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ORNL ISOTOPIC POWER FUELS

QUARTERLY REPORT

Period Ending March 31, 1972

Eugene Lamb

R. G. Donnelly

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ORNL ISOTOPIC POWER FUELS QUARTERLY REPORT
FOR PERIOD ENDING MARCH 31, 1972

Eugene Lamb

Isotopes Division

R. G. Donnelly

Metals and Ceramics Division

JUNE 1972

OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37830
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

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ORNL ISOTOPIC POWER FUELS QUARTERLY REPORT
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Eugene Lamb and R. G. Donnelly

SUMMARY

A vacuum hot-press for pressing pellets up to 1-in. diameter was assembled and tested. A process and the necessary hot-cell equipment to make $\sim 250\text{-}\mu\text{m}$ -diam $^{244}\text{Cm}_2\text{O}_3$ microparticles have been developed. These particles are strong enough to be blended with metal powder to form cermets. The curium source test is being disassembled and the equipment salvaged. Causes of the transfer of curium fuel from the pellet channels to the upper interior sections of the capsule have been analyzed. Four samples of the curium fuel were taken during the disassembly for spark source mass spectrometry, x-ray diffraction, and helium release analyses.

Two cylindrical SrTiO_3 pellets and four spherical Gd_2O_3 pellets were used to test the operation of the impact test unit. Three sabot heaters have been designed to heat the specimens to their expected operating temperature before impacting them. Construction of the laser system for velocity measurement is expected to be completed in April.

The Pt-Rh-W alloys were found to be relatively insensitive to atmosphere contaminants such as those found in radio-isotope thermoelectric generators. Hemispheres of Pt-26% Rh-8% W and Pt-30% Rh-8% W-0.25% Hf-0.1% Ti have been successfully fabricated. Iridium has been zone refined into single-crystal bar, which can be cold swaged 40% without cracking.

Much higher oxygen levels can be tolerated by T-111 without embrittlement at temperatures higher than present Pioneer operating temperatures. T-111 embrittled by oxygen contaminants at 825°C can be ductilized by a heat pulse equivalent to that received by a Pioneer heat source upon reentry into the earth's atmosphere. Molybdenum alloys and coatings on T-111 continue to show relative insensitivity to contaminating environments.

INTRODUCTION

The development of fuel forms with optimum design for use at temperatures up to 2000°C involves obtaining the characteristics of isotopic power and heat sources for anticipated applications in aerospace, terrestrial, and marine environments. The physical and chemical properties of the

compound and source form, such as thermal conductivity, density, gas retention, and melting point, must be determined. Compatibility of the fuel form with container materials must be established to ensure adequate containment during the intended lifetime of the mission.

CURIUM-244 FUEL DEVELOPMENT

(Division of Space Nuclear Systems Program 04 30 05 03)

Curium-244 Oxide Fuel Development and Properties

Heat Capacity Cm_2O_3

The hot cell has been tested and is now ready for beginning the heat capacity experiment. When the cell is operated under an argon purge of $6 \text{ ft}^3/\text{min}$, the concentration of oxygen has been less than 50 ppm. These levels were reached in less than 3 hr after the cell had been converted from an air purge to an argon purge.

The Pt-Pt10Rh and the W5Re-W26Re thermocouples used in this equipment have been calibrated to 1400°C . Changing from all Pt-Pt10Rh to Pt-Pt10Rh and W5Re-W26Re thermocouples necessitated a change in the computer program for analyzing data.

Vacuum Hot-Press

A vacuum hot-press for pressing pellets up to 1-in. diameter was assembled. The out-of-cell check-out of the vacuum hot-press has been completed. The hot-press is designed to press $3/4$ -in.-diam pellets of curium oxide at 4000 psi and 1550°C .

Five Gd_2O_3 pellets were pressed. The only modifications found necessary were shortening and shimming the transmitter rod to provide more travel and to reduce wobble.

Curium-244-Noble Metal Compound Fuel Development and Properties

The vacuum furnace, which will be used to study the reaction of $^{244}\text{Cm}_2\text{O}_3$ with Pt, Rh, and Ir to above 2000°C , has been installed in the hot cell.

Curium-244 Cermet Fuel Development and Properties

This task involves the preparation of sized $^{244}\text{Cm}_2\text{O}_3$ particles for use in cermets and the determination of ranges of fabrication parameters for noble metal- $^{244}\text{Cm}_2\text{O}_3$ cermets. The preparation of cermets requires sized particles of Cm_2O_3 which are incorporated into the metal matrix to form the composite fuel. Of the several methods available to produce sized

particles, the ion-exchange procedure offers the potential advantages of efficient utilization of ^{244}Cm without recycle, adaptability to manipulator cell operation, and simplicity of procedure.

Our aim is to develop cermet fuel forms with the most desirable combination of properties and to reduce the in-cell development requiring curium. We are specifically attempting to structure the cermet to provide for helium release.

Preparation of Sized $^{244}\text{Cm}_2\text{O}_3$ Particles

We have completed development of a process and the equipment to make $^{244}\text{Cm}_2\text{O}_3$ microparticles that have a diameter of approximately 250 microns and are strong enough to allow blending with metal powder to form cermets. Development was done using inactive gadolinium as a stand-in for ^{244}Cm . The hot-cell equipment for the preparation of $^{244}\text{Cm}_2\text{O}_3$ particles by the ion-exchange procedure is being used to prepare approximately 500 g of Gd_2O_3 for stand-in tests for $\text{Ir}-^{244}\text{Cm}_2\text{O}_3$ cermet fabrication. These runs have indicated the need for minor changes in the equipment. Approximately 300 g of Gd_2O_3 particles has been prepared.

The process chosen for development is based on the use of ion-exchange beads. The essential steps in the process are: (1) an ion-exchange resin is loaded with gadolinium; (2) the organic material is decomposed in an inert atmosphere; (3) the carbon is removed by oxidation; and (4) the particles are sintered. Good quality particles have been produced using the ion-exchange resins Rexyn-102H and IRC-72; both are of the carboxylic or weak acid type.

The ion-exchange method has the advantages of using simple, readily available equipment and requiring very little mechanical manipulation. The uniformity and size of the particles can be easily controlled. Very little airborne dust is formed; therefore, the danger of the spread of contamination and the decontamination problems following the use of the process are reduced. Furthermore, since yields are approximately 100%, there will be no waste oxide requiring reprocessing during normal operation.

Helium Release in $^{244}\text{Cm}_2\text{O}_3$ Cermets

The movement of helium through dense pure $^{244}\text{Cm}_2\text{O}_3$ bodies has been adequately defined empirically. While the mechanisms of helium diffusion in $^{244}\text{Cm}_2\text{O}_3$ are not clearly established, all the data support a conclusion that radiation effects are a paramount consideration. Experiments have been initiated to determine the effect of alpha damage on the diffusion of helium in metals. These experiments serve a twofold purpose: (1) to indicate mechanisms of helium release from cermets, and (2) to further substantiate the effect of radiation on helium release in $^{244}\text{Cm}_2\text{O}_3$. Our hypothesis is that at lower temperatures (<1000°C) the principal mechanism for helium diffusion in $^{244}\text{Cm}_2\text{O}_3$ is along a network of dislocation loops. It is well known that at temperatures below approximately 2000°C helium does not diffuse through metals at a measurable rate. However,

if sufficient dislocation loops can be introduced into a metal foil by alpha irradiation, and if our hypothesis is correct, then helium should diffuse through the alpha-damaged metal foil. These experiments are being conducted using $^{244}\text{Cm}_2\text{O}_3$ in contact with metal foils so that the dynamic effect of irradiation on helium diffusion can be evaluated.

