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***Mound Laboratory Isotopic
Power Fuels Programs:
October-December 1971***

March 24, 1972

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MOUND LABORATORY

Miamisburg, Ohio

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MONSANTO RESEARCH CORPORATION

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for the

U. S. ATOMIC ENERGY COMMISSION

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Foreword

This report presents the technological achievements of Mound Laboratory in its isotopic fuels programs during the past three months. The separate reports compiled here represent the work of the following sections of the Nuclear Operations Department (Director W. T. Cave): Nonweapons Programs (Manager R. E. Vallée), and Quality and Reliability (Manager D. P. Kelly).

This work is supported by the AEC Division of Space Nuclear Systems, Division of Isotopes Development, and Division of Reactor Development and Technology.

Summaries of all sections are compiled at the front of this report. Brief introductions to the work are included with each section.

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Plutonium-238 Fuels

FUEL PREPARATION

Multihundred Watt Development Spherical plutonium-238 fuel forms are being developed to meet the requirements of the multihundred watt heat source program. Spheres from 1.4-1.5 in. in diameter are being vacuum hot pressed. During this quarter seven spheres were prepared from pure plutonium oxide (PPO). Five spheres in the SP0 series had been prepared previously.

Sphere SP0-6 was fabricated with hydroxide-precipitated plutonium-238 dioxide (297 μm) which was sintered at 1200°C for 3 hr. The sphere was vacuum hot pressed in a 1.5 in. POCO-AXF graphite punch and die assembly at a 2500 lb load and 1480°C. Closure of the punches occurred about 6 min after the load was increased to 9000 lb. The sphere was at temperature for 30 min. The sphere was cooled at a rate of 10°C/min to ambient temperature. The sphere was cut from the die assembly. The pressed sphere showed no visible surface cracks. A hairline crack from pole to pole was observed during gaging five days after fabrication. SP0-6 is still intact 75 days after fabrication and has not shown any visible surface changes as of this time. The sphere had a calorimetry value of 112.38 W and a neutron emission of 4980 n/sec/g Pu. The gaging data indicated a 0.012 in. out-of-roundness. Figure 1 shows SP0-6 after removal from the graphite die.

Sphere SP0-7 was fabricated with hydroxide-precipitated plutonium-238 dioxide. The feed was fabricated by forcing uncalcined hydroxide through a 63 μm screen. The feed was sintered and oxygen-16 exchanged at 1150°C for 4 hr. The sphere was vacuum hot pressed in 1.5 in. POCO-AXF graphite punch and die assembly at 2500 lb and 1480°C. The pressure was increased to 5900 lb to ensure punch closure. The sphere was at temperature for 35 min. The sphere was cooled at a rate of 10°C/min to ambient temperature. A hairline crack was observed from pole to pole shortly after the sphere was removed from the die. The sphere was intact for two days when it was accidentally broken. The gaging data indicated a 0.021 in. out-of-roundness. The neutron emission was 7620 n/sec/g Pu, and the theoretical density was 81.2-84.6%.

Sphere SP0-8 was fabricated with oxalate-precipitated plutonium dioxide. The feed was outgassed at 1000°C for 1.5 hr. The feed was sieved through a 105 μm screen. The sphere was vacuum hot pressed in a 1.5 in. POCO-AXF graphite punch and die assembly at 2500 lb and 1480°C. Closure of the punches occurred 11 min after temperature was attained. The sphere was cooled to ambient temperature at 10°C/min. The sphere was broken into two half sections when it was removed from the die. The gaging data on the re-assembled sphere indicated a 0.037 in. out-of-roundness and a theoretical density of 84.5-91.0%.

Sphere SP0-9 was fabricated with hydroxide-precipitated plutonium-dioxide. The feed was <297 μm , which had been sintered at 1200°C for 3 hr. The sphere was vacuum hot pressed in a 1.45 in. POCO-AXF graphite punch and die assembly at a 2500-lb load and 1480°C.

FIGURE 1 -- SPO-6 after removal from graphite die.

