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LOS ALAMOS SCIENTIFIC LABORATORY
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Quarterly Status Report on

# Plutonium-238 Space Electric Power Fuel Development Program (U)

July 1-September 30, 1969

UNITED STATES
ATOMIC ENERGY COMMISSION
CONTRACT W-7405-ENG. 36

AEC RESEARCH AND DEVELOPMENT REPORT

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This LA...MS report presents the status of the Plutonium-238 Space Electric Power Fuel Development Program of Group CMB-11 of LASL. Previous reports in this series, classified Confidential RD, are:

LA-4068-MS
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# Plutonium-238 Space Electric Power Fuel Development Program (U)

July 1-September 30, 1969

to

Space Isotopic Fuels and Materials Branch

Space Electric Power Office

Division of Space Nuclear Systems



UNITED STATES
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PROGRAM 07433

# PLUTONIUM-238 SPACE ELECTRIC POWER FUEL DEVELOPMENT

Person in Charge: R.D. Baker

Principal Investigator: J.A. Leary

## I. INTRODUCTION

Several programs sponsored by SEPO/SNS during FY 1969 demonstrated advantages of solid solution ceramics and cermets as radioisotopic heat source fuel forms. In order to utilize the principal advantages of each fuel type, a new program direction was established for FY 1970. The objective was to synthesize, fabricate, and characterize a solid solution cermet (SSC) fuel for the Transit application. The following fuel properties were established as requirements:

1. Fuel to be fabricated in modular form as right circular cylindrical discs nominally 2.15 in. dia by 0.21 in. thick.
2. The ceramic phase in the cermet to be a solid solution of $ThO_2$ in $^{238}PuO_2$.
3. The metal phase in the cermet to be molybdenum.
4. Power density to be 3.2 watts per cc of fuel, or greater.

These experiments define the limits of porosity, $ThO_2$, and Mo that can be used in the fuel. The following deployment was established for the immediate goal:

1. Ceramic phase to consist of 10 percent by wt. $ThO_2$, 90 percent by wt. $^{238}PuO_2$ (80 percent $^{238}Pu$ enrichment), and approximately 6 percent by volume porosity.
2. Cermet to contain 12.8 percent by wt. [illegible] percent by vol.) of Mo.
3. The cermet disc to be "overcoated" with a 0.004 in. thick layer of Mo.

Fuel simulant discs are also required for large capsule tests such as impact and re-entry simulation. A comparison of estimated fuel properties and simulant properties is given in Appendix II. Present efforts are directed towards measuring fuel properties, increasing fabrication capabilities, and determining some of the more important simulant properties.

The tasks and major milestones established for this program are itemized in Appendix I and in Section IX, respectively.

## II. OUTLINE OF PROCESS

It should be emphasized that most of the specialized pieces of apparatus required for this work such as the hot press and the barrel coater were designed, purchased, assembled, and placed in operation during this report period. A limited amount of developmental studies were required, of course, but all efforts were directed toward a SSC fuel product which met the requirements as noted above. The flow sheet with the various production process steps is shown in Fig. 1. Those steps will be discussed in detail in the following sections of this report. For ease and convenience, those sections are arranged in the same format as the

[redacted]

