~~FOR REFERENCE
NOT TO BE TAKEN
FROM THIS ROOM~~

MLM-MU-78-64-0003

MILLIWATT GENERATOR HEAT SOURCE
PROGRESS REPORT

January 16, 1978 - April 15, 1978

Wayne R. Amos
Program Manager

MOUND FACILITY

Miamisburg, Ohio

operated by

MONSANTO RESEARCH CORPORATION

a subsidiary of Monsanto Company

for the

U. S. DEPARTMENT OF ENERGY

Contract No. EY-76-C-04-0053

Monsanto

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DLC

MILLIWATT GENERATOR HEAT SOURCE
PROGRESS REPORT

I. Introduction

Activities at MRC associated with the Milliwatt Generator Heat Source efforts over the period January 16, 1978, to April 15, 1978, are presented below.

II. $^{238}\text{PuO}_2$ /Titanium Compatibility Studies (P. E. Teaney, A. R. Kiefer and D. L. Roesh)

Continuing are the compatibility studies of various materials as previously described (Section IV, MWG Progress Report, April 16 - July 15, 1977). Completed during the report period were the metallographic and microprobe analyses of the PuO_2 /titanium compatibility specimens. The specimens were tested at 800°C and 1000°C as shown in the test matrix (Table I). Compatibility specimens were tested for time periods ranging from 32 days to 720 days at 800°C , and from 30 days to 180 days at 1000°C .

Table I

Ti/ PuO_2 Compatibility Test Matrix

<u>Temp. ($^\circ\text{C}$)</u>	<u>Time (Days)</u>					
800	32	61	90*	180	361	720
1000	30	60	90*	180		

* duplicate specimens and a blank were tested for 90 days at each temperature

The configuration of the compatibility specimen is shown in Figure 1. The specimen consisted of three (3) capsules. The inner (titanium) capsule was gas tungsten arc welded after being loaded with fuel. The fueled titanium specimen was subsequently electron beam welded in a tantalum capsule followed by enclosure in an outer container of Hastelloy-X. The outer container provided oxidation resistance for the high temperature heat treatment in air. The purpose of the tantalum

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Configuration of Titanium/Plutonium
Dioxide Compatibility Specimens

FIGURE 1

capsule was to protect the titanium liner from possible nitrogen diffusion through the Hastelloy-X during the long term-high temperature exposure. The tantalum also served as a barrier to prevent an eutectic reaction between the titanium and the Hastelloy-X.

Prior to assembly, the tantalum and titanium capsules were chemically cleaned in a 10ml HF, 10ml HNO₃, 30ml lactic acid solution to assure that no protective oxide barrier existed on the surface of the specimens.

The impurity content of the fuel used for the tests is shown in Table II. The fuel contained less than 1.9 weight percent total impurities.

All of the specimens tested at 1000°C were bulged, especially in the area of the specimen that was not in contact with the fuel. A blank (non-fueled) specimen that was tested for 90 days was bulged in all areas of the specimen. The bulging resulted from internal pressure due to the high temperature aging. The area of the fueled capsules that was in contact with the fuel was not as distorted, but was embrittled with respect to the upper portion of the capsule and contained numerous stress cracks. One of the most severe conditions is shown in Figure 2. The bottom portion of the capsule apparently was embrittled by solid state diffusion of oxygen from the fuel early in the test. Therefore, during the test the upper (more ductile) portion of the capsule deformed while the lower portion developed stress cracks.

The fuel-liner interface of a specimen after 30 days at 1000°C is shown in Figure 3. Reaction along the inside edge of the specimen is indicated by the presence of porosity and a two-phase microstructure which ranged in depth from 50 to 85 µm from the fuel/metal interface. The reaction zone has a Widmanstätten structure consisting of plutonium and titanium. Electron microprobe analysis indicated that the lighter phase was predominately titanium (approximately 95 weight percent) while the darker phase consisted of approximately 33 weight percent plutonium in titanium. One of the

Table II

Fuel Impurities
(Percent as Metal)

Ni - 0.05

Fe - 0.36

Sn - trace

Al - 0.11

Ca - 0.07

B - 0.04

Mn - 0.06

Pb - 0.23

Si - trace

Cr - 0.41

Mo - <0.14

Cu - <0.04

Co - 0.28

Mg - 0.07

Zn - 0.04

Na - trace

Total <1.90%

Liner Sidewall

Titanium Compatibility Capsule
after 181 days
at 1000°C

PuO₂/Ti interface

Bottom of titanium
capsule

Tantalum barrier

25X (as polished)