The sphere was at temperature for 11 min. The sphere was cooled to ambient temperature at a rate of $10^{\circ}\text{C}/\text{min}$. The gaging data indicated an 0.018 in. out-of-roundness and an 82.0-85.1% theoretical density. The neutron emission was 8990 n/sec/g Pu. The sphere developed a hairline crack from pole to pole about an hour after removal from the die. The crack had not propagated 11 days after fabrication when it was drop tested. The sphere survived an 8 in. drop test onto a hood floor covered with tantalum foil. The pole-to-pole crack widened and about 1/4 of the sphere broke off when it was dropped from 12 in.

Sphere SPO-10 was fabricated with hydroxide-precipitated plutonium dioxide, which was sized to $<297\ \mu\text{m}$ and sintered at 1200°C for 3 hr. The sphere was vacuum hot pressed in a 1.45 in. POCO-AXF graphite punch and die assembly at 2500 lb and 1480°C . Closure of the die occurred 6 min after temperature was reached. The sphere was cooled at a rate of $10^{\circ}\text{C}/\text{min}$ to ambient temperature. The sphere developed a pole-to-pole crack shortly after it was removed from the die. The gaging data indicated an 0.018 in. out-of-roundness and an 80.8-83.8% theoretical density. The neutron emission was 4420 n/sec/g Pu. The sphere was drop tested six days after fabrication. The sphere broke into two sections when dropped from 8 in. The fracture occurred along the pole-to-pole crack.

Sphere SPO-11 was fabricated with hydroxide-precipitated plutonium dioxide which was sized to $<297\ \mu\text{m}$ and sintered at 1200°C for 3 hr. The sphere was vacuum hot pressed in a 1.45 in. POCO-AXF graphite punch and die assembly at 2500 lb and 1480°C . Closure of the die occurred about 10 min after temperature was reached. The sphere was cooled at a rate of $10^{\circ}\text{C}/\text{min}$ to ambient temperature. The sphere developed a pole-to-equator crack shortly after it was removed from the die. The equator was relatively smooth. The knife edge thickness of the punches was increased from 0.001 to 0.004 in. for this pressing. The sphere was photographed, neutron counted, and calorimetered. The neutron emission was 5330 n/sec/g Pu and the calorimetry value was 100.7 W. The gaging data indicated a 0.015 in. out-of-roundness and an 81.5-84.1% theoretical density.

The sphere was oxygen-16 exchanged for 30 min to remove any residual surface carbon. The skin temperature of the insulated sphere was 615°C during the oxygen-16 treatment. The sphere was drop tested six days after fabrication. The sphere survived successive drops of 8, 14, 20, 20, and 20 in. onto the glovebox floor which was covered with tantalum foil. The sphere fragmented into four sections on the fourth successive drop from 20 in. Carbon analysis showed the polar sample to be <100 ppm carbon, and the average carbon content of the equatorial sample was 185 ppm.

SPO-12 was fabricated with hydroxide-precipitated plutonium dioxide particles <297 μm which were sintered at 1200 C for 3 hr. The sphere was vacuum hot pressed in a 1.45 in. POCO-AXF graphite punch and die assembly at a 2500-lb load and 1480°C. Closure of the punches occurred 15 min after temperature was reached. The sphere was cooled at a rate of 10°C/min to ambient temperature. The sphere developed a pole-to-equator crack shortly after removal from the graphite die. The sphere had a power level of 101.1 W and a diametrical range of 1.453 to 1.467 in. No neutron data have yet been collected on this sphere. (W. A. Zanotelli and B. R. Kokenge)

Table 1

SPO SPHERE DATA

Sphere	Range of Diameters (20°C)(in.)	T.D. Range (%)	Power (W)	Specific Neutron Emission Rate (n/sec/g Pu)	Comments
SPO-6	1.506-1.518	82.4-84.4	112.4	4.98×10^3	Sphere intact 75 days after fabrication. Hydroxide feed <297 μm .
SPO-7	1.504-1.525	81.2-84.6	108.5	7.62×10^3	Hydroxide feed, green, sized <63 μm .
SPO-8	1.469-1.506 ^a	84.5-91.0 ^a	110.7	18.1×10^3	Oxalate-prepared $^{238}\text{PuO}_2$ feed; feed outgassed at 1000°C for 1.5 hr. Sphere in 2 pieces upon removal from die.
SPO-9	1.448-1.466	82.0-85.1	101.4	8.99×10^3	Hydroxide feed <297 μm .
SPO-10	1.451-1.469	80.8-83.8	100.5	4.42×10^3	Hydroxide feed <297 μm .
SPO-11	1.453-1.468	81.7-84.2	100.7	5.33×10^3	Hydroxide feed <297 μm .
SPO-12	1.453-1.467	81.6-84.0	101.1	-----	Hydroxide feed <297 μm .