Cermet Test Program

Strength deterioration and reduced helium permeability of $^{244}\text{Cm}_2\text{O}_3$ -bearing cermets upon aging are of particular concern to the development of an isotopic power fuel form. We are investigating these effects in simulated Mo-ThO₂ cermets. Aging of the simulant materials for 1000 hr at 1200 and 1500°C began on March 28 and April 6, 1972, respectively, and should be completed during the third week in May.

One circular and two rectangular pieces, machined from each of ten different Mo-ThO₂ cermets, are being aged in a vacuum of $<2 \times 10^{-5}$ torr at 1200 and 1500°C. The various compositions and hot-pressing temperatures are given in Table 1. The round specimens will be used for permeability and impact strength measurements; the bars will be cut into compressive yield strength and metallographic specimens. Specimens could not be machined from the 80 vol % Mo-ThO₂ disks hot-pressed at either 1200 or 1450°C because of the extreme brittleness of the cermet. Prior to aging, but after machining, all specimens were annealed for 1 hr at 900°C in vacuum to clean their surfaces of volatile contaminants and also to reduce internal stresses from the machining step. After the anneal, the aging specimens were characterized according to weight, dimensions, open and closed porosity, and room-temperature helium permeability.

To minimize oxygen contamination during the 1000-hr aging treatment, each set of one circular and two rectangular specimens were contained in 0.020-in.-thick tantalum boxes, which in turn were placed in a larger tantalum boat and wrapped with tantalum foil. The specimens however are not in contact with either the tantalum or each other because tungsten wire of 0.020-in. diameter was positioned around each specimen to limit supporting surface contact.

For our fully active and simulated studies on noble metal- $^{244}\text{Cm}_2\text{O}_3$, all primary suppliers failed to bid on a requisition for 1100 g of iridium powder, stating that a major oil company had purchased their next two years' production. However, we placed an order for the material with a chemical supply house. The price is \$7.25/g instead of the prior market price of \$5.10/g. Delivery of the iridium powder is expected the second week of May.

An Ir-Gd₂O₃ program has been prepared for out-of-cell studies simulating noble metal- $^{244}\text{Cm}_2\text{O}_3$ cermets. Our aim is to reduce the in-cell development requiring curium. A reasonable simulation should be obtained since the Gd₂O₃ powder of 62- to 500-μm principal particle size range was prepared by the ion-exchange resin technique developed for making Cm₂O₃ particles. Because of the high cost of iridium, we will determine the

pertinent fabrication and aging characteristics from a limited number of specimens. These specimens will be hot-pressed and machined pellets containing 0, 20, 40, 60, and 80 vol % Gd_2O_3 .

Table 1. Composition and Hot-Pressing Temperatures of Mo-ThO₂ Cermets for Aging Study

Core Order Number	Composition ^a (vol %)	Hot-Pressing Temperature (°C)
1257	Mo-20.9 ThO ₂ -14.4 Voids	1200
1258	Mo-21.0 ThO ₂ -5.3 Voids	1450
1259	Mo-20.1 ThO ₂ -2.6 Voids	1700
1260	Mo-39.1 ThO ₂ -19.8 Voids	1200
1261	Mo-42.1 ThO ₂ -5.3 Voids	1450
1262	Mo-40.3 ThO ₂ -2.4 Voids	1700
1263	Mo-51.6 ThO ₂ -29.4 Voids	1200
1264	Mo-60.4 ThO ₂ -9.4 Voids	1450
1265	Mo-60.5 ThO ₂ -2.2 Voids	1700
1268	Mo-80.5 ThO ₂ -2.0 Voids	1700

^a Specimen dimensions (in.): A - 0.50 diam by 0.20 thick; B - 1.0 long × 0.35 wide × 0.20 thick; C - 0.50 long × 0.35 wide × 0.020 thick.

Recovery of Curium-244 from Fuel Reprocessing Waste

During previous work on ²⁴²Cm isotopic power programs, a solvent extraction process (differential extraction) and a process flow sheet (using either TBP or D2EHPA) were designed, based on experimental data, for the recovery of ²⁴²Cm from irradiated ²⁴¹Am. This work is being reexamined for its applicability to the recovery of ²⁴⁴Cm. Differential extraction offers several possible advantages over conventional solvent extraction procedures:

1. Very low capital cost (usually about 90% of total costs in radiochemical separations).
2. Low volume, easily managed waste streams.
3. Low sensitivity to high radiation levels due to short organic phase contact times.
4. Adequate separation capability.

Fabrication of Spherical $^{244}\text{Cm}_2\text{O}_3$ Source Forms

One concept for the fueling of a proposed isotopic power generator with $^{244}\text{Cm}_2\text{O}_3$ requires $^{244}\text{Cm}_2\text{O}_3$ spheres of approximately 0.75-in. diameter. A split die assembly (see Fig. 1) has been tested using Gd_2O_3 . Pressed spheres have the same polar and equatorial diameter within approximately 1 mil. No defects in the spheres are visible at the junctures of the die parts. Near theoretical densities have been obtained in all pressed spheres. If the die assembly is not precisely filled, a slight concave crease is formed in the sphere at the points where the punches terminate. Overloading of the die results in a cylindrical section at the equator of the sphere. It is expected that this die design will result in longer life for the die assembly due to elimination of knife edges.

Fig. 1. Split Die Assembly.

Curium Source Test

Disassembly and salvage of equipment used in the curium source test have begun. All equipment exterior to the cells has been removed.

The causes of the transfer of curium fuel from the pellet channels to the upper interior sections of the capsule have been analyzed in more detail than given previously.¹

The heat source is shown in Fig. 2 with an approximate outline of the transferred fuel deposits. Decay helium leaving the Cm_2O_3 passed up through a small hole in the disk over the fuel form. It then entered the spiral capillary inside the disk and passed to the external capillary. The purpose of the internal capillary was to allow the helium to leave the high-temperature capsule while allowing only a very small amount of curium to enter the external capillary. The design anticipated approximately 1-atm pressure in the heat source.

A temperature history of the heat source is shown in Fig. 3. The temperature of the center of the base averaged 1281°C (ref. 2) during early measurements rather than the design temperature of 1650°C . The interior of the heat source was evacuated in an effort to get a higher temperature. Evacuation was carried out every 2-4 days to remove decay helium, and pressures varied over the range of 8-200 microns during most of the test.

Deposits of material were observed on the metal disk directly above the individual cylinders of $^{244}\text{Cm}_2\text{O}_3$ and on the metal matrix around the cylinders. A quantity of loose powder was also found above and below the disk. The original location of this powder cannot be determined. The process of cutting open the capsule involved laying it on its side and rotating it. The powder could have passed easily through the hole connecting the two volumes. According to calorimetric analysis, the loose material consisted of $^{244}\text{Cm}_2\text{O}_3$ having lower watts per gram than pure fuel; these data indicate that impurities in the original fuel were transferred preferentially or part of the capsule material was transferred.

The deposits on the metal surfaces were expected and were produced by migration of Cm_2O_3 vapor from the hot surface of the Cm_2O_3 cylinders to the nearest cooler surfaces. However, harder, more compact deposits had been anticipated.

Fig. 2. Heat Source.

Fig. 3. Curium Heat Source Temperature History.