Figure 2

PuO_2/Ti Reaction
after 30 days at 1000°C

250X (as polished)

Figure 3

sites of electron microprobe analysis is shown in Figure 4A in addition to photomicrographs from the cathode ray tube display of the electron microprobe. A density distribution of the area scanned was obtained using backscattered electrons from the sample (Figure 4B) while the concentrations of plutonium in the area are shown in Figure 4C (obtained using plutonium m_{α} x-radiation). The concentrations of plutonium (4C) corresponded to the higher density areas in 4B and to the darker phase areas in 4A. Most of the pores in the specimen did not contain a reaction product. However, when a reaction was present, it was enriched in plutonium and depleted in titanium with respect to the matrix. In addition to the observed reaction, plutonium diffusion was detected to a depth of 325 μm from the fuel-metal interface.

Reactions in the remaining 1000°C specimens were similar to those in the 30 day specimen. However, the amount of porosity and reaction increased with additional time at 1000°C. Plutonium penetrated the grain boundaries of the specimens more severely in some areas of the specimens than in others. Plutonium penetrated entirely through the liner (80 mils) at one site in a 90 day specimen and at four locations in the 181 day specimen. The areas of severe reaction appeared to coincide with highly stressed locations in the liner. Disregarding these localized penetrations of plutonium, an attempt was made to measure the general depth of plutonium diffusion in the specimens tested at 1000°C. The results are summarized in Table III.

Table III

Plutonium Diffusion in Titanium (1000°C)

<u>Time (hr)</u>	<u>Depth of Bulk Diffusion of ^{238}Pu in μm (ΔX)</u>	<u>ΔX^2 or μm^2</u>
30	325 μm	105625
60	550	302500
90	575	330625
90	710	504100
181	755	570025

A) Specimen after 30
Days at 1000°C
(showing site of
electron microprobe
analysis)

250X (as polished)

B) Density Distribution of
the Area from Figure 4A

C) Plutonium Distribution of
the Area from Figure 4A

Figure 4

These data were fitted to the parabolic rate equation $\Delta X^2 = kt + b$ where ΔX is the reaction depth in microns, t is the time in hours and k and b are constants. The resulting rate curve ($\Delta X^2 = 118t + 1.1 \times 10^5$) is shown in Figure 5. The curve is meant to simply illustrate a trend in the data, and is not intended to prove that a parabolic rate law is being followed.

All of the specimens tested at 800°C were integral and there were no visible signs of capsule distortion due to internal pressure. The inside edge of the 800°C specimens appeared to be friable in nature after exposure to the fuel. All specimens (except blanks) showed indications of material flaking off into the fuel. The only indication of fuel-liner reaction after 32 days at 800°C was a slight ($<5\mu\text{m}$) loss of material from the inside edge of the liner. The 61 day specimen was also slightly irregular along the inside edge. In addition at one location in the liner, small plutonium enriched precipitates delineated the grain boundaries to a depth of $28\mu\text{m}$ from the inside edge.

Duplicate specimens were tested for the 90 day time period. One specimen showed no evidence of reaction except for flaking or loss of material from the inside edge. The remaining specimen was similar to the 61 day specimen with localized grain boundary penetration of plutonium to a depth of $280\mu\text{m}$.

No plutonium diffusion or grain boundary precipitation was detected in the 180 day specimen. However, irregularity along the inside edge of the liner indicated approximately $10\mu\text{m}$ loss of material into the fuel.

Plutonium enriched grain boundary precipitates were detected to a depth of $170\mu\text{m}$ in one area of the 361 day specimen. Plutonium diffused to a depth of $300\mu\text{m}$ into the titanium matrix at that location.

The only test at 800°C showing general migration of plutonium into the titanium matrix was the 720 day specimen.

At the shorter time periods, plutonium penetrated the matrix only at widely scattered locations. The typical appearance of the fuel-metal interface after 720 days at 800°C is shown in Figure 6. Loss of material into the fuel is indicated by the irregularity along the inside edge. Voids and plutonium enriched inclusions are present generally for a depth of approximately 320 μm. Plutonium penetrated the grain boundaries to a depth of 850 μm in localized areas of the specimen.