^a Measurements made on re-assembled broken sphere.

Coating of PMC Discs with Molybdenum and Tungsten A study has been initiated to develop a method for coating PMC (Pu-Mo cermet) discs with either of the refractory metals, molybdenum or tungsten. A parametric investigation is presently under way using solid molybdenum discs as simulant substrates for the PMC discs. The first method to be studied is the hydrogen reduction of the metal hexafluorides in a barrel coater.

Thus far, six simulant discs have been coated with tungsten under various conditions. Although more data are needed, initial results are encouraging in that tungsten deposition does not appear very condition sensitive. Dense, uniform, continuous, one-mil coatings have been deposited. Efforts are continuing to increase the coating rate, and thus, obtain thicker coating of comparable quality.

In addition, 10 simulant discs have been coated with molybdenum under various conditions. As expected, molybdenum deposition is much more condition sensitive; thus more work is needed to optimize the coating quality and deposition rate. Several of the runs have yielded acceptable coatings but only at very low deposition rates.

(R. R. Jaeger)

FUEL CHARACTERIZATION

Evaluation of Molybdenum-Coated PMC Discs Two PMC discs [PM-56-B and PM-56-T; Type (-3)] were coated at Battelle Memorial Institute in Columbus, Ohio, by the molybdenum hexafluoride-hydrogen CVD (chemical vapor deposition) barrel-coating process. The results of all chemical and physical analyses on PM-56-B (BMI-12152) were reported.¹ PM-56T (BMI-10752) has been sectioned and submitted for photomicrographic and microprobe analyses of the PMC-molybdenum overcoat interface. The results of the metallographic and microprobe analyses will be reported as they are obtained. (G. N. Huffman)

Destructive Analyses of PMC Process Control Discs Production grade PMC discs are randomly selected from the production cycle for destructive analyses to ensure control of the process. Pie-shaped specimens are cut from the disc for metallographic, isotopic, heavy element, chemical, and spectrographic analyses. All data not previously reported in quarterly reports are listed in Table 2. Photomicrographs representative of the microstructure of the discs not previously reported are shown in Figures 2-4.² The physical analyses on the three most recently submitted discs, PM-105T, PM-115B, and PM-139T, are presented in Table 3.

Table 2

DESTRUCTIVE ANALYSES OF PRODUCTION GRADE PLUTONIA-MOLYBDENUM

Isotopic Analyses (wt % of Total Pu)	Process Control Disc Designation			
	PM-73B	PM-76B	PM-89B	PM-96T
²³⁶ Pu	<0.0001	<0.0001	<0.0001	<0.0001
²³⁸ Pu	79.9	80.0	80.0	80.0
²³⁹ Pu	16.4	16.5	16.5	15.9
²⁴⁰ Pu	2.75	2.71	2.71	2.80
²⁴¹ Pu	0.72	0.66	0.64	0.93
²⁴² Pu	0.17	0.19	0.15	0.39

Table 2 (Continued)

Heavy Element Analyses
(wt % of Total Pu)

Mass No.	Assignment	Process Control Disc Designation			
		PM-73B	PM-76B	PM-89B	PM-96T
227	-	<0.01	<0.01	<0.01	<0.01
231	-	<0.01	<0.01	<0.01	<0.01
233	U	<0.01	<0.01	<0.01	<0.01
234	U	0.70	0.41	0.60	0.69
235	U	<0.01	0.01	<0.01	<0.01
236	U	<0.01	0.01	<0.01	<0.01
237	-	0.04	0.05	0.03	0.06
241	Am	0.0764	0.0857	0.0739	0.1224

Isotopic Analyses
(wt % of Total Pu)