The loose powder may have come from surface deposits broken free when the capsule was cut open. Powder could also have been formed by the rapid cooling of helium gas containing Cm_2O_3 vapor. This cooling would have occurred in thermal convection currents inside the capsule. Also, hot gas from above the Cm_2O_3 cylinders moved rapidly to cooler parts of the system during the periodic evacuations.

Calorimetric measurement of the external capillary showed only a small quantity of $^{244}\text{Cm}_2\text{O}_3$ passed through the spiral capillary. The capillary was not plugged at the end of the test, and it can be concluded that the vented capsule design was a success under the conditions of the test which were more severe than originally planned.

Calculations using the data from the source experiment show that the capillary would not have plugged even if the temperature had been 1650°C as originally planned, provided a helium atmosphere had been maintained. An increase in temperature to the design value would have caused a 4100-fold increase in the Cm_2O_3 diffusion rate. However, a pressure of 1 atm (design condition) would have caused a 16,900-fold decrease in the rate of diffusion. Thus, the transport of Cm_2O_3 would have been less than observed in the test.

Calculations were made to determine if the quantity of curium which had left the surface of the $^{244}\text{Cm}_2\text{O}_3$ cylinders was compatible with the calculated internal temperatures. The temperatures were estimated from external temperatures previously reported.² The most reliable values are considered to be those obtained by an optical pyrometer measurement at the center of the bottom of the capsule. The average of five values obtained over a period of 39 days is 1281°C . The average temperature of the top of the matrix was calculated to be 80°C higher, or 1361°C .

The center-to-surface ΔT of the Cm_2O_3 cylinders was estimated to be 200°C . However, radiant loss of heat was expected to reduce this value to about 110°C on the exposed upper surfaces of the cylinders. This loss leads to a calculated maximum surface temperature of about 1471°C . The average surface temperature is estimated to be 1416°C .

The amount of Cm_2O_3 which had left the cylinders, obtained from the data of Ramey and Haff,¹ was 37.2 g, which is equivalent to $8.4 \times 10^{-8} \text{ g/cm}^2\text{.sec}$ from the exposure time of the Cm_2O_3 . Equation (1) by Smith and Peterson³ was used to calculate the rate of evaporation of Cm_2O_3 from the exposed surfaces of the pellets.

$$\log \frac{W}{\text{at}} \frac{\text{g}}{\text{sec.cm}^2} = 10.33 (\pm 0.26) - \frac{29,050}{T^\circ\text{K}} - 1/2 \log T^\circ\text{K} . \quad (1)$$

The calculated rate of evaporation, $\frac{W}{\text{at}}$, is plotted as a function of temperature in Fig. 4. The confidence belt is calculated from the limits of uncertainty of the constants in the equation. These limits are stated by the authors to be the standard deviations. The authors state that this

equation is valid over the range of 1800–2600°K. Consequently, there is some uncertainty in its use in the 1673–1773°K range. A phase change in Cm_2O_3 occurring at about 1600°C increases this uncertainty.

The observed average evaporation rate of $8.4 \times 10^{-8} \text{ g/cm}^2\cdot\text{sec}$ occurs at 1570°C. The estimated average surface temperature was 1416°C. The significance of this difference is uncertain because there are many uncertainties in the calculations. For example, the actual pellet temperature could have been higher than that calculated or the area of the pellets from which vaporization occurred could have been larger than the superficial area of the top pellet surface.

During the disassembly of the curium source test,¹ four samples of the curium fuel were taken for a series of analyses. These samples are described below:

<u>Sample Designation</u>	<u>Sample Description</u>
A	Scrapings from top of pellets, 1.76 W/g
B	Material chipped from pellets, 1.83 W/g
C	Scrapings from bottom of vent disk, 1.70 W/g
D	Powder from inside vent disk, 1.2 W/g

The results of the spark source mass spectrometry, x-ray diffraction, and helium release analyses are given in this report. Other data will be reported as acquired.

Samples of each of the above materials were sent for spark source mass spectrometric analyses. The results are presented in Table 2. The values reported are visual estimates taken from a standard plate and using a common graphite matrix. These values are to be interpreted as approximations only. Actual values should be within the range times 1/2 to times 2. The data given for Sample A do not differ significantly from the original $^{244}\text{Cm}_2\text{O}_3$ except for tungsten contamination. Sample D, which was collected from the coldest and most remote surface of the capsule interior, contains appreciably higher concentrations of the more volatile impurities found in the $^{244}\text{Cm}_2\text{O}_3$ (La, Mg, Na, and Si). Sample C contains less of the relatively low

Fig. 4. Calculated Rate of Vaporization as a Function of Temperature.

Table 2. Spark Source Mass Spectrometry
Results of Curium Source Fuel

Element	Material (ppm)			
	A	B	C	D
Aluminum	150	150	500	>10,000
Barium	20	5	2	50
Calcium	20	50	70	~2,000
Niobium	<1	<1	<1	<1
Chromium	30	30	100	10
Copper	<1	2	5	20
Iron	30	100	30	100
Potassium	<5	<5	<5	15
Magnesium	5	10	<1	200
Manganese	3	10	<1	10
Sodium	<1	5	<5	500
Nickel	5	20	5	2
Phosphorus	<1	1	<1	5
Silicon	10	100	30	1,000
Strontium	5	1	10	10
Tantalum	30	100	<10	<10
Thorium	15	15	2	5
Titanium	<10	20	20	~2,000
Vanadium	3	1	10	3
Tungsten	300	1,000	1,000	30
Zinc	<10	10	<10	10
Zirconium	1,000	1,000	100	10
Sulfur	15	30	30	30
Yttrium	Trace ^a	Trace ^a	Trace ^a	Trace ^a
Lanthanum	10	3	20	10
Cerium	3	1	3	10
Praseodymium	3	1	3	1
Neodymium	10	10	10	10
Europium	<3	<3	<3	<3
Gadolinium	~3	~3	10	<10
Dysprosium	<10	<10	<10	<10
Holmium	<3	<3	<3	<3
Erbium	<5	<5	<5	<5
Thulium	<3	<3	<3	<3
Ytterbium	<5	<5	<5	<5
Lutetium	<5	<5	<5	<5
Mass 240-248		Major Components		

^aLess than 1 ppm.

volatility zirconium than does Sample B. Sample D contains even less zirconium than Sample B. The high values for aluminum and titanium in Sample D are anomalous. These data as well as those previously given **strongly** support the conclusion that $^{244}\text{Cm}_2\text{O}_3$ transfer was by vaporization. These data also show that, at least with $^{244}\text{Cm}_2\text{O}_3$, the primary factor in a vented capsule may be plugging of the vent by volatile impurities in the fuel.

A 100-mg sample of material B was studied by x-ray diffraction. The results showed an fcc crystal structure identified as CmO_2 . There were other faint lines present; however, these were of such low intensity, they were not identifiable. The analyses were performed approximately one month after the samples were submitted. Thus, there was ample time for the sample to have oxidized to CmO_2 . The identification of only one crystal structure would show that there was no significant reaction product in the bulk Cm_2O_3 pellets.

Helium release experiments have been made on material B. Three experiments have been completed using a total of 0.364 g of the fuel. The 6.55-g sample of material B was initially removed as pieces and placed in a container on December 17, 1971. The helium release experiments were completed approximately two months after the packaging. The calorimetric data for material B were used to calculate the amount of helium generated during this time. These results are presented in Table 3.