In summary, the data show that titanium is not a desirable encapsulant for plutonium dioxide in the 800°C to 1000°C temperature range. This is not surprising. Thermodynamically, reaction between the materials would be expected. At 927°C, the free energy of reaction for the equation

is -29.8 Kcal¹. There was the possibility, however, that the reaction product might form a protective layer inhibiting further reaction. The results show that this did not occur. Also, it was hoped that if a reaction did occur, a rate could be determined that might allow use of the material as an encapsulant with a predictable life expectancy. Unfortunately, the erratic nature of the plutonium grain boundary reaction, especially in the highly stressed areas of the specimen, made this determination impossible.

III. Hardware Production (R. W. Saylor)

The liner cap blanking die has been modified with a hardened tool steel punch replacing the previous carbide material. Carbide chipping in the blanking die punches has been a common occurrence and to date, four dies have been modified in the above manner. Additional dies have performed well, requiring only routine maintenance.

An additional (unscheduled) 45 strength member bodies were fabricated to replace hardware lost through engineering

¹F. L. Oetting, Chem. Rev., 67:3, 261 (1967)

Reactions along Fuel-metal Interface
of Titanium Specimen after 720 Days at 800°C

62.5X (as polished)

250X (as polished)

Figure 6

evaluation and the abnormally high dye penetrant rejects found in the Sheet 16, Lot 7 raw material (Section II, MWG Progress Report, October 16, 1977 - January 15, 1978).

Efforts are underway to standardize all gage masters at the low limit of the product tolerance range. A uniform system for mastering gages will simplify their use and lessen the chance for error.

Two lathes equipped with a digital readout system and optical comparator are now operating continuously to meet production commitments. An EE Monarch lathe is being upgraded with this equipment to provide back-up in case of problems on the present lathes.

Hardware continues to be produced on schedule with high acceptance rates for each of the seven components. Shown in Table IV are the number of components produced to date and the acceptance rates. Also shown are the cost of defectiveness and the dollar percent defectiveness values.

IV. Encapsulation (C. E. Burgan)

Twenty-five pressure burst capsules were fabricated from Lot 8 T-111. These units will be used to qualify the T-111 for production usage.

Also fabricated were ten simulant units (filled with a mixture of tungsten and molybdenum). A portion of these units will be used as mock-ups for fueled units in establishing impact gun parameters for an upcoming reimbursable order.

A new torch drive system was installed for the strength member and clad welding operations.

Encapsulation of production subassemblies and assemblies continues on schedule with high acceptance rates. To date, 472 units have been encapsulated through the liner, 429 units through the strength member, and 386 units through the clad. DoE has now accepted a total of 243 heat sources.

Shown in Table V is the Quality Report on Assemblies and the dollar percent defectiveness values. To date, for the entire program (hardware and encapsulation), the total cost of defectiveness is \$20,136, the total value of all product is \$919,170, and the dollar percent defectiveness is 2.2%.

Table IV
Quality Report on Hardware

<u>Component</u>	<u>Fabricated</u>	<u>Number Prime</u>	<u>Number Example Weld</u>	<u>Eng. Eval.</u>	<u>Number Scrap</u>	<u>Process Yield (%)</u>
Liner Shim	615	611	-	-	4	99.3
Liner Cap	615	612	3	-	0	100.0
Liner Body	570	557	11	-	2	99.6
Strength Member Cap	630	607	17	-	6	99.0
Strength Member Body	630	532	69	12	17	97.3
Clad Cap	555	546	7	-	2	99.6
Clad Body	555	540	7	-	8	98.6

Overall Process Yield 99.0%

Dollar Value of Fabricated Hardware \$190,193

Cost of Defectiveness \$ 1,973

Dollar Percent Defectiveness 1.0%

Table V
Quality Report on Assemblies

Liner Assembly	Fabricated	572
	Rejected	6 ¹
	Yield	98.7%
	Cost of	
	Defectiveness	\$3,720
	Value of	
	Fabricated Units	\$288,920
Strength Member Assembly	\$ % Defective	1.3%
	Fabricated	429
	Rejected	11 ²
	Acceptable	418
	Yield	97.4%
	Cost of	
	Defectiveness	\$6,754
Clad Assembly	Value of	
	Fabricated Units	\$187,682
	\$ % Defective	3.6%
	Fabricated	386
	Rejected	11 ³
	Acceptable	375
	Yield	97.2%
	Cost of	
	Defectiveness	\$7,689
	Value of	
	Fabricated Units	\$252,375
	\$ % Defective	3.0%

Remarks:

¹ 3 - dye indications 1 - power failure 1 - bad weld
 1 - fuel problem

² 11 - ultrasonic indications in the weld area

³ 10 - outside diameter in the heat affected zone too large
 1 - nick on outside diameter of cap

V. Pressure Burst Capsule Evaluation (D. A. Pawlak)

Twenty-five pressure burst capsules were fabricated for production qualification of Lot 8 T-111, and testing of these capsules has been initiated. Results to date are shown in Table VI.