# CERMET FLOW SHEET

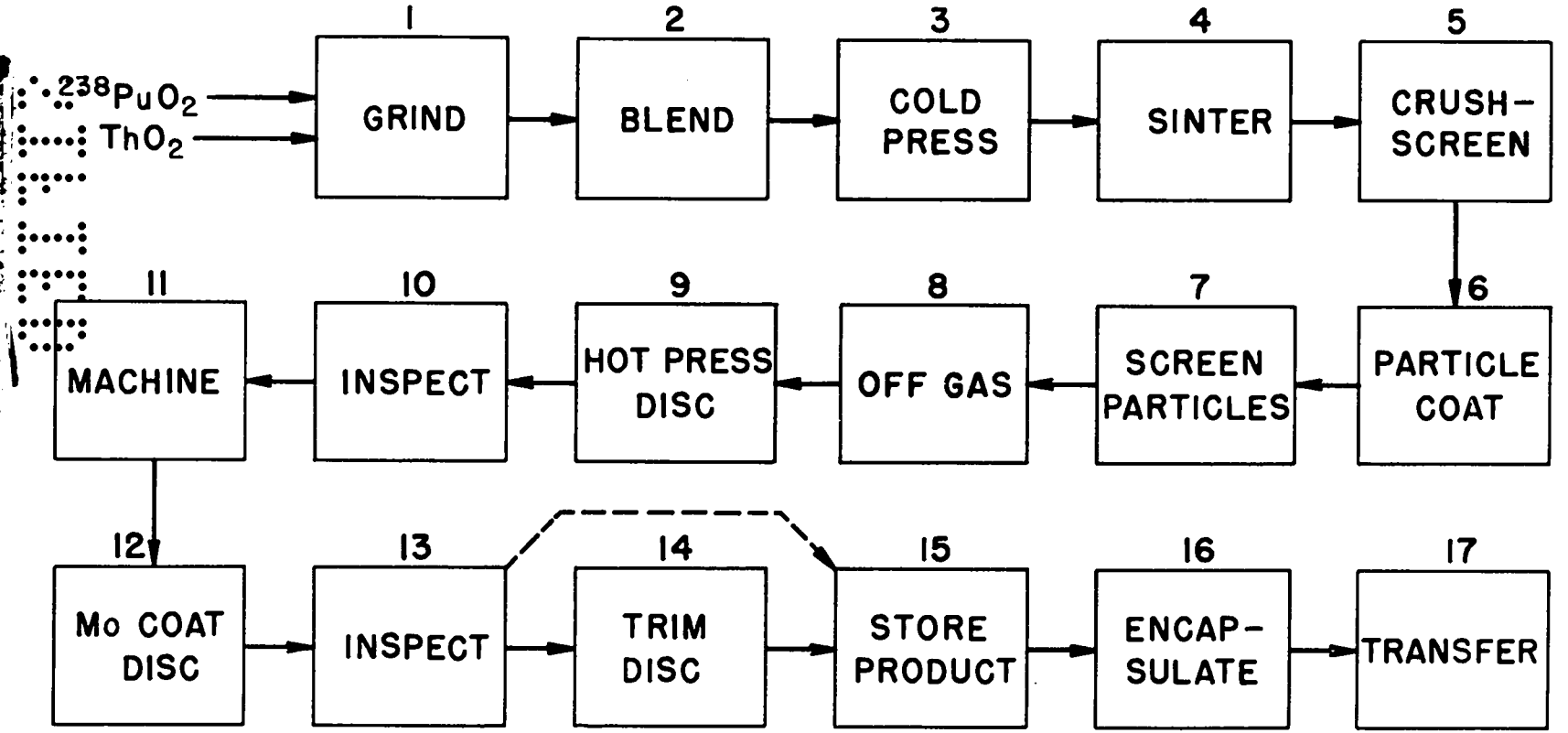



Figure 1

weekly reports to the SNS/SEPO office.

## III. SYNTHESIS AND FABRICATION OF SOLID SOLUTION CERMETS

Before any of the operational or process steps on the flow diagram are initiated, the "as received" $^{238}PuO_2$ is outgassed at ≥ 1000°C for 1 hour. Incoming $ThO_2$ feed powder is also outgassed under identical conditions.

### A. Preparation of Feed Material (Steps 1 - 5 on Flow Diagram)

The outgassed $^{238}PuO_2$ and $ThO_2$ feed materials are ground in separate ball mills. The 3 in. dia mills have tungsten carbide liners and use stainless steel milling balls. Maximum loadings are 125 g each. Conditions for a typical milling are 80 hours at 100 rpm for the $ThO_2$ and 24 hours at 100 rpm for the $^{238}PuO_2$. Essentially 100% of the product is ≤ 100μ at the conclusion of a typical milling operation.

The separately ground oxide feed materials are blended in another ball mill with the final mixture adjusted to contain 90 w/o $^{238}PuO_2$.

The blended powders are "cold-pressed" at 14,000 psi for 1 minute to form 1.4 in. dia discs. A typical disc weighs 100 g. These discs are sintered at 1600° for 2 hours in at atmosphere of $CO_2$. This sintering temperature was chosen to eliminate the "dusty" product obtained with low-fired discs.

After cooling and removal from the furnace, the discs are ground in a vibratory grinder and the resulting powder is screened to concentrate the 105 - 177μ size particles. Approximately 35 w/o of the disc is recovered in the desired size range. The remainder of the $^{238}PuO_2$-$ThO_2$ is recycled back to the powder blending step.

### B. Coating of Powder (Step 6 on Flow Diagram)

The sized particles are coated with Mo by the CVD (chemical vapor deposition) process. The coating involves the gas-phase decomposition of $MoF_6$ at 607°C on the surface of the $^{238}PuO_2$-$ThO_2$ solid solution particles. The reacting gas is a mixture of $MoF_6$, $H_2$, and Ar. The quantities of each constituent are controlled by gas flowmeters in each of the incoming lines. Equilibration times of 2 hours are required at the following flow rates to deposit 12.8 w/o Mo on the oxides: $MoF_6$ = 18 cc/min, $H_2$ = 1500 cc/min, and Ar = 2300 cc/min. The coated particles are rescreened to 105 - 177μ followed by a second outgassing (Step 8). Figure 2 shows a typical lot of coated feed powder.

### C. Hot Pressing (Step 9 on Flow Diagram)

The coated particulate feed powder is next subjected to a hot pressing operation to form the high density cermet product. Specimens are pressed at 2100°C for 10 min at 12,500 psi. The die and punch material is POCO AXF graphite coated with 0.002 in. NbC. A 0.0003 in. Ta liner is also used in the die. Twelve cermet specimens have been pressed using these operational parameters. These cylindrical specimens all were 0.25 in. dia x 0.3 in. high. Average immersion densities of 95.1% of theoretical were obtained from the twelve specimens along with average power densities of 3.31 w/cc. The hot pressing operation is followed by appropriate visual, X-ray radiography, dimensional, and gravimetric inspection. Any machining to size that may be required is done at this time (Steps 10 and 11 on Flow Diagram). A photomicrograph of typical $^{238}Pu$-$ThO_2$ SSC is shown in Fig. 3.

### D. Overcoating (Step 12 on Flow Diagram)

The hot-pressed products are overcoated with 0.004 in. molybdenum for safety in subsequent handling

50μ

REPRESENTATIVE SAMPLE OF $^{238}PuO_2$-$ThO_2$ SOLID SOLUTION COATED WITH VAPOR DEPOSITED Mo PRIOR TO HOT PRESSING
(200 X A. P.)

Figure 2.

$^{238}PuO_2$ - $ThO_2$ S.S. CERMET



(100X)



(250X)

Figure 3

and manipulation. The process is chemically similar to Step 6 above, although slightly different equilibration parameters are used. In addition, since the disc is now formed, a different reaction vessel is utilized for the overcoating process. This vessel is called the "barrel" coater and is essentially a 4 in. diameter graphite tube heated resistively. The tube may be rotated and it is positioned at an angle of 15° above horizontal. Therefore, the disc undergoes a mild and gentle tumbling action while being coated with molybdenum. It is planned to overcoat only one disc at a time. Equilibrium conditions are 1 hour at 620°C with flow rates as follows: $MoF_6$ = 31 cc/min and $H_2$ = 1900 cc/min.

E. Machining

Any final machining or trimming is done at this point using a jeweler's lathe. The final fuel form is inspected and, if satisfactory, transferred to storage for future use.

IV. PROPERTIES

A. Impact Testing

Six $^{238}PuO_2$-$ThO_2$ (3.5 watts/cc) pellets and six $^{238}PuO_2$ pellets were shipped to Mound Laboratory for impact testing at 325 and 250 ft/sec. Some of the pellets will be aged prior to impact to determine this effect. Pellet characteristics are given in Table I. Densities were measured by immersion of a representative pair of each type of material.