Table 3. Theoretical Helium Produced from Material B

Date Experiment Completed	Theoretical Helium Produced (cm^3/g)	Measured Helium Released (cm^3/g)
Feb. 11, 1972	0.3546	0.2653
Feb. 15, 1972	0.3799	0.2652
Feb. 17, 1972	0.3926	0.2716

In all of these experiments the measured helium content per gram of material was less than the calculated helium produced by a 1-g sample during the storage period.

The tube in which the sample is located must be evacuated to approximately 500 microns before measurements begin. The elapsed time for this pumpdown is approximately 30 sec. There may be some helium evolved during this period. Also the sample had oxidized and the powder may be of such a particle size that a significant fraction of the alphas was emitted by recoil from the surface. This emission would lower the total helium inventory in the sample. Since the measured stored helium is lower than the calculated value, no valid concentration of helium in the original fuel sample can be inferred.

Metallography of the curium source test fuel is continuing; the optical photomicrographs have been obtained. The sample showed two or possibly three phases. The fuel will be examined with the electron microprobe, which may show the nature of the phases. An x-ray diffraction pattern will be obtained on this same piece of fuel. These analyses are not complete yet.

Curium Source Neutron Dose Measurement

The water shielding tank for the curium source neutron dose measurement experiment has been designed and is being fabricated. It should be completed in April.

Impact Testing of Heat Source Materials

High-speed movies (~ 3000 frames per second) were taken of two projectiles fired in the impact tester to determine the feasibility of using photographic equipment already available at ORNL.

All electronic parts, including the helium-neon laser, have been ordered for the velocity measuring system, and design of the yoke on which the laser system will be mounted has been started. Design has also begun on an electrically heated sabot which will permit heating a specimen to its expected operating temperature before impacting. This will allow more exact simulation of conditions when studying impact characteristics of radioactive heat source materials.

Impact Tests

High-speed movies were taken of impact tests of two cylindrical SrTiO_3 pellets and four spherical Gd_2O_3 pellets to check the operation of the unit, the movie equipment, and debris particle size analysis. The velocity of the SrTiO_3 pellets was determined with the aid of time markings on the film and a 1-ft scale pictured in the background of the film. The velocity of the Gd_2O_3 pellets was measured with the electric eye timing circuit. Table 4 is a summary of the data of these six tests.

Table 4. Summary of Data from SrTiO_3 and Gd_2O_3 Pellet Impact Tests

Test No.	Material	Sabot Mass (lb)	Firing Pressure (psig)	Velocity (ft/sec)
1 ^a	SrTiO_3	1.52	190	291
2	SrTiO_3	1.51	185	256
3 ^b	Gd_2O_3	1.52	190	286.5
4	Gd_2O_3	1.52	190	c
5	Gd_2O_3	1.52	125	231.5
6	Gd_2O_3	1.52	125	234.2

^aIn tests 1 and 2, velocity was determined from high-speed film.

^bIn tests 3, 4, 5, and 6, velocity was determined with electric-eye timing device.

^cTiming mechanism did not trigger.

The particles of Gd_2O_3 from test 6 were collected and analyzed by sieving for size distribution. The size distribution data for this test are presented in Table 5.

Table 5. Particle Size Distribution Data
for Gd_2O_3 Pellet Impact Test No. 6

Size Range (microns)	Weight of Particles (g)	Weight Fraction (%)
>2380	20.7850	75.708
2000-2380	1.2205	4.446
850-2000	1.7888	6.516
590-850	0.4003	1.458
420-590	0.3418	1.245
297-420	0.3647	1.328
250-297	0.2400	0.874
177-250	0.4649	1.693
150-177	0.2562	0.933
88-150	0.8104	2.952
63-88	0.3048	1.110
45-63	0.2048	0.746
<45	0.1245	0.453
Unaccounted for	0.1480	0.539
Total	27.4540	100.001

Velocity Measurement

The construction of the laser system for velocity measurement is expected to be completed in the latter part of April 1972. For interim use while waiting for this system, several other systems were tried. The first was a system in which two metal foil strips, a measured distance apart, were placed in the path of the impact specimen. The impact specimen would break these foils, consequently breaking the circuit, and triggering and subsequently stopping a timing device. This system did not work because the air blast preceding the sabot was of sufficient force to break the thin foil strips and give false time readings. A thin wire was substituted for the foil, but this failed too as a result of the air blast breaking the wires. Heavier wires and foils could not be used because of their effect on the projectile.

A second triggering system using photoelectric cells was constructed and has proven satisfactory. This system was calibrated against a strobe light. The results of this calibration are given in Table 6.

Table 6. Strobe Light Calibration
of Photoelectric Cell Timing System

Test	Velocity (ft/sec)		% Variation
	Strobe Light Measured	Timing System Measured	
1	44.8	47.2	5.4
2	95.3	90.3	5.5
3	99.4	94.2	5.5
4	134.7	122.1	10.3

Sabot Heaters

Three different sabot heaters have been designed. The first two heaters (Fig. 5) had a relatively short life (~ 6 hr). The heating element, a double coil of nichrome wire, burned out in each case due to overheating of the inner coil.

The third heater (Fig. 6) has a single coil heater. This design limits the pellet size that can be tested to 1-in. diameter (including a capsule to contain the particles). Table 7 gives the steady-state temperatures of the specimen cavity (cup) and the outside temperature of the sabot (jacket) at several heater power inputs. In the test, power was applied to the heater and the heater was allowed to sit for 1 hr before the readings were taken. The heater was insulated with $\sim 1/4$ in. of insulating material. The heater weighed 490 g (1.08 lb).

Drawings for the sabot heater and the modifications to the impact gun have been completed. Several of the heaters are being built in the shops. The heaters will be undersized by 0.017 in. to allow for thermal expansion in the impact tests. Figure 7 is a drawing of the electrical connection to be installed in the impact gun gas chamber for the sabot heaters.

Fig. 5. Sabot Heater No. 1.

Fig. 6. Sabot Heater No. 2.

Fig. 7. Electrical Connections for Sabot Heaters.

Table 7. Steady-State Temperature Data for Sabot Heater Test

Power (W)	Cup Temperature (°C)		Jacket Temp (°C)	Jacket Diam (in.)
	Thermocouple	Optical Pyrometer		
0	—	—	—	2.766
100	503	—	100	—
130	578	—	115	—
150	692	772	143	2.780
170	758	828	164	2.782
190	819	880	175	2.783
210	859	920	186	2.784
240	925	980	207	2.785
260	969	1025	217	2.787

Particle Size Determination

Mr. Stan Bronisz of LASL was contacted by telephone to discuss the particle size determination methods they use in their plutonium fuels impact studies. LASL impacts the fuel in a closed container to assure collection of all particles. The impacted container is then opened under liquid freon-TF, and a wet sieving process is used for particles over 10 microns in diameter. The particles of less than 10 microns in diameter are dispersed in water, cast on a standard microscope slide, and shadowgraphed and photographed on an electron microscope. The particles are measured directly from the photograph. They have used a quadrant image analyzer but have found that direct measurement is faster.

LASL has also used a Coulter counter and a variable spot analyzer. They are interested in the unit produced by Micromeritics Instrument Corporation, which we have been investigating.

