 1500°C , a specially designed cold press, a balance, and a variety of hand tools. Operations performed in this box included breakdown of the original 10-gram shipment to smaller batches, reduction,

70-386

Figure 2-5. Transfer of CmO_2 from Shipping Container to Gold Plated Storage Container on Balance

pelletizing, sintering, and bagout to the encapsulation box. Oxygen purity level ranged from 25 to 100 ppm during these operations.

The encapsulation box has a specially fabricated hood within the box for actual opening of the transfer bag, placing the curia pellet in the capsule, putting a thick metal disc on the top of the fuel pellet, smearing the weld joint for radioactive contamination, and placing the lid on the capsule. Figure 2-6 shows the pellet being held by vacuum tweezers in transit from the transfer container on the left to the capsule on the right. Figure 2-7 shows the loading of the metal disc on top of the fuel pellet already in the capsule. Oxygen purity of the argon in the box ranges from 100 to 200 ppm during the encapsulation operations.

Transfer from the encapsulation box to the electron beam welder is performed in air with the capsule lid in place. Lids are welded in a Hamilton Standard 6-kw electron-beam welder. Typical capsules containing curia are shown in Figure 2-8. All 6 curia capsules have been further encapsulated in tungsten secondary and tantalum tertiary capsules for safer high-temperature exposure.

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Figure 2-6. Transfer of Cm_2O_3 Pellet to Capsule

Figure 2-7. Loading Metal Disc

70-377

Figure 2-8. Typical Capsule Appearance of W, W-25Re, and Re (Left to Right)

2.4 PLUTONIA-MOLYBDENUM CERMETS

Six plutonia-molybdenum cermets fabricated at Battelle-Columbus Laboratories were encapsulated previously for exposure at 1800° and 2000°C. Two capsules completed 1000-hour exposures and were shipped to Battelle-Northwest for helium-release measurement. Gas measurements and analyses are listed in Table 2-3 (Reference 5). Table 2-4 provides information on fabrication dates and estimated residual helium at fabrication (Reference 6), exposure conditions, and calculated helium release. The estimated value of approximately 40% to 43% of helium generated being released is a strong function of the estimate of the amount retained during fabrication, which is at best a crude estimate.

Four more cermets are being exposed at 1800° and 2000°C and have attained 3000 hours of exposure time.

Table 2-3
PLUTONIA-MOLYBDENUM CERMET GAS ANALYSIS

Gas	Capsule		Blank
	AA-55	AA-52	
Gas Volume (cc at STP)	0.56	0.57	--
Mass Spec Analysis (Mole %):			
CO ₂	0.07	0.06	0.72
Ar	0.14	0.11	1.43
O ₂	4.30	3.01	42.4
N ₂	5.33	4.61	52.7
CO	0.10	0.10	0.73
He ⁴	89.7	90.9	0.01
H ₂	0.42	1.33	2.06

Table 2-4
HELIUM RELEASE DATA

Characteristic	Capsule	
	AA-55	AA-52
Battelle-Columbus Fabrication Date	4/23/69	4/22/69
Cermet Weight (g)	4.18	4.06
Estimated Residual Helium at Fabrication (cc at STP)	0.418	0.406
Exposure Temperature (°C)	1800	2000
Exposure Time (hr)	1000	1000
Exposure Completion Date	8/26/69	8/26/69
Calculated Helium Generated from Fabrication to Exposure Completion (cc at STP)	0.821	0.788
Total Helium Stored (cc at STP)	1.239	1.194
Helium Measured (cc at STP from Table 2-3)	0.503	0.518
Estimated Percent Released	40.6	43.4

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Section 3

CONCLUSIONS

Conclusions to date include:

1. Substoichiometric plutonia is less reactive than $\text{PuO}_{2.0}$ in contact with W, W-25Re, and Re.
2. Substantial loss of oxygen from molybdenum alloy capsules probably resulted in reduced reactions compared to what would have occurred without oxygen loss.
3. Rhenium transports rapidly in the presence of oxygen and a thermal gradient.
4. Although difficult to work with, curia can be encapsulated in contamination-free containers.
5. Approximately 40% of stored helium is released from plutonia-molybdenum cermet heated to 1800° or 2000°C for 1000 hours in closed containers.

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Section 4
REFERENCES

1. R. L. Andelin and J. D. Watrous. Plutonia/Curia Compatibility Testing Fourth Quarterly Report, MDC G1665, October 1969.
2. P. E. Potter. The Ternary System - Plutonium-Carbon-Oxygen. AERE-R5544, Atomic Energy Research Establishment, Harwell, V. K., August 1967.
3. R. E. Fryxell. Chemical Properties and Behavior of Urania Above 1500°C. GEMP-439, General Electric Company, Nuclear Materials and Propulsion Operation.
4. Seventh Annual Report. AEC Fuels and Materials Development Program, GEMP-1003, February 29, 1968.
5. R. Teats. Collection and Analysis of Helium Gas from Six Tungsten-25% Rhenium Clad Capsules Containing a Plutonia-Molybdenum Cermet, RM-C353, letter to J. D. Watrous, January 13, 1970.
6. W. M. Pardue, et al. Final Report for the Program to Develop Composite Fuel Forms of $\text{Pu}^{238}\text{O}_2$. BMI-1839, September 1969.

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