Table I

Impact Samples Sent to MLM on September 4, 1969

| Pellet No. | Composition, w/o | Density, g/cc |
|---|---|---|
| 81081-1 | 82% $PuO_2$-18% $ThO_2$ | 10.2 |
| 81081-2 | " | " |
| 81081-5 | " | " |
| 81081-6 | " | " |
| 81081-7 | " | " |
| 81081-8 | " | " |
| 81101-1 | 100% $PuO_2$ | 11.1 |
| 81101-2 | " | " |
| 81101-3 | " | " |
| 81101-4 | " | " |
| 81101-5 | " | " |
| 81101-6 | " | " |

B. Compatibility

A tungsten mesh furnace for use in compatibility testing in the 1500°C region was received late in the quarter, and the installation order has been issued.

During the quarter two capsules, LP-7 and -8, were assembled and placed in test at 900°C to evaluate the compatibilities of $^{238}PuO_2$- 18 w/o $ThO_2$ solid solution, Mo, and Ta - 10 w/o W. Capsules containing TZM against two compositions of $^{238}PuO_2$-$ZrO_2$ solid solution at 900°C (D) and containing TZM against $^{238}PuO_2$ and $^{238}PuO_2$-$ThO_2$ solid solution at 1800°C (HP-1 and HPT-1) were removed from test and are now being examined. The current status of the various tests is given in Table II.

C. Mechanical Properties of $^{238}Pu$ Fuel Forms

The necessary hardware for measuring compressive strains (with strain gauges) in $^{238}PuO_2$ ceramics during room-temperature compressive testing is now being assembled. A device that will allow all strain gauge connections to be made in an open-faced hood is being assembled, and the necessary cables and plugs to carry the out-put signal from the glove box containing the Instron tester to the instrumentation are being installed. Initially, compression tests will be attempted with 90-degree rosette strain gauges on the specimens in order to measure both Young's and Poisson's ratio. (S. E. Bronisz and R. E. Tate)

VI. HELIUM MIGRATION FUNDAMENTAL STUDIES

A. Alpha-bombardment of $ThO_2$

Electron microscopy: Transmission electron microscopy of alpha-bombarded $ThO_2$ is being directed primarily toward examination of flakes extracted from bulk material by a replication process. One flake thus removed from the spalled surface of a $ThO_2$ disc is shown in Fig. 4. The disc had been irradiated to a dose of $3.8 \times 10^{17}$ ions $cm^{-2}$ and then heated to 1000°C for 1 h, after which spallation to a depth of ~15 μ was observed. The bimodal nature of the fracture is illustrated in Fig. 4, the smooth spall surface being seen at left center and the rough spall surface at the right.

Figure 5 shows a transmission electron micrograph of the lower edge of the flake. It illustrates a variation that has been observed in the defect structure of the $ThO_2$. The damage shown at the left was caused

[redacted]

Table II

Compatibility Test Program Summary (September 15, 1969)

| Capsule No. | Interfacial Arrangement[a] | Test Temp., °C | Status |
|---|---|---|---|
| D | $ZrO_2$\|Y\| /TZM/$^{238}PuO_2$ - 35 $ZrO_2$\|Y\| /TZM/ $^{238}PuO_2$ - 7 $ZrO_2$\|Y\| | 900 | Test completed after 6671 hr. |
| HP-1 | $^{238}PuO_2$/TZM/$^{238}PuO_2$/TZM | 1800 | Test completed after 1000 hr. |
| HP-3<br>HP-4 | Same as HP-1 | 1800 | Test continuing, 2600 hr. to date. |
| HPT-1 | $^{238}PuO_2$ - 53 $ThO_2$/TZM/$^{238}PuO_2$ - 55 $ThO_2$/TZM | 1800 | Test completed after 1000 hr. |
| HPT-2 | Same as HPT-1 | 1800 | Test continuing, 2600 hr. to date. |
| HPT-3<br>HPT-5 | $^{238}PuO_2$ - 56 $ThO_2$/TZM/$^{238}PuO_2$ - 56 $ThO_2$/TZM | 1800 | Test continuing, 2600 hr. to date. |
| LP-1<br>LP-2<br>LP-3<br>LP-4 | $ThO_2$/TZM/$^{238}PuO_2$ - 56 $ThO_2$/TZM/$^{238}PuO_2$ | 900 | Test continuing, 4000 hr. to date. |
| LP-5 | TZM/Pt-20 Rh/$^{238}PuO_2$/Pt-20 Rh/$^{238}PuO_2$ - 56 $ThO_2$/Pt-20 Rh/$ThO_2$/Pt-20 Rh/TZM | 900 | Test continuing, 2400 hr. to date. |
| LP-6 | Same as LP-5 except Pt-40 Rh instead of Pt-20 Rh | 900 | Test continuing, 2400 hr. to date. |
| LP-7 | Mo/Ta-10W/$^{238}PuO_2$-18 $ThO_2$/Mo/Ta-10W/ $^{238}PuO_2$ - 18 $ThO_2$/Mo | 900 | In test 8/22/69, 600 hr. to date. |
| LP-8 | Mo/Ta-10W/$^{238}PuO_2$ - 18 $ThO_2$/TZM | 900 | In test 8/22/69, 600 hr. to date. |

[a]Compositions given in weight percent.

Fig. 4. Extracted flake from spall surface of alpha-bombarded $ThO_2$. 16,000X.