CLADDING MATERIALS PROGRAM

(Division of Space Nuclear Systems Program 04 30 05 04)

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Metals and Ceramics Division

The purpose of this program is to develop alloys with a superior combination of properties to better assure reliable containment of radioisotopic fuels such as $^{238}\text{PuO}_2$ and $^{244}\text{Cm}_2\text{O}_3$ under both operating and accident conditions for space thermoelectric generators. Ideally the encapsulating material should be insensitive to the operating environment and capable of surviving launch aborts, reentry heating, and earth impact, as well as provide maximum post-impact containment of the fuel. At the same time it must be both fabricable and weldable.

We feel these goals can best be accomplished with high-strength, noble-based alloys having melting points above 2000°C.

Preparation of Pt-26% Rh-8% W Sheet

To make the desired encapsulation components for isotopic heat sources, fabricable sheets of a Pt-Rh-W alloy 0.025 to 0.030 in. thick by greater than 8 in. square are required. We have fabricated 1- and 4-lb ingots of the Pt-26% Rh-8% W alloy into sheets 0.030 in. thick by approximately 5-1/2 and 10-1/2 in. square with very little difficulty. Although the initial sheet exhibited low ductility (1 to 5% elongation), we have successfully drawn blanks into 7/8- and 1-1/4-in.-diam hemispheres (see Fig. 8), with small increments of reduction between anneals. In this material, failure always appeared to occur at the grain boundaries. Thus, improvement in quality control and fabrication procedures appeared necessary to raise the elongation to 15 to 20% obtained on sheet specimens prepared from some buttons of chemically pure metal ingredients.⁴

The alloy ingots have been made by separately electron-beam melting platinum-rhodium scrap obtained from Mound Laboratory and virgin rhodium powder and then electron-beam melting these together with arc-melted and

Fig. 8. Photograph of Electron-Beam-Melted Ingot, Rolled Sheet, and Fabricated Parts from Pt-26% Rh-8% W Alloy.

crushed tungsten. Examination of sheet with poor ductility revealed microporosity near the surface, random contamination (primarily aluminum and silicon) of the grain boundaries, and tungsten segregation. The surface microporosity was eliminated by scalping the hot-rolled ingot prior to cold rolling. Repeated melting reduced the aluminum content from 500 to 200 ppm and the silicon content from 300 to 100 ppm. The observed tungsten segregation was in the form of small undissolved chips at the surface of the hot-rolled plate which we expect to overcome by improved melting procedures.

We have fabricated 0.030-in.-thick sheet from 1-lb drop-cast electron-beam-melted ingots of both the platinum-rhodium scrap and the scrap with the virgin rhodium added to make up the platinum-rhodium base alloy for Pt-26% Rh-8% W. Blanks from each of these materials were cold drawn without difficulty to make both 7/8- and 1-1/4-in.-diam hemispherical cups. Tensile specimens from each of the alloys heat treated at 1000 and 1200°C showed about 37% elongation for the Pt-10% Rh scrap and 43% elongation for the Pt-28.3% Rh base alloy. Published data⁵ indicate about 35 and 33% elongation, respectively, for these two alloys in the annealed condition. Therefore, we now feel there is no problem of purity in the alloy constituents.

We are presently preparing another 4-lb ingot. The arc-melted tungsten will be replaced by hydrogen heat-treated tungsten powder, and the alloy will be compounded initially as 1-lb buttons in the arc furnace to assure dissolution of the tungsten prior to electron-beam melting. We expect this change in melting procedure along with changes in the fabrication procedure to improve the ductility of the final sheet.

Development of Improved Alloys

The mechanical properties of hafnium- and titanium-stabilized Pt-Rh-W alloys in the recrystallized condition (1 hr at 1200°C) were determined at 1316°C. A comparison of the tensile properties of the recently developed platinum-base alloys with other candidate alloys at 1316°C is made in Table 8. The tensile strength of the Pt-Rh-W alloys increase with tungsten content. Hafnium and titanium additions further improve the strength. Both the ternary and the hafnium- and titanium-modified alloys are stronger than Pt-30% Rh and are comparable to iridium or TZM, but weaker than T-111. In terms of the impact strength (i.e., fracture strain times tensile strength), the Pt-30% Rh-8% W-1% Hf-0.2% Ti alloy is the best among the candidate alloys.

The tensile properties of Pt-30% Rh-8% W-1% Hf-0.2% Ti alloy were determined in the stress-relieved condition (1 hr at 1000°C); these data are presented in Table 9 along with the recrystallized data. The hafnium- and titanium-stabilized alloy is very strong in the stress-relieved condition, even up to 1093°C. The ductility of the alloy is lower in the stress-relieved condition and does not increase significantly with temperature below its recrystallization temperature (i.e., 1200°C).

Table 8. Comparison of the Tensile Properties of Platinum-Base Alloys^a with Iridium, TzM, and T-111 at 1316°C

Composition (wt %)	Tensile Strength (psi)	Elongation (%)	Impact Strength (in.-lb/in. ³)
Pt-30 Rh	10,000	26.5	2,650
Pt-30 Rh-6 W	17,500	55.0	9,600
Pt-26 Rh-8 W	21,200	45.0	9,550
Pt-30 Rh-10 W	25,500	50.5	12,900
Pt-30 Rh-8 W-0.25 Hf-0.1 Ti	21,600	52.0	11,200
Pt-30 Rh-8 W-0.5 Hf-0.2 Ti	25,000	44.5	11,100
Pt-30 Rh-8 W-1.0 Hf-0.2 Ti	27,700	54.5	15,100
Iridium	26,000	38	9,900
TzM	22,000	30	6,600
T-111	37,000	36	13,300

^a0.020-in.-thick sheet recrystallized 1 hr at 1200°C, strain rate 0.05 in./min.

Table 9. Tensile Properties of Pt-30% Rh-8% W-1% Hf-0.2% Ti in Stress-Relieved and Recrystallized Conditions

Test Temperature (°C)	Tensile Properties			
	Elongation (%)		Tensile Strength (psi)	
	Stress Relieved ^a	Recrystallized ^b	Stress Relieved ^a	Recrystallized ^b
Room	5.5	11.7	243,000	130,000
760	5.7	26.3	186,000	108,000
1093	7.5	28.1	102,000	42,000
1316	54.5 ^c	54.5	27,700 ^c	27,700

^aStress relieved 1 hr at 1000°C.

^bRecrystallized 1 hr at 1200°C.

^cEstimate from the recrystallized value.

To further qualify the use of the newly developed platinum-base alloys as cladding material for space isotopic heat sources, 23-mil-thick sheet specimens were exposed to oxygen at 1×10^{-5} torr. Table 10 shows the tensile properties of Pt-Rh-W alloys after a 253-hr exposure at 1100°C, and Table 11 shows the data of Pt-Rh-W-Hf-Ti alloys after a 1000-hr exposure at 1000°C. The Pt-Rh-W alloys show only a small reduction of the room-temperature ductility, but no change in the 825°C ductility. It is important to note that this result is independent of the tungsten content. If an activation energy for oxidation of 27.5 kcal/mole (ref. 6) is used

to extrapolate the data to a lower exposure temperature, the data in Table 10 predict no change of the 825°C ductility of Pt-Rh-W alloys after a 2400-hr exposure at 825°C (the Pioneer service temperature).

As indicated in Table 11 the modified alloys show a moderate reduction of ductility at room temperature and lesser degree of reduction at 825°C. The room-temperature ductility is dependent on the hafnium and titanium level, the alloy containing 0.25% hafnium and 0.1% titanium has better ductility after oxygen exposure than the alloys containing 0.5% hafnium and 0.2% titanium. However, the latter alloys still have 7 to 9% elongation at room temperature and 16 to 21% at 825°C.