	Process Control Disc Designation		
	PM-105T3	PM-115B6	PM-139T6
^{236}Pu	<0.0001	<0.0001	<0.0001
^{238}Pu	80.2	80.3	80.4
^{239}Pu	15.7	15.8	15.2
^{240}Pu	2.78	2.76	2.73
^{241}Pu	0.92	0.86	1.22
^{242}Pu	0.37	0.37	0.49

Heavy Element Analyses
(wt % of Total Pu)

Mass No.	Assignment			
227	-	<0.01	<0.01	<0.01
231	-	<0.01	<0.01	<0.01
233	U	<0.01	<0.01	<0.01
234	U	0.57	0.69	0.36
235	U	<0.01	<0.01	<0.01
236	U	<0.01	<0.01	<0.01
237	-	0.06	0.06	0.07
241	Am	0.1228	0.1287	0.1231

Spectrographic Analyses
(ppm of Disc Weight)

Aluminum	-	-	-
Barium	-	-	-
Calcium	N.D.	N.D.	N.D.
Chromium	<50	<50	<50
Cobalt	N.D.	N.D.	N.D.
Copper	<50	<50	<50
Iron	580	900	600
Lead	<25	-	-
Magnesium	<25	<25	<25
Manganese	<50	<50	<50
Nickel	<50	<50	<50
Silicon	<50	<50	<50
Sodium	-	-	-

Chemical Analyses
(wt % or ppm of Disc Weight)

Molybdenum, %	18.72	17.78	18.15
Thorium, %	0.14	0.12	0.12
Carbon, ppm	-	<130	104
Chlorine, %	<0.02	-	-
Fluorine, %	<0.01	<0.01	<0.01
Total Pu, %	70.92	72.23	72.24

Table 3

PHYSICAL CHARACTERISTICS OF PLUTONIA-MOLYBDENUM
CERMET PROCESS CONTROL DISCS

	PM-105T3	PM-115B6	PM-139T6
Disc Type	-3	-6	-6
Weight, g	103.4	129.3	136.4
Volume, cm ³	9.664	12.28	12.67
Density, g/cm ³	10.7	10.5	10.8
Power, W	33.05	41.64	43.78
Neutron emission, n/sec	3.31×10^5	4.03×10^5	5.67×10^5
Power density, W/cm ³	3.42	3.39	3.46
Specific Power, W/g	0.320	0.322	0.321
Specific neutrons, n/sec/g ²³⁸ Pu	5700	5500	7400
Dimensions corrected to 20°C			
Diameter, in.	1.7493/1.9306	2.1128	2.1122
Thickness, in.	0.2185	0.2155	0.2225

FIGURE 2 - Cross section photomicrograph of PM-105T (125X) as polished.

FIGURE 3 - Cross section photomicrograph of PM-115B (125X) as polished.

FIGURE 4 - Cross section photomicrograph of PM-139T (125X) as polished.

Simple Method for the Determination of the Molybdenum Concentration of Molybdenum-Coated Plutonium Dioxide Particles A cermet composed of molybdenum and plutonium dioxide (PMC) is used as heat source material for SNAP (Systems for Nuclear Auxilliary Power) applications.

Since the molybdenum concentration has a definite effect on the power density and physical characteristics of the fuel material it must be accurately determined prior to hot pressing into the desired shape. The prepressed material consists of plutonium-238 dioxide particles (105 to 250 μm) which are coated by the chemical reduction of MoCl_5 by hydrogen. This technique is carried out in a fluid bed.

In the past the molybdenum concentration has been determined by a wet chemical method which requires a minimum of 3 hr to complete. The inherent corrosive nature of this method makes it undesirable for routine analysis in a stainless steel glovebox. As a result a method has been developed which requires no acids or bases, but instead utilizes the inherent oxidation characteristics of molybdenum.

At temperatures above 725 $^{\circ}\text{C}$, catastrophic oxidation of molybdenum and rapid volatilization of MoO_3 has been shown to occur.³ These distinctive qualities are very favorable to the simple technique of oxidizing the molybdenum coating, volatilizing the MoO_3 , and subsequently calculating the molybdenum concentration from the sample weight loss.

Experimental Initial studies were carried out using a thermogravimetric analysis apparatus previously described.⁴ This technique was employed in an attempt to follow the oxidation and volatilization that occurred during heating.