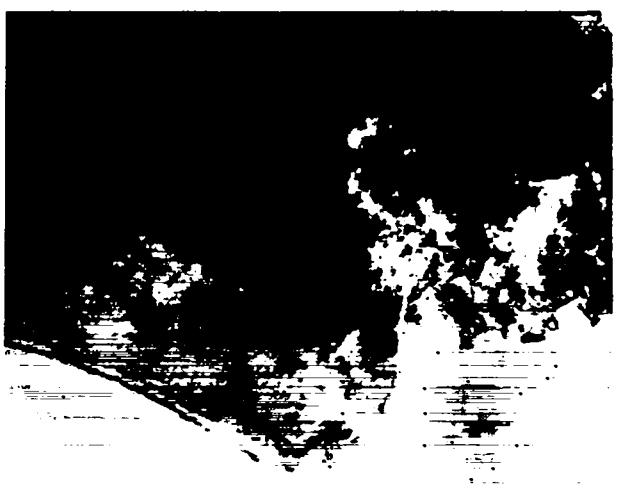


Fig. 5. Transmission electron micrograph of extracted flake shown in Fig. 3. 43,000X.

[redacted]

by the penetration of alpha particles through the flake and into the $ThO_2$ beyond the depth, after first having traversed a sintering void. This structure consists of a fine dispersion of defects characteristic of radiation-damaged material. The damage at the right, however, resulted from the deposition of helium ions in the flake itself. Here, where severe distortion seems to have accompanied the fracture, high content of dislocations typical of deformed material is seen in addition to the fine dispersion of defects.

Currently, other studies are underway to determine the nature of the defect structure of bombarded $ThO_2$ as a function of depth, i.e. original surface, mid-depth, and spall surface. Also, beam heating in the electron microscope is being utilized to study the annealing behavior of defects found at the different depths. Defects that are initially finely dispersed in flakes will, after having been annealed at high temperature, coalesce into dislocation loops, as shown in Fig. 6. The sample illustrated in this figure had been bombarded to a dose of $1.9 \times 10^{17}$ ions $cm^{-2}$.

Although it is rather difficult to be able to study the behavior of defects in a region of helium deposition, because of the profusion of superimposed damage, in one sample where such a study was possible (see Fig. 7), helium bubbles were found after the sample had been beam heated. This sample had been irradiated to a dose of $3.8 \times 10^{17}$ ions $cm^{-2}$. These

Fig. 6. Alpha-bombarded $ThO_2$ after beam heating, showing dislocation loops. 105,000X.

Fig. 7. Alpha-bombarded $ThO_2$ after beam heating, showing helium bubbles. 105,000X.

bubbles show crystallographic surfaces approximately parallel to the <113> direction. They were found to be very resistant to high-temperature annealing, neither changing in size nor becoming mobile even when the sample was heated to near its melting point.

Helium release from $ThO_2$: A $ThO_2$ disc that had been bombarded to the relatively low dosage of $9.4 \times 10^{16}$ ions $cm^{-2}$ was heated in a gas-release detection apparatus. The heating rate was $\sim 20^{\circ}C\ min^{-1}$, and the disc did not spall. Preliminary evaluation of the results indicates that bursts of gas occurred between 1200 and 1500°C, with the maximum rate of gas release occurring at 1380°C.

Annealing of lattice damage: An attempt was made to determine the lattice-damage annealing curve for a $ThO_2$ disc that had been bombarded to a dose of $1.9 \times 10^{17}$ ions $cm^{-2}$. The average temperature attained by the disc during bombardment was 260°C. X-ray lattice parameter determinations were utilized to monitor the damage, and thus reflect atomic-level, point-defect strains rather than larger-scale damage such as dislocation loops and point-defect clusters. The lattice parameter for the disc was determined (at room temperature) before bombardment, after bombardment, and after each successive 1-hr anneal in 100°C increments between 100 and 700°C. The initial lattice dilation amounted to 0.67% and, after 1 hr at 600°C, was 0.40%, i.e., 40% of the damage had been recovered at the end

of the 600°C anneal. Spallation of a portion of the bombarded region occurred during the 1-hr anneal at 700°C, thus terminating the experiment. (F.W. Clinard, Jr.)

B. Release Studies

Temperature-ramp experiments: Eight temperature-ramp experiments were done with $^{238}PuO_2$ samples. Included were one 1/4 in. dia x 1/4 in. thick pellet, one sample of Lot 93 PTF microspheres, and six samples of various sizes of powders made by crushing 1/4 in. x 1/4 in. pellets. The powders were graded through a series of sieves, the grain size of the material, approximately 20 μm, invariably being smaller than the particle size. Ceramography indicated that the original pellets were well sintered and had no apparent interconnected porosity.

An attempt was made to heat the samples at a linear rate of 20°C $min^{-1}$. Although the actual rate attained was not quite linear, it was close to linearity over the range of fast release (10 to 90% of the helium).

The results are summarized in Table III. The mean particle diameters listed are the averages of 100 to 150 microscopic measurements of the shortest dimension of the particles, which were not always equiaxed. The standard deviations of the particle diameters are about 15%. The temperatures at which 10, 50, and 90% release was observed are given in the columns headed $T_{10}$, $T_{50}$, and $T_{90}$. $T_{max}$ is the temperature at which the maximum rate occurred.

Temperature-ramp experiments offer the possibility of resolving simultaneous processes having different temperature dependences. The resolution, if present, shows up as more than one release rate peak at different temperatures. Such multiple rate peaks have not been seen in the present experiments. Thus, we conclude that if more than one release process is operative, all processes show their major contribution over about the same temperature range of 1200 to 1600°C.

Since temperature is varied, a single experiment yields information about the temperature dependence of the release phenomenon. The results for two of the experiments have been analyzed through use of the mathematics for a time-dependent diffusion coefficient to provide plots of log D' vs 1/T. Instead of the hoped-for straight line, the points describe a curve. Thus, a single pair of Q and $D'_0$ for the Arrhenius law $D' = D'_0 \exp(-Q/RT)$ does not apply. If, however, a straight line is forced on the data, a slope giving an activation energy of 70-80 kcal is obtained. These data are being further analyzed.

Aging effects: A new batch of 1/4 in. dia $^{238}PuO_2$ pellets was received in April, 1969. The oxide had been precipitated 3 days prior to the date of the sintering operation, which was April 4, 1969. One pellet (12967) was run isothermally at 1397°C for 7 days, following sintering. $D/a^2$ computed from the 50% release time was $0.53 \times 10^{-5}$ $sec^{-1}$. Another pellet (12702) from the same batch was run at 1442°C for 138 days following sintering. The corresponding $D/a^2$ was $5.4 \times 10^{-5}$ $sec^{-1}$. These results, along with those for the four $^{238}PuO_2$ pellets run previously, are given in Table IV, where the data are arranged in order of increasing temperature.