To demonstrate the formability of the alloy, two 2-in.-diam blanks of hafnium- and titanium-stabilized alloys were made from 30-mil-thick sheet stock fabricated by hot-rolling at 1230°C followed by cold-rolling at room temperature. After recrystallizing 1 hr at 1200°C, the blank was formed over a 1-1/4-in.-diam mandrel at room temperature. The first blank cracked at the last stage when we attempted to form a complete hemisphere in one pass. With two intermediate anneals at 1200°C, the second blank was fabricated to a 1-1/4-in.-diam hemisphere without cracking (Fig. 9).

Table 10. Mechanical Properties of Pt-Rh-W Alloys at Room Temperature and 825°C after Oxygen Doping at 1100°C and 1×10^{-5} Torr for 253 hr

Composition (wt %)	Condition	Elongation (%)	Ultimate Tensile Strength (psi)
<u>Room Temperature</u>			
Pt-30 Rh-6 W	As-recrystallized	26	112,000
	Doped	16.3	88,000
Pt-26 Rh-8 W	As-recrystallized	20 ^a	115,000 ^a
	Doped	13.5	90,000
Pt-30 Rh-10 W	As-recrystallized	14.5	118,000
	Doped	10	82,000
<u>825°C</u>			
Pt-30 Rh-6 W	As-recrystallized	30 ^a	71,000 ^a
	Doped	31.5	52,000
Pt-26 Rh-8 W	As-recrystallized	30 ^a	76,000 ^a
	Doped	30	54,000
Pt-30 Rh-10 W	As-recrystallized	30 ^a	85,000 ^a
	Doped	31	66,000

^aData obtained from composition or temperature extrapolation.

Table 11. Tensile Ductility of Pt-Rh-W-Hf-Ti Alloys at Room Temperature and 825°C after Oxygen Doping at 1000°C and 1×10^{-5} Torr for 1000 hr

Composition (wt %)	Condition	Tensile Elongation (%)
<u>Room Temperature</u>		
Pt-30 Rh-6 W-0.5 Hf-0.2 Ti	Recrystallized	19.3
	Doped	8.7
Pt-30 Rh-8 W-0.25 Hf-0.1 Ti	Recrystallized	18.5
	Doped	10
Pt-30 Rh-8 W-0.5 Hf-0.2 Ti	Recrystallized	19.3
	Doped	7.3
<u>825°C</u>		
Pt-30 Rh-6 W-0.5 Hf-0.2 Ti	Recrystallized	30 ^a
	Doped	21.3
Pt-30 Rh-8 W-0.25 Hf-0.1 Ti	Recrystallized	30 ^a
	Doped	22
Pt-30 Rh-8 W-0.5 Hf-0.2 Ti	Recrystallized	30 ^a
	Doped	16

^aData estimated from temperature extrapolation.

Fig. 9. A Pt-30% Rh-8% W-0.25% Hf-0.1% Ti 1-1/4-in.-diam Hemisphere Formed by Cold Drawing from 2-in.-diam by 0.03-in.-thick Disk with Two Intermediate Anneals at 1200°C.

Characterization of Iridium

The tensile properties of 20-mil-thick sheet iridium specimens recrystallized 1 hr at 1500°C were determined at 1316°C. The results are presented in Table 12 along with low-temperature data reported previously.¹ Although iridium is weak at low temperatures, it has almost the same strength as the Pt-30% Rh-8% W-1% Hf-0.2% Ti (Table 8) alloy at 1316°C. Thus, the excellent high-temperature strength of iridium is confirmed.

Table 12. Room- and Elevated-Temperature Tensile Properties of Iridium Sheet Recrystallized 1 hr at 1500°C

Testing Temperature (°C)	Ultimate Tensile Strength (psi)	Elongation (%)
Room	56,000	5.7
760	56,000	23.5
1093	35,000	19.8
1316	26,000	38.0

Recent work⁷ on iridium indicates that as-fabricated iridium hemispheres, as well as sheet, contain numerous inclusions (in stringer and globular forms) and surface microcracks. Silica-type beads were also observed on the surface of and in welds. These results indicate the presence of impurities which may be the cause of the low ductility at room temperature (see Table 12) and the difficulty in fabrication.

In order to improve the physical and mechanical properties of iridium, we are now working on the purification of iridium by a zone-refining technique. Two rectangular specimens 0.05 × 0.125 × 3-1/2 in. were cut from iridium plate purchased from Englehard Industries, then zone refined without difficulty in ultravacuum. The resulting zone-refined iridium single crystal bar was cold swaged 40% in area without cracking.

PHYSICAL METALLURGY OF REFRACTORY ALLOYS

(Division of Reactor Development and Technology Program 04 40 02 05 1)

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The purpose of this program is to provide a base technology evaluation of high-temperature materials for use in space applications of radioisotope thermoelectric generators (RTG's). Emphasis is presently on tantalum and molybdenum alloys used as containment materials for ²³⁸PuO₂.

Effect of Oxygen Contamination on the Mechanical Properties of T-111

Previous work¹ indicated that T-111 can tolerate 300 and 750 ppm oxygen when contaminated in low oxygen pressure at 825 and 1000°C respectively. The fractured surfaces of brittle specimens were examined by scanning electron microscopy. The fractograph of a specimen containing 730 ppm oxygen doped at 1000°C (Fig. 10) indicates that grain boundary separation (location A) and cleavage (location B) are competitive fracture modes. It is interesting to note that slip traces (location C) are observed on some grain boundary areas. The ductility of the contaminated specimen increases with heat treatment at high temperatures. Figure 11 shows the dimple-type ductile fracture surface of a specimen annealed 15 min at 1700°C after doping with 3640 ppm oxygen. Here HfO_2 precipitates (about 0.3-micron diameter) are observed at the bottom of the crests on the fracture surface.

In order to show the effect of a heat pulse during reentry of the Pioneer heat source on the tensile properties of oxygen-contaminated T-111, 20-mil sheet specimens containing 700, 1700, and 3150 ppm oxygen were subjected to the thermal history outlined in Table 13, then tested at room temperature. As shown in Table 14, the simulated heat pulse ductilizes oxygen-embrittled T-111 to the extent that the alloy can now tolerate an oxygen level between 1700 and 3150 ppm. Assuming a linear contamination rate of 1/20 ppm per hour (based on the data of Pioneer test capsules PF-3 and PF-7), the results in Table 14 suggest that the T-111 strength member of the Pioneer heat source can be effectively ductilized by the reentry heat pulse after five years at 825°C.

Fig. 10. Scanning Electron Microscope Fractograph of T-111 Doped with 730 ppm Oxygen at 1000°C Exhibiting 2.2% Elongation at Room Temperature (3000X).

Fig. 11. Scanning Electron Microscope Fractograph of T-111 Doped with 3460 ppm Oxygen, Heat-Treated 15 min at 1700°C. Test at 10.5% elongation at 760°C (3000X).

Table 13. A Possible Heat Pulse^a During Reentry of Pioneer Heat Source

Time Elapsed (sec)	Temperature (°F)
0	1517
1180	2000
1350	2500
1400	2600
1460	2500
1560	2400

^aInformation obtained from A. P. Litman, AEC-SNS, Washington, DC.