Table VI
Pressure Burst Test Results
of
Lot 8 T-111 Capsules (1010°C)

<u>Capsule</u>	<u>Internal Pressure (psia)</u>	<u>Rupture Time (hrs)</u>	<u>Failure Location</u>
MPT-01H	8001.2	24.49	Cap/body weld - body interface
MPT-02H	6500.5	90.38	Cap/body weld

Rupture times compare favorably with prior data from Lot 7 capsules (both the lot qualification values and the TMS values).

VI. Surveillance (D. A. Pawlak)

A portion of the surveillance activities include the long range storage (at 210°C and 410°C) of pressure burst capsules, with subsequent testing of the stored units at various time intervals to FY2003 (SLA BB Drawing 309768). Protection of the T-111 from air oxidation during these long time periods at elevated temperatures will be accomplished by encapsulation of each pressure burst capsule in a Hastelloy C-276 sleeve with end caps.

Each constant temperature oven will contain direct drive mechanisms, which will eliminate malfunctions due to bearing, pulley, or belt problems. Each will also contain solid state proportioning control systems, with uniformity within $\pm 0.75\%$ of the set point and a control accuracy of $\pm 0.5^\circ$.

Although the Hastelloy C-276 and the constant temperature ovens have been on order for several months, vendor delays

have resulted in deliveries now projected for June, 1978. Upon receipt of the materials and equipment, the first surveillance pressure burst capsules will be put on test.

VII. Ultrasonics (W. A. Dudley)

Efforts are being made to ultrasonically evaluate pressure burst capsule welds. This presently cannot be done because of pressure burst capsule stem interference with the ultrasonic fixturing. An order has been placed for a specially built ultrasonic transducer.

Also being investigated is the feasibility of non-destructively evaluating T-111 sheet material for microinclusions by acoustical microscopy. A contract was placed with Sonoscan, Inc. The initial results of their study with "typical" T-111 sheets of .040" thickness are expected in May 1978.

VIII. Reimbursables

Fabricated and delivered to LASL for the U.S. Navy were five heat sources of the MWG design, with the exception that the wattage level was 4.5 watts (E-45064). (A total of six were delivered because wattage requirements were not met in one unit - the sixth unit will be returned to Mound.)

Essentially completed is a Sandia reimbursable order (E-40549) for fabrication and delivery of 32 fueled units. Shipment has been made on 21 units, with the remaining 11 units to be shipped to GEND in late April, 1978.

Recently received from SLA were two more reimbursable orders. One is for disassembly of two RTG's and evaluation of the non-Mound fabricated heat sources (E-45062). The other order calls for fabrication, impact, and evaluation of eight fueled units (E-45061).

The total programmatic FY-78 reimbursables to date is 204.6K.

X. GEND TMS Units

Fabricated and evaluated were 25 WR heat sources for GEND TMS activities. These units, which will be shipped to GEND

in late April, 1978, were fabricated as part of the overall P&S funding. This completes Mound's obligations to GEND (delivery of capability, feasibility, and TMS units) until shipment of production units is initiated in late FY-78.

IX. Savannah River Interface

With the first encapsulation responsibilities being transferred to Savannah River in FY-80, communications between the sites have been initiated to simplify the eventual technology transfer. Copies of the hardware drawings, welding fixtures, alpha boxes, and associated purifying systems, have been sent to Savannah River personnel in addition to all the operation sheets for liner welding and non-destructive testing.

Many of the technical details were discussed at meetings at Savannah River in mid-February and mid-April, with Mound personnel in attendance. Six persons representing SRP and DuPont engineering visited Mound on February 24, 1978, and two SRP personnel observed the liner welding operations on March 15, 1978. Another Mound visit of SRP, SRL, and DuPont engineering personnel is tentatively planned for May 10, 1978.

In late June, 1978, SRP will ship to Mound sufficient oxide for encapsulation of 12 sources. These units will be subjected to various compatibility and impact tests, identical to those previously performed on Mound units. The data from these 12 units will then allow comparison between SRP oxide (oxalate process) and Mound oxide (hydroxide process). Although some of the compatibility tests will not be completed for two years, the initial data is expected to provide sufficient information for meaningful long range predictions.