Table III

Helium Release During Temperature-Ramp Experiments

| Experiment No. | Mean Particle dia (μm) | $T_{10}$, °C | $T_{50}$, °C | $T_{90}$, °C | $T_{max}$, °C | Remarks |
|---|---|---|---|---|---|---|
| — | 86 | 1030 | 1170 | 1500 | 1090 | Lot 93 microspheres |
| 12695A | 211 | 1275 | 1440 | 1590 | 1430 | Duplicate samples |
| 12695B | 189 | 1285 | 1425 | 1555 | 1360 | Duplicate samples |
| 12695C | 345 | 1275 | 1450 | 1585 | 1440 | |
| 12695D | 262 | 1250 | 1420 | 1550 | 1430 | |
| 12695E | 74 | 1165 | 1325 | 1480 | 1295 | |
| 12695F | 122 | 1245 | 1380 | 1525 | 1360 | |
| 12696 | — | — | — | >1500 | >1600 | 1/4" x 1/4 " pellet |
| 12694B | 270 | 1250 | 1405 | 1555 | 1390 | |

Table IV

Helium Release Aging Effects

| Experiment No. | Temperature (°C) | $(D/a^2)_{50} \times 10^5$ ($sec^{-1}$) | Age (days) | $T_{50}$ (sec) |
|---|---|---|---|---|
| 12585 | 1364 | 0.058 | 193 | 53180 |
| 12697[a] | 1397 | 0.53 | 7 | 5876 |
| 12584 | 1412 | 0.77 | 220 | 4026 |
| 12702[a] | 1442 | 5.4 | 138 | 575 |
| 12582 | 1466 | 1.13 | 178 | 2752 |
| 12583 | 1812 | 2.75 | 182 | 1127 |

[a] New batch

It can be seen that the 7-day old pellet released what little helium it had at a rate comparable with those of the previous samples, but that No. 12702 exhibited a faster release rate at 1442°C than did the old batch at 1612°C. Although this comparison was made in order to reveal aging effects, the observed variations are believed to result from inherent

differences among the samples rather than from age. Another pellet is now being run to recheck the anomalously fast release of 12702.

Data analysis on $^{238}PuO_2$ Pellets: Further analysis of the isothermal release data from the four $^{238}PuO_2$ pellets that had been run previously has now been completed. As described earlier, the extraction of "instantaneous" effective diffusion coefficients, D', from the fractional release vs time data showed that D' varied during the course of a run, thus suggesting that a classical diffusion model with constant D' was inadequate to describe the data. The fractional release plots from these experiments also showed that the release rate became very slow before 100% release of the helium inventory could be attained. The fractional release vs time thus leveled out at less than 100%, and some fraction of the helium was released very slowly or not at all. The amount thus retained in the samples appeared to be temperature dependent, ranging from 15% at 1412°C to 5% at 1614°C. Examination of the release rates at the ends of the runs shows that the rates were constant, thus some sort of steady state was observed in three of the four samples run.

It can be shown that for a constant D' (= $D/a^2$) the time for release of 99% of the helium is: $t_{99} = 0.42/D'$. At that time, the fractional rate is: $dF/dt = 0.090\ D'$. Approximately values of D' were obtained from the 50% release times for the samples, and the observed and calculated rates at $t_{99}$ may be compared in Table V. $R_{99}$ is the rate predicted at 99% release; $R_{obs}$ is the rate actually measured at $t_{99}$.

In each instance, the observed rate is seen to be less than the steady-state value, suggesting that diffusion release was complete. The empirical model suggested by this result and by the leveling out of the fractional release is that only part of the helium is released by diffusion and that the remainder is, in essence, not released on the time scale of our experiments. By adjusting the diffusion equations to allow for leveling out, a better, although still imperfect, fit can be obtained for a constant D'. Data pertaining to the amount of helium that appears to be permanently trapped are given in Table VI. Colume 4 is the predicted inventory at $t_{99}$ (1% of the initial inventory), column 5 is the difference between column 4 and the actual inventory at $t_{99}$, and column 6 is the fraction of the initial inventory that was permanently trapped, $F_T$.

Table V

Observed and Calculated Helium Release Rates at $t_{99}$

| Experiment No. | T (°C) | D' x $10^5$ ($sec^{-1}$) | Calc $T_{99}$ (sec) | Calc $R_{99}$ x $10^6$ (cc-$sec^{-1}$) | $R_{obs}$ x $10^6$ (cc-$sec^{-1}$) |
|---|---|---|---|---|---|
| 12582 | 1465 | 1.13 | 37200 | 0.60 | 0.2 |
| 12583 | 1612 | 2.75 | 15300 | 1.29 | 0.2 |
| 12584 | 1412 | 0.77 | [illegible] | [illegible] | [illegible] |
| 12585 | 1364 | 0.058 | 720000 | [illegible] | [illegible] |

Table VI

Fraction of Helium Permanently Trapped

| Temperature (°C) | Plateau (fraction) | Retained (cc/g) | Calculated Steady State (cc/g) | Trapped (cc/g) | Fraction trapped |
|---|---|---|---|---|---|
| 1465 | 0.84 | 0.042 | 0.003 | 0.039 | 0.15 |
| 1612 | 0.95 | 0.010 | 0.003 | 0.007 | 0.03 |
| 1412 | 0.75 | 0.065 | 0.003 | 0.062 | 0.24 |
| 1364 | > 0.80 | < 0.104 | 0.003 | < 0.101 | < 0.39 |

As far as can be seen from the four data points available, $F_T$ increases with decreasing temperature. A not unreasonable linear fit to the data is to assume: $F_T = 1 - 0.00059\ T(^{\circ}C)$, which has the properties that at 1700°C no trapping occurs, and that at 0°C all the helium is trapped, none being available for release by diffusion.