Table 14. Effect of a Pioneer Heat Pulse on the Mechanical Properties of Oxygen-Contaminated T-111

Oxygen Added (ppm)	Heat-Pulse Treatment	Mechanical Properties at Room Temperature		
		Elongation (%)	Ultimate Tensile Strength (psi)	Fracture Mode
0	No	28	101,000	Ductile
700	No	1	135,000	Brittle
700	Yes	17.3	112,000	Ductile
1700	No	0 ^a	—	Brittle
1700	Yes	10.2	151,000	Ductile
3150	No	0 ^a	—	Brittle
3150	Yes	1.8	234,000	Brittle

^aFracture within elastic limit.

The critical condition which ductilizes T-111 during reentry is believed to be the 110 sec (1.83 min) at temperatures between 1371 and 1427°C (see Table 13). To verify this, the kinetics of the ductilization of T-111 specimens containing 3000 ppm oxygen at 1400°C were studied. The results in Table 15 show that the ductility increases and strength decreases continuously with annealing time. The oxygen-contaminated specimen was only partially ductilized after the 2-min anneal at 1400°C, which is consistent with the results in Table 14. Examination by transmission electron microscopy reveals numerous HfO₂ precipitates about 100 Å in diameter (Fig. 12). The ductilization is due to the continuous coarsening of fine precipitates with annealing time (Fig. 13).

Table 15. Effect of Annealing Time at 1400°C on the Room-Temperature Tensile Properties of T-111 Containing 3000 ppm Oxygen

Annealing Time (min)	Elongation (%)	Tensile Strength (psi)
0	0.4	110,000
2	1.7	233,000
5	3.6	220,000
30	10.5	177,000
240	13.0	142,000

Fig. 12. Transmission Electron Micrograph of T-111
As-doped with 2650 ppm Oxygen at 1000°C (88,750X).

Based on these studies, we believe that oxygen contamination of T-111 at still higher temperatures can result in significant strengthening with only moderate reduction of ductility. In other words, T-111 can tolerate much higher levels of oxygen when it is used at higher temperatures. A series of T-111 specimens were thus doped with oxygen at a pressure of 1×10^{-5} torr at 1200°C and tested at room temperature. The results in Table 16 show that T-111 can tolerate 4000 to 5000 ppm oxygen which is more than an order of magnitude higher than the permissible level when doped at 825°C.

Fig. 13. Transmission Electron Micrograph of T-111 As-doped at 1000°C with 2650 ppm Oxygen and Annealed 5 min at 1400°C (88,750X).

Table 16. Room-Temperature Mechanical Properties of T-111 Oxygen Doped at 1200°C

Oxygen Added (ppm)	Tensile Strength (psi)	Elongation (%)
1375	114,000	18.7
2655	125,000	16.7
3940	147,000	11.0
5120	178,000	2.2
6550	40,000 ^a	0 ^a

^aFractured within elastic limit.

Effect of Oxygen on the Mechanical Properties of 0.090-in.-thick T-111

The embrittlement of 0.020- and 0.040-in.-thick T-111 by oxygen has been reported to be dependent on the contaminating temperature as well as the specimen thickness.¹ Because of the importance of the relationship between oxygen contamination and the ductility of the strength member in the Pioneer heat source, it was deemed necessary to conduct similar studies on 0.090-in.-thick T-111. The tensile properties at 825°C of 0.090-in.-thick T-111 specimens, which were machined from blanks after doping with oxygen at a rate of about 1.5 ppm/hr, are summarized in Table 17. The data show that the ductility remains constant at about 18% elongation to an oxygen level of at least 290 ppm oxygen, but drops sharply from there to zero ductility between 686 and 1070 ppm. Within experimental scatter, the ductility of T-111 as a function of the oxygen content at 825°C of the 0.090-in.-thick specimen is the same as the ductility of the 0.020-in.-thick specimen. Table 18 shows that the ductility of T-111 at room temperature for a given level of oxygen decreased as the specimen thickness increased.

Table 17. Effect of Oxygen on the 825°C Tensile Properties of 90-mil-thick T-111^a

Amount of Oxygen Added (ppm)	Tensile Strength (psi)	Elongation (%)
Control ^b	59,200	18.0
185	72,500	20.5
290	77,500	18.5
422	75,500	11.5
560	71,900	5.2
686	74,600	2.8
1070	50,800	0.0

^a3/4 × 2-1/2 × 0.090 in. blanks doped with oxygen at 1 × 10⁻⁶ torr prior to machining tensile specimens.

^bAnnealed 1 hr at 1650°C. Analysis: 10 ppm oxygen, 10 ppm nitrogen, 3 ppm hydrogen and 24 ppm carbon.

Table 18. Effect of Specimen Thickness on the Room-Temperature Ductility of T-111

Oxygen Added (ppm)	Elongation (%)		
	0.020 in. Thick	0.040 in. Thick	0.090 in. Thick
170	23	26	16.8
244	21	12	6.0
362	10	1	3.2

Contamination Studies of T-111 and TZM by Impurities Outgassed from Graphite and Min-K 1301

Tensile specimens of bare T-111, molybdenum-coated T-111, and TZM have been exposed at 825°C to gases outgassed from graphite and Min-K 1301 under conditions that approximate those in the Pioneer radioisotope thermoelectric generator.* The reaction rates of 0.020-in.-thick sheet specimens of T-111 with the impurity gases transported through a 0.020-in.-diam orifice are shown in Table 19. These results show that oxygen contamination varies linearly with the exposure time. The calculated reaction rates of 0.6 to 0.8 ppm/hr for 0.090-in.-thick specimens contaminated from one side are somewhat higher than the 0.16 ppm rate observed for PF-7 (ref. 8) in a 1000-hr test. This difference is attributed mainly to differences in the volume ratios of the test components, to the geometry of the separate systems, and to the use of different outgassing procedures.

Table 19. Reaction Kinetics of T-111 in the Simulated Pioneer Heat Source Environment

Exposure (hr)	Contamination Rate for 0.020-in.-thick T-111 ^a (ppm/hr)	Contamination Rate for 0.090-in.-thick T-111 ^a (ppm/hr)
280	7.21	0.80
506	5.72	0.63
1004	6.57	0.73

^aBased on weight gain; specimen contaminated from both sides.

^bCalculated rate for 0.090-in.-thick T-111 contaminated from one side.

The contamination rate of T-111 decreases as the thickness of molybdenum coating increases as shown in Table 20. Table 21 shows that the oxygen contamination of T-111 coated with 0.0012 in. of molybdenum is 16 to 27 times lower than the uncoated specimens and that the tensile ductility of the coated specimens is not seriously impaired by the simulated Pioneer environment. The uncoated specimens were completely brittle as would be expected for specimens containing 2000 to 6600 ppm oxygen.

*Argon at 600 torr plus gases from ATJ graphite and Min-K at 538°C getterred with both bare and palladium-wrapped zirconium foil. Graphite previously vacuum outgassed 4 hr at 1200°C and Min-K outgassed 48 hr in air at 400°C plus 2 hr at 600°C in vacuum.

Table 20. Effect of Molybdenum Coating on Contamination of 0.020-in.-thick T-111 in Simulated Pioneer Environment

Exposure (hr)	Thickness Molybdenum (in.)	Contamination Rate (ppm/hr)
204	none	11.8
534	none	11.1
204	0.0001 ^a	4.0
204	0.0002 ^a	2.2
534	0.0002 ^a	1.5
280	0.0012 ^b	0.27
506	0.0012 ^b	0.35
1004	0.0012 ^b	0.29

^aVacuum-evaporated molybdenum.