A 16-mg sample of molybdenum-coated plutonium dioxide was heated in air at 3 $^{\circ}\text{C}/\text{min}$ up to 910 $^{\circ}\text{C}$. The resulting thermogram, Figure 5, exhibited a weight gain from 490 $^{\circ}\text{C}$ to about 710 $^{\circ}\text{C}$. The weight remained constant until 740 $^{\circ}\text{C}$, at which point a rapid loss began to occur and continued to 810 $^{\circ}\text{C}$. At this temperature the rate of weight loss decreased noticeably, but continued until 910 $^{\circ}\text{C}$ was reached after which time no further loss was observed.

Originally attempts were made to calculate the molybdenum concentration from the weight gain at 710 $^{\circ}\text{C}$, assuming that it was oxidized to MoO_3 and no volatilization occurred. In every analysis the weight gain was insufficient to account for the known quantity of molybdenum. It was then assumed the probable cause of this error was the competing reactions of oxidation and volatilization occurring simultaneously. Efforts were made to volatilize the molybdenum by raising the temperature to 825 $^{\circ}\text{C}$ and holding until no further weight loss was observed. The concentration of molybdenum was then calculated from the weight loss. This technique resulted in insufficient weight loss to account for the known quantity of molybdenum.

In an effort to explain these anomalies, metallographic and electron microprobe examinations were made of the heated materials. The results exhibited the presence of an intermediate phase. Figures 6 and 7 are photographs of electron microprobe line scans for plutonium and molybdenum of a sample heated in air at 710 $^{\circ}\text{C}$ for 30 min. The horizontal line on the photos is the exact location of the scan, while the vertical peaks depict the intensity of the plutonium and molybdenum in Figures 6 and 7, respectively.

The darker region which shows no plutonium and a high molybdenum concentration is very likely MoO_3 . The intermediate region exhibits the presence of both plutonium and molybdenum, while the grey portion depicts a high concentration of plutonium and no molybdenum. These results can be compared to identical line scans of unheated material shown in Figures 8 and 9. The dark grey area is unoxidized molybdenum and, as expected, exhibits a high molybdenum concentration and the absence of plutonium. The lighter

FIGURE 5 - TGA thermogram of molybdenum-coated plutonium dioxide.

FIGURE 6 - A line scan for plutonium of a molybdenum-coated plutonium dioxide particle (13 wt % Mo) heated at 710°C for 30 min in air.

FIGURE 7 - A line scan for molybdenum of the same particle shown in Figure 6.

grey portion depicts the reverse element concentration. Virtually no intermediate phase is present. These results suggest that the intermediate phase is a ternary complex of Pu-Mo-O. This reaction would prevent all of the molybdenum from forming MoO_3 under the previously described conditions and, as a result, account for the insufficient weight gain for the correct calculation of the known quantity of molybdenum. This incomplete formation of MoO_3 would also effect the calculation of the molybdenum concentration from weight loss due to vaporization.

Further investigation showed that this ternary phase was readily decomposed at temperatures above 925°C under vacuum or air, since all the molybdenum could be accounted for by weight loss determinations in samples heated to this temperature. In addition to this no evidence of the ternary complex in the remaining plutonium dioxide was found by metallographic examination.

With these background data in mind, a simple oxidation-vaporization apparatus, shown in Figure 10, was designed and fabricated for this technique. It consists of a quartz vacuum chamber which houses a suspended platinum sample pan. The chamber is heated by a resistance furnace and can be evacuated or purged with oxygen as desired. A flowmeter is used to monitor a flow rate in the 300 to 400 ml/min range. The sample temperature is measured by a chromel-alumel thermocouple located in proximity to the sample pan.

The analysis involved weighing the sample pan, adding the sample, reweighing, then introducing the pan into the quartz vacuum chamber. The oxygen flow was adjusted to about 400 ml/min, and the sample temperature was raised to between 950-980°C. The length of heating was dependent upon sample size (maximum of 500 mg); however, 1 hr was found to be sufficient for a 200-to-300-mg specimen. After 1 hr, the chamber was evacuated with a roughing pump to a pressure of about 10 mm of Hg for 5 min, and the sample was reweighed. This was repeated until no further

weight loss occurred. A time parameter can be established for the selected sample weight.