Another feature of the measured release rate curves is the presence of far more "noise" than is inherent in the electronics of the gas release apparatus. Helium appears to be released in many short bursts during the isothermal period. The bursts constitute a small fraction of the release rate during the period when the major part of the helium is being released, but are quite important during the plateau period when the rate has become small and constant. A further refinement of the above model, in that the bursts represent helium released from "permanent" traps, is suggested. Such an erratic release is not at all consistent with a bulk diffusion process, but is consistent with release along grain boundary channels or, possibly, with the disappearance of a trap, as through annealing, and the consequent release of the trapped helium.

Helium storage near the surface of a solid: Alpha

particles generated near the surface of a solid have some probability of escaping and, thus, of not being stored as helium in the lattice if the location of the decaying nucleus is closer to the surface than the penetration distance of the particle. An X-ray diffraction pattern from a sample will be characteristic of material close to the surface, since the penetration distance of the X-rays is smaller than the range of alpha particles for high z-number elements. Therefore, it is of interest to compare the amount of helium stored close to the surface of a sample with that stored deep within the sample. An expression for fractional storage as a function of depth is thus desired.

Consider a volume element, dV = dxdydz, located at depth z within the solid. The alpha particles that come to rest in dV will be generated by atoms lying on the surface of a sphere centered on dV and having radius a, the penetration distance. Since the material is homogeneous, dV cannot store more than it generates and the fraction stored, F, will be unity for $z > a$. For $z < a$, the sphere penetrates the surface and its only part contributing to storage in dV will be that lying below the surface.

Using the usual spherical coordinates to calculate the surface area of the protruding part of the sphere $A_p$:

$$dA = r d\theta \cdot r \cos\theta \, d\Phi = a^2 \cos\theta \, d\theta \, d\Phi$$

$$A_p = 2 \int_{\theta = \arcsin z/a}^{\pi/2} \int_{0}^{\pi/2} a^2 \cos\theta \, d\theta \, d\Phi$$

$$A_p = 2a^2 \pi (1 - z/a) .$$

The area of the sphere lying below the surface is:

$$A_B = 4\pi a^2 - 2\pi a^2 (1 - z/a) .$$

The fractional area below is:

$$F = 1/2 (1 + z/a) \quad 0 \le z \le a$$

and $F = 1 \quad z > a$

The fraction F, defined for the two ranges of z, is the fractional distribution of stored helium as a function of depth from the surface, z.

Next, consider a surface layer of thickness d, where $d \le a$. An element of volume dxdydz at depth z within this layer will generate Q dxdydz, where Q is the generation rate per unit volume. The amount stored in the volume element is F·Q dxdydz. And the total amount stored in a column having the dimensions dx by dy by dz is:

$$\int_0^d F \cdot Q \, dx dy dz = Q \, dx dy \cdot \frac{d}{2}\left(1 + \frac{d}{2a}\right)$$

The total generated in the column is: Q dx·dy·d.

The fraction stored in the column (and hence in the surface layer) is: total stored/total generated. The final result, for the fraction stored near the surface, is:

$$F_S = 1/2 \left(1 + \frac{d}{2a}\right) \qquad 0 \le d \le a$$

where d is the depth of the surface layer, a is the range of the particles in the solid, and $F_S$ is the fraction of generation stored in the layer of depth d.

For the case where the X-ray penetration depth is $d = 2\mu m$ and the alpha particle range is $a = 15\mu m$, $F_S = 0.53$. Thus 53% of the helium generated in the $2\mu m$ surface layer will be stored, and assuming a steady generation rate, effects on the diffraction pattern caused by helium storage in the surface layer will accumulate between 0.5 and 0.53 times as fast as do the same effects in the interior of the sample.

General comments about helium release: Experience with two different batches of $^{238}PuO_2$ pellets makes it increasingly evident that sample variability is a serious problem. At present, there are insufficient data for one to be able to specify the critical properties of a pellet, but some likely possibilities are grain size, pore size, inclusion content, and density. Since engineering predictions of helium release will be based on laboratory measurements, it is of great importance that the production fuel be uniform and that the measurements be made on the same material that is used for fuel.

In order to provide data for engineering predictions of helium release from a new fuel form, isothermal release measurements should be made in the range of capsule operating temperatures and temperature-ramp experiments should be performed. Since the release rate will, presumably, be slow at operating temperatures,

the isothermal runs should be continued as long as is practicable. A minimum of three tests would be required: two isothermal runs (one each of the maximum and minimum operating temperatures) and one temperature-ramp test, which would be continued until all the helium were released or the maximum reentry temperature were reached. Microstructural changes, particularly the formation of bubbles or cracks, and changes in the dimensions or gross density of the sample should be looked for.

Consideration is being given to the possibility of measuring the helium inventories on pellet samples held for long periods in sealed capsules in order to obtain long time data. Since compatibility testing involves this sort of treatment, perhaps the samples coming from compatibility tests could be analyzed for helium content. Such analysis should be a valuable supplement to the three tests proposed above.

Vapor pressure enhancement by knock-out: An experiment was done to examine the transport of $^{238}Pu$ from $^{238}PuO_2$ by self radiation knock-out of surface material. The technique used was to make a standard vapor pressure determination using collimated geometry to define a molecular beam from the sample. The beam was collected on a copper target which was subsequently counted to determine the plutonium deposit. Two exposures were made, one for 48 hr at 298°K, the other for 115 hr at 1263°K. The total alpha count on the two targets was 66 and 145 c/m, respectively. An open crucible was used instead of the normal Knudsen cell to gain sensitivity, but exact conversion of the results to pressure data was thus precluded. However, if it is assumed that the deposit consisted entirely of $^{238}Pu$, a rough estimate gives $2 \times 10^{-16}$ atm as the pressure at both 1263 and 293°K. The vapor pressure of $PuO_2$ calculated by extrapolation from high-temperature data is $2 \times 10^{-16}$ atm at 1263°K and $2 \times 10^{-90}$ atm at 298°K. These data thus suggest that transport by knock-out may occur and may produce an enhanced "vapor pressure" at low temperatures. (B. Mueller and R.N.R. Mulford)