Data shown in Table 4 compare the results of this technique with those of the wet chemistry method. The maximum disagreement is 0.9 wt % molybdenum for 11 determinations. This technique does have the shortcoming that any volatile impurities present will be calculated as molybdenum. However, the particles are normally heat treated to 700 to 800°C in a hydrogen atmosphere after coating and are examined metallographically. Otherwise the maximum error is the weighing accuracy which has a limit of ± 0.4 mg.

The data in Table 5 show calorimetry values for plutonium-238 before and after analysis. These determinations were made to check for possible loss of plutonium during the decomposition of the previously discussed Pu-Mo-O phase. It is obvious from the results that no loss occurred.

Conclusion This method has desirable features that are amenable to routine analysis in a stainless steel glovebox, namely:

- a) no requirement of corrosive acids or bases,
- b) it is a relatively rapid analysis, requiring about 1 hr,
- c) during most of the analysis the apparatus can be unattended,
- d) the apparatus is simple and economical to fabricate.

Since no coated standards were available, the method accuracy was compared only to the results obtained by the previously mentioned wet chemistry technique. The accuracy is believed to be affected mainly by the volatile impurities and the weighing accuracy, which in this work is estimated to be $\pm 1\%$.

During the course of this investigation a reaction was discovered between the molybdenum coating and the plutonium dioxide when they were heated in air at 710°C. Metallographic and electron microprobe examinations revealed the

FIGURE 8 - A line scan for plutonium of a molybdenum-coated plutonium dioxide particle (13 wt % Mo); unheated.

FIGURE 9 - A line scan for molybdenum of the same particle shown in Figure 8.

presence of both molybdenum and plutonium in this phase. This strongly suggests a Pu-Mo-O ternary complex. This is not surprising since other group IV/actinide complexes have been reported in the literature.⁵ (D. E. Etter and R. L. Deaton)

FIGURE 10 - Oxidation-vaporization apparatus.

Table 4

A DATA COMPARISON OF THE OXIDATION-
VAPORIZATION AND THE WET CHEMISTRY METHODS
FOR THE DETERMINATION OF MOLYBDENUM CONCENTRATION

<u>Batch No.</u>	<u>Oxidation-Vaporization (wt % Molybdenum)</u>	<u>Wet Chemistry (wt % Molybdenum $\pm 0.5\%$)</u>
PC1-191, 192	17.1	17.3
PC1-196-L	13.9	14.1
PC1-191-L	25.5	25.5
PC1-195, 196-S	11.9	11.6
PC1-195, 196-S	11.8	11.6
PC1-91, 94-R-5	14.8	14.9
PC1-195, 196-S-E2	21.3	20.9
PC1-195, 196-S-E2	21.2	20.9
PC1-195, 196-S-E2	21.2	20.9
PC1-195, 196-S-E2	21.0	20.9
PC1-195, 196-S-E2	21.1	20.9

Table 5

A COMPARISON OF CALORIMETER DATA BEFORE
AND AFTER ANALYSIS

<u>Batch No.</u>	<u>Before Heating (W/g $\pm 0.3\%$)</u>	<u>After Heating (W/g $\pm 0.3\%$)</u>
195-196-S-1	0.3086	0.3091
195-196-S-2	0.3071	0.3082
195-196-S-3	0.3087	0.3097
195-196-S-4	0.3076	0.3086

Capsule Design and Testing

FUEL/CAPSULE MATERIAL COMPATIBILITY TESTS

Plutonium-238 Dioxide/Mo-50 wt % Re at 800 and 1000°C Two Mo-50 wt % Re capsules containing plutonium-238 dioxide powder were examined after one had been heat treated at 800°C for 360 days and the other at 1000°C for 180 days. Configuration of the compatibility capsules is given in Figure 11. Chemical analysis of the plutonium dioxide is given in Table 6.

FIGURE 11 - Configuration of capsule used in plutonium-238 dioxide/Mo-50 wt % Re compatibility test.

800°C Results After exposure to plutonium dioxide for 360 days at 800°C, Mo-50 wt % Re normally develops a thin ($\sim 1\ \mu\text{m}$) surface layer as seen in Figure 12. Examination of this layer with the electron microprobe* found about 80 wt % molybdenum, ≤ 15

*Analysis of this layer with the electron microprobe was difficult due to the thinness of the reaction product relative to the size of the electron beam which was 1 to 2 μm . Thus the quantitative analysis should be considered very approximate.

FIGURE 12 - Mo-50 wt % Re after exposure to plutonium dioxide for 360 days at 800 °C. 1210X, unetched.

Table 6

CHEMICAL ANALYSIS OF PLUTONIUM DIOXIDE
POWDER USED IN COMPATIBILITY TEST WITH
Mo-50 wt % Re

Impurity	Concentration (wt %)
Ni	<0.002
Fe	0.06
Al	0.07
Ca	0.03
B	<0.01
Si	trace
Cr	<0.03
Cu	trace
Mg	0.01
Zn	<0.03
Na	trace
Total	<0.26

wt % rhenium, 1 wt % iron*, possibly a small amount of plutonium, with oxygen assumed to be present. At the outer edge of this layer are small particles (indicated by A in Figure 12) of a second oxide. These particles were too small to be analyzed by the electron microprobe but visually appear to be plutonium dioxide observed in another portion of the capsule. Small metallic particles (indicated by B in Figure 12) can be seen at the oxide/base metal interface. These particles were also too small to analyze by the electron microprobe.

A thicker (~10 μm) reaction product was observed several times along the capsule walls and is described by the photomicrograph in Figure 13 and x-ray strip chart analysis in Figure 14. The reaction product appears to be an oxide which is optically active under polarized light. Analysis of the oxide found about 17 wt % iron, 63 wt % molybdenum, <12 wt % rhenium,** with oxygen assumed to be present.

*0.06 wt % iron was present as an impurity in the plutonium dioxide.

**Quantitative values for the molybdenum and rhenium were obtained by using the 52.6 wt % molybdenum, 47.4 wt % rhenium base metal as a standard. The iron determination was made using a 100 wt % iron standard.

FIGURE 13 - Mo-50 wt % Re after exposure to plutonium dioxide for 360 days at 800°C. Line indicates traverse of electron beam for x-ray strip chart analysis of Figure 14. 1210X, unetched.

This oxide appears to penetrate the base metal to depths of about 5 to 7 μm . Only in these areas did oxide penetration occur. Metal particles are dispersed at the outer edge of the oxide (in the area indicated by A) and in the base metal just below the oxide (denoted by B). The metallic particles, which seem similar to those indicated by B in Figure 12, appear to be enriched in rhenium and iron and depleted in molybdenum.

1000°C Results Figure 15 is a photomicrograph of the Mo-50 wt % Re capsule bottom after heat treating for 180 days at 1000°C. Figure 16 is an x-ray strip chart analysis which helps characterize the plutonium dioxide/Mo-50 wt % Re reaction zone. The outer phase of the reaction zone identified by A contains plutonium, about 81 wt % molybdenum*, with oxygen assumed to be present. The darker particles in this oxide were too small to resolve with the electron microprobe but appear higher in plutonium than the oxide matrix. Maximum thickness of the oxide reaction product was about 10 μm . The inner phase of the reaction zone identified by B is present as a surface layer which is about 2 to 7 μm thick and is found in the grain boundaries of the base metal to a maximum depth of 20 to 25 μm . This phase appears metallic and contains 57 to 67 wt % rhenium, 27 to 35 wt % molybdenum, and 5 to 7 wt % iron**. An intermetallic compound (assumed to be the X-type electron compound) was observed in the grain boundaries below the reaction zone. The intermetallic compound present in the reaction zone visually appeared different from the intermetallic observed in the base metal.

*This value for molybdenum was obtained by using the 52.6 wt % molybdenum base metal as a standard.

**Quantitative values for molybdenum and rhenium were obtained by using the 52.6 wt % molybdenum, 47.4 wt % rhenium base metal as a standard. The iron determination was made using a 100 wt % iron standard.

FIGURE 14 - X-ray strip chart analysis of reaction zone found on Mo-50 wt % Re after 360 days at 800°C. Area analyzed is indicated in Figure 13.

FIGURE 15 - Mo-50 wt % Re after exposure to plutonium dioxide for 180 days at 1000°C. Line indicates traverse of electron beam for x-ray strip chart analysis of Figure 16. 1210X, unetched.