C. X-ray Line Broadening Analysis:

A high-purity $^{238}PuO_2$ disc has now been examined at weekly intervals for a period of 18 wks to determine what changes, if any, occur as a function of time. So far, changes have been anything but dramatic. A slow, apparent increase in lattice constant, amounting to 0.0004Å, has occurred during the period, and the integral breadth of the 622 line, which initially showed a slight decrease, has not increased slightly. (The 622 line is the most sensitive of those being studied because it is at the largest value of $2\theta$.) A possible explanation for this unexpected result is that, initially, the radiation damage relieved lattice stresses that had not been relieved by a thermal anneal, and that now the radiation damage is slowly accumulating and causing the line breadth to increase. (R.B. Roof, Jr.)

V. DESIGN AND INSTALLATION

A. 150 Ton Cold Press and Enclosure

Parts, procurement, assembly, and installation of this unit was completed. The unit is now in operation.

B. 50 Ton Hot Press

Design drawings for this unit were initiated during this quarter. Procurement of parts for the press and enclosure was completed. Installation of services is now in progress.

C. High Temperature Oxidizing Furnace

Installation of this unit was also completed during this quarter. However, the automatic controls supplied with the unit were found to be defective and a manually controlled power supply has been adapted. This temporary hook-up will allow any required runs to be completed until the new controls arrive. Gases available for this furnace are Ar, $CO_2$, and Ar - 6% $H_2$.

D. Ultrasonic Machine Tool Facility

An ultrasonic machine tool for grinding, shaping, drilling, etc., operations on the finished cermet product discs has been ordered. This unit will augment the jeweler's lathe now in use. The $^{238}Pu$ enclosure for this tool has also been ordered.

E. Ball Mill Blender

A new blender mill has been installed and is operational.

[redacted]

F. Oscillating Grinder and Lathe

The oscillating grinder and lathe have been installed in the 150 ton press enclosure.

VII. MEETINGS

A. On August 12, 1969, J.A. Leary and F.W. Schonfeld presented a review of the Solid Solution Cermet program at an Advanced Planning Committee Meeting at AEC Headquarters.

B. On August 18, 1969, representatives of GE-Evendale and GE-Valley Forge met at LASL to discuss procurement of Solid Solution Cermet Simulants (SSCS).

C. On August 19 and 20, 1969, Los Alamos served as host of the Second Meeting of the Isotope Fuels and Materials Committee. Attendees were AEC/SNS/SEPO Headquarters, AEC/DAO, and MLM.

D. On August 21, 1969, further meetings among AEC/DAO, MLM, and LASL were held to determine the scope of product disc specifications.

E. On August 26, 1969, J.A. Leary and M.W. Shupe met with representatives of GE-Evendale.

F. On September 3, 1969, M.W. Shupe attended a Transit Capsule Design Review Meeting at TRW.

G. On September 19, 1969, a review meeting was held at LASL for representatives of GE-Evandale and TRW.

H. On September 29, 1969, J.A. Leary and T.K. Keenan met with GE representatives at Evendale to discuss simulant specification, procurement, and schedules.

I. On September 30, 1969, J.A. Leary and T.K. Keenan attended the Transit Schedule Meeting at MLM.

VIII. SIMULANTS

On September 16, 1969, LASL purchase order CMO-6990-1 was executed directing GE-Evendale to manufacture a number of cermet discs. These discs were primarily $ThO_2$ and contained 14 v/o Mo. A specification sheet, CMB-11-9528, was issued which listed criteria and acceptance standards for these discs. Photomicrographs of typical Solid Solution Cermet Simulant (SSCS) fuel are shown in Fig. 8. The dimensions of such discs (2.15 in. diameter and 0.21 in. high) closely approximates that of the final $^{238}PuO_2$-$ThO_2$-Mo cermet fuel form.

Discs are to be assigned as follows: 1300 pieces to Atomics International, Canoga Park, California, of which 45 revert to Mound Laboratory, Miamisburg, Ohio, after suitable machining and grinding; 119 pieces to Isotopes, Incorporated, Timonium, Maryland; 80 pieces to Mound Laboratory for combination with the 45 machined pieces into capsule loadings. Thirty pieces are to be sent to LASL for quality control evaluation. The balance remain at Atomics International for assembly into capsule sets. All finished capsule sets are to be subjected to various impact, fireball and other re-entry simulation testing.

IX. MILESTONES

The following milestones were attained during this report period:

| | |
|---|---|
| Task I.1 | Complete installation of large press and furnace. |
| Task I.2 | Develop process to produce $^{238}PuO_2$-$ThO_2$ pellets. |
| Task I.3 | Order and install particle sizing equipment. (This was initially planned for 200 w/week. It has been tested at the 100 w/week level.) |
| Task II.1 | Done during last quarter. |
| Task II.2 | Complete $^{238}PuO_2$ development work on particle coating unit No. 1. |
| Task II.3 | Complete fabrication of particle coating unit No. 2. |
| Task II.4 | Complete cold testing of particle coating unit No. 2. |
| Task II.5 | Complete testing and installation of particle coating unit No. 2. (This unit has been completed and tested. However, it was found that unit No. 1 was sufficient for 100 g/week production. Unit No. 2 remains on standby.) |
| Task IV.1 | Fabricate Mo overcoating unit. |
| Task V.1 | Develop hot pressing parameters for small specimens. |

X. TECHNICAL ASSISTANCE TO OTHER CONTRACTORS

A total of 56 engineering drawings on 12 processing items along with procurement information and data on 34 LASL items has been sent to MLM.

[redacted]



[redacted]

# TYPICAL PHOTOMICROGRAPHS OF FUEL SIMULANT ($ThO_2$ CERAMIC)



100X



500X

Figure 8



APPROVED FOR PUBLIC RELEASE

[redacted]

XI. APPENDIX 1

The tasks and milestones associated with this program are listed below.