Figure 17 is a photomicrograph of the top of the capsule and is typical of the Mo-50 wt % Re not in intimate contact with plutonium dioxide. Presence of the Pu/Mo oxide and the substantial decrease in the amount of the Re/Mo/Fe phase appears correlated with direct contact between plutonium dioxide and Mo-50 wt % Re.

Summary and Discussion At both 800 and 1000°C, plutonium dioxide selectively oxidized the molybdenum in a Mo-50 wt % Re alloy. At 800°C, the reaction product consisted of a 1 μ m thick oxide layer containing 80 wt % molybdenum, ≤ 15 wt % rhenium, and ≤ 1 wt % iron, with several 10 μ m thick deposits of an oxide containing 63 wt % molybdenum, 17 wt % iron, and < 12 wt % rhenium. At 1000°C, the reaction product consisted of an oxide containing 81 wt % molybdenum, and plutonium. Maximum thickness of this oxide was 10 μ m. Formation of molybdenum-bearing oxide has not been observed in any of the $^{238}\text{PuO}_2/\text{Mo}$ compatibility couples previously reported⁶⁻⁹ and therefore appears to depend on the presence of rhenium.

The $^{238}\text{PuO}_2/\text{Mo-50 wt % Re}$ interaction also resulted in the formation of a Re/Mo/Fe phase. At 800°C, this intermetallic compound was observed as small particles at the oxide/base metal interface and dispersed at the outer edge of the thicker oxide. At 1000°C, the Re/Mo/Fe formed a 2 to 7 μ m thick surface layer and was found in the grain boundaries to a maximum depth of 20-25 μ m. Formation of the Re/Mo/Fe phase could be due to the enrichment of iron and/or the enrichment of rhenium which would result from the selective removal of molybdenum during the oxide formation mentioned above. Possible identification of this intermetallic compound includes the σ and χ electron compounds.

Oxide penetration of the Mo-50 wt % Re occurred below the 10 μ m thick oxide deposits on the 800°C sample. Maximum depth of penetration was about 7 μ m. No oxide penetration of the 1000°C sample was observed. (D. R. Schaeffer)

FIGURE 16 - X-ray strip chart analysis of reaction zone of Mo-50 wt % Re indicated in Figure 15.

FIGURE 17 - Mo-50 wt % Re after exposure to plutonium dioxide for 180 days at 1000 °C; top of capsule. 1210X, unetched.

References

1. Mound Laboratory Isotopic Power Fuels Programs: April-September, 1971, MLM-1827, (Jan. 14, 1972), pp. 32-33.
2. Mound Laboratory Isotopic Power Fuels Programs: April-September, 1971, MLM-1827, (Jan. 14, 1972), pp. 33-38.
3. M. Simmad and Aija Spilners, Trans. AIME, 203, 1011 (1955).
4. D. E. Etter and W. H. Smith, "A Compact Microthermogravimetric Analysis Apparatus," to be published in J. Chem. Ed.
5. O. A. Ustinov, M. A. Andrianov, N. T. Chebotarev, and G. P. Noveselov, Zh. Neorgan. Khim, 15 (2), 582 (1970).
6. J. E. Selle, J. R. McDougal, and D. R. Schaeffer, The Compatibility of Plutonium-238 Dioxide With Platinum and Platinum-Rhodium Alloys: Interim Report, MLM-1684 (Jan. 30, 1970), 124 pp.
7. J. E. Selle, J. J. English, P. E. Teaney, and J. R. McDougal, The Compatibility of $^{238}\text{PuO}_2$ with Various Refractory Metals and Alloys, Interim Report, MLM-1706, (Oct. 23, 1970), 214 pp.
8. J. E. Selle, A Summary of the Phase Diagrams and Compatibility of PuO_2 with Various Materials, MLM-1589, (Apr. 1969), 38 pp.
9. W. C. Pritchard, K. A. Johnson, J. A. Leary, and W. J. Maraman, Compaction and Sintering of PuO_2 -Mo Powder Mixtures, LA-2621, Los Alamos Scientific Laboratory, Los Alamos, New Mexico (Nov. 1961).