TASK SCHEDULE FOR DEVELOPING SOLID SOLUTION CERMET; 10/8/69

| | | SCHEDULED | STATUS |
|---|---|---|---|
| **TASK I: SYNTHESIS OF SINTERED PARTICLE FEED** | | | |
| Subtask | 1. Complete installation of large press and furnace | 8/15/69 | installation of furnace complete; now being calibrated |
| | 2. Develop process to produce $^{238}PuO_2$-SS pellets | 8/31/69 | Done |
| | 3. Order and install particle sizing equipment (200 watts/week) | 8/30/69 | Tested at 100 w/week level |
| **TASK II: PARTICLE COATING** | | | |
| Subtask | 1. Complete cold testing of Coating Unit No. 1 | 6/30/69 | Done |
| | 2. Complete $^{238}Pu$ development work on Unit No. 1 | 7/31/69 | Done |
| | 3. Complete fabrication of Unit No. 2 | 8/15/69 | Done |
| | 4. Complete cold testing of Unit No. 2 | 9/1/69 | Done |
| | 5. Complete installation and testing of Unit No. 2 | 9/15/69 | Agreed don't need at 100 g/week -- held as back-up |
| **TASK III: LARGE DISC HOT PRESSING** | | | |
| Subtask | 1. Procure motor generator and press | 9/1/69 | Generator here with press; part of generator missing |
| | 2. Complete installation of MG set press and enclosure | 9/30/69 | To 10/30 depending on delivery of above part |
| | 3. Complete process development | 10/30 | To 11/30 due to above |
| **TASK IV: PRODUCT COATING** | | | |
| Subtask | 1. Fabricate Mo Coating Unit | 8/15/69 | Done |
| | 2. Develop coating process on $^{238}Pu$ | 9/1/69 | 10/30 |
| | 3. Develop coating process for small specimens | | 10/30 |
| **TASK V: DEVELOP PROCESS FOR SMALL SPECIMENS** | | | |
| Subtask | 1. Develop hot pressing parameters | 8/10/69 | Done |
| | 2. Characterize product (chemistry, density, structure) | 8/20/69 | 10/30 ( density and structure OK; waiting on another group for chemistry) |
| **TASK VI: FUEL CHARACTERIZATION** | | | |
| Subtask | 1. Small Specimens | 12/69 | |
| | 2. Product Specification for QC and QA | 12/69 | |
| | 3. Large Discs | | |
| | 4. Aging Effects | | |





[redacted]

## ESTIMATED PROPERTIES OF SSC FUEL DISCS AND SSCS SIMULANT

### I. Thermal Expansion

Percent Expansion (± 15%) on Heating from 25°C to:

| Temp., °C | SSC Fuel | SSCS Simulant |
|---|---|---|
| 500 | 0.38 | 0.34 |
| 1000 | 0.98 | 0.89 |
| 1500 | 1.59 | 1.48 |
| 2000 | 2.21 | 2.07 |

### II. Thermal Conductivity

(estimated same for both SSC and SSCS)

| Temp., °C | k, cal/cm sec °C (± 15%) |
|---|---|
| 100 | 0.033 |
| 500 | 0.027 |
| 1000 | 0.024 |
| 1500 | 0.023 |
| 2000 | 0.022 |

### III. Thermal Diffusivity

(must be measured)

### IV. Heat Content

| Temp., °C | $H_T - H_{298}$, kcal/mole(1) | |
|---|---|---|
| | SSC Fuel | Simulant |
| 900 | 14 | 12 |
| 1650 | 28 | 25 |
| 2000 | 40 | 30 |

(1) 207 g/mole SSC and 198 g/mole SSCS

### V. Heat Capacity

| Temp., °C | Heat Capacity, cal/mole °K | |
|---|---|---|
| | SSC Fuel | Simulant |
| 25 | 13.3 | 11.5 |
| 900 | 17.5 | 15.3 |
| 1650 | 18.2 | 16.8 |
| 2000 | 18.6 | 17.3 |

### VI. Melting Point

| | |
|---|---|
| SSC Fuel, Solid Solution Ceramic Phase | 2400°C |
| SSC Fuel, Molybdenum Phase | 2620°C |
| Simulant, $ThO_2$ Ceramic Phase | 3300°C |
| Simulant, Molybdenum Phase | 2620°C |

### VII. Heat of Melting

| | |
|---|---|
| SSC Fuel | 65 cal/gram |
| Simulant | 69 cal/gram |

### VIII. Density

| | |
|---|---|
| SSC Fuel | 10.44 ± 0.10 g/cc |
| Simulant | 9.3 g/cc |

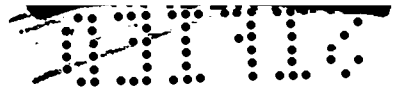
### IX. Composition

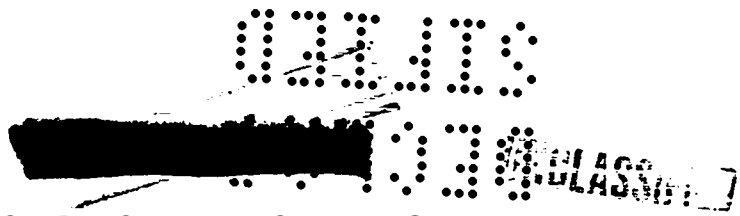
SSC Fuel:

- Cermet: 86 v/o ceramic, 14 v/o molybdenum
- Ceramic: $^{238}PuO_2$ - 10 w/o $ThO_2$ at 94% T.D.
- Molybdenum: 0.004 in. thick molybdenum overcoat (approximately 4.5 v/o of total fuel): all molybdenum 98% dense

Simulant: Same as SSC Fuel, except $PuO_2$-$ThO_2$ ceramic is replaced by $ThO_2$.

Note: Isotopic composition of $^{238}PuO_2$ is "as supplied" by AEC.





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Group 1 - Excluded from automatic downgrading and declassification

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