^b0.0002-in. vacuum-evaporated molybdenum plus 0.001-in. CVD molybdenum.

Table 21. Effect of a 0.001-in.-thick Molybdenum Coating on the Contamination and Room-Temperature Properties of 0.020-in.-thick T-111

Exposure (hr)	Level of Oxygen Contamination ^a		Tensile Properties of Coated Specimens	
	(ppm)		Tensile Strength (psi)	Elongation (%)
	Uncoated	Coated		
280	2020	76	83,300	15.0
506	2900	179	100,000	15.3
1004	6620	293	102,500	10.7

^aCalculated from weight gain of specimens.

Table 22 summarizes the tensile properties of TZM after 2004-hr exposure to the simulated environment. In general, no significant differences were noted in the tensile strengths; however, the ductility decreases steadily with exposure times to values of 12-15% elongation. Although chemical analyses have not been obtained yet, the extent of contamination based on the weight change of the specimens was very small. From the standpoint of compatibility with the Pioneer heat source environment, it is concluded that both molybdenum-coated T-111 and TZM would be suitable alternate strength members.

Table 22. Tensile Properties of 0.020-in.-thick TZM at Room Temperature and 825°C after Exposure to Simulated Pioneer Heat Source Environment

Exposure (hr)	Ultimate Tensile (psi)	Elongation (%)
<u>Room Temperature</u>		
Control	79,600	33.5
534	77,800	35.7
1030	78,400	32.8
2004	79,300	15.0
<u>825°C</u>		
Control	45,000	24.8
534	43,800	20.0
1030	43,700	21.8
2004	46,300	12.0

Effect of Oxygen Contamination on the Mechanical Properties of Molybdenum-Base Alloys

The mechanical properties of molybdenum-base sheet specimens contaminated with oxygen at 825°C and 1×10^{-5} torr oxygen pressure were determined at various temperatures. The results are given in Tables 23 and 24 together with data obtained previously at room temperature and 825°C.¹ Oxygen contamination of TZM at 825°C causes only a small decrease of ductility at room temperature, and the ductility remains at a level of 25% after 2000 hr of exposure. However, as shown in Table 23, TZM suffers a moderate reduction of ductility at 825 and 1316°C and a more serious reduction at 1093°C. These results clearly indicate that increasing the test temperature does not improve the ductility of oxygen-contaminated TZM. The same was found in T-111. The tensile strength of TZM does increase some with doping time.

The response of the Mo-46% Re alloy to an oxygen environment is quite different from TZM. Mo-46% Re specimens show no change in ductility at room temperature after 1000 hr of contamination, but show a sharp drop after the 2000-hr exposure, assuming that the reported value of 1.3% elongation in Table 24 is not due to defects in the specimen. However, increasing the test temperature to 825°C, restores the ductility of the specimen contaminated for 2000 hr. The difference in behavior of these two alloys is believed to be due to the retention of oxygen in solution in the Mo-Re alloy, but in TZM oxygen reacts with zirconium and titanium to form oxide precipitates.

Table 23. Tensile Properties of 20-mil-thick TZM Sheet Specimens at Various Test Temperatures after Contamination with Oxygen at 1×10^{-5} Torr and 825°C

Doping Time (hr)	Tensile Strength (psi)	Elongation (%)
<u>Room Temperature</u>		
0	79,300	35.3
100	81,200	25.2
500	85,000	29.2
994	84,000	31.0
2000	85,000	24.5
<u>825°C</u>		
0	45,000	24.8
994	46,800	18.0
2000	51,200	17.7
<u>1093°C</u>		
0	33,000 ^a	24 ^a
500	41,000	15.3
994	40,000	12.2
2000	42,000	6.6
<u>1316°C</u>		
0	22,000 ^a	30 ^a
500	25,000	23
994	25,500	14.2
2000	28,700	10.0

^aData collected from General Electric Company, *Multi-Hundred Watt, Radioisotope Thermoelectric Generator Program*, GESP-7034 (March 1970).

Table 24. Tensile Properties of 20-mil Mo-46% Re Sheet Specimens at Room Temperature and 825°C after Contamination with Oxygen at 1×10^{-5} Torr and 825°C

Doping Time (hr)	Tensile Strength (psi)	Elongation (%)
<u>Room Temperature</u>		
0	195,000	8.2
1000	192,000	9.2
2000	153,000	1.3
<u>825°C</u>		
1000	116,000	13.7
2000	115,000	9.6

Effect of CO Contamination on the Mechanical Properties of Molybdenum-Base Alloys

The tensile properties of TZM sheet specimens contaminated with CO at 825°C and 1×10^{-5} torr gas pressure have been determined at elevated temperatures. The results are given in Table 25 together with those obtained previously¹ at room temperature and 825°C. TZM shows a moderate decrease in ductility and a moderate increase in strength with doping time; however, TZM has more than 15% elongation after 2000 hr of exposure. We thus believe that TZM is reasonably compatible with CO.

Table 25. Tensile Properties of 20-mil-thick TZM Sheet Specimens at Various Temperatures after Contamination with CO at 825°C and 1×10^{-5} Torr

Doping Time (hr)	Tensile Strength (psi)	Elongation (%)
<u>Room Temperature</u>		
0	79,000	37.0
0	79,600	33.5
196	79,500	33.2
1000	83,000	30.0
2000	82,000	27.9
<u>825°C</u>		
0	45,000	24.8
2000	46,300	22.5
<u>1093°C</u>		
0	33,000 ^a	24 ^a
1000	38,800	15.2
<u>1316°C</u>		
0	22,000 ^a	30 ^a
196	27,600	23.0
1000	30,000	18.0
2000	30,700	15.5

^aData collected from General Electric Company, *Multi-Hundred Watt, Radioisotope Thermoelectric Generator Program*, GESP-7034 (March 1970).

The effect of CO contamination on the mechanical properties of Mo-46% Re is also shown in Table 26. The tensile data obtained at room temperature and 825°C indicate that CO at 825°C has no effect whatsoever on the mechanical properties of Mo-46% Re alloy.

Table 26. Tensile Properties of 20-mil-thick Mo-46% Re Sheet Specimens at Room Temperature and 825°C after Contamination with CO at 825°C and 1×10^{-5} Torr

Doping Time (hr)	Tensile Strength (psi)	Elongation (%)
<u>Room Temperature</u>		
0	195,000	8.2
1004	190,000	10.7
2006	186,000	12.0
<u>825°C</u>		
1004	115,000	10.5
2006	123,000	9.7

Contamination Studies of TZM by Water Vapor

Table 27 shows the tensile properties of TZM after exposure to 1×10^{-5} torr water vapor at 825°C. The room-temperature tests show only a small decrease in ductility for exposures to 1000 hr; however, after 2000 hr the specimen was completely brittle. The tensile properties at 825°C after exposures to 2000 hr are only slightly different from the control specimen.

Table 27. Tensile Properties of 0.020-in.-thick TZM at Room Temperature and 825°C after Exposure to 1×10^{-5} Torr Water Vapor

Exposure (hr)	Ultimate Tensile (psi)	Elongation (%)
<u>Room Temperature</u>		
Control ^a	79,600	33.5
457	83,200	31.0
1002	80,600	29.3
1995	74,500	0.3
<u>825°C</u>		
Control	45,000	24.8
457	45,600	20.2
1002	46,000	16.3
1995	44,600	20.0

^a Recrystallized 1 hr at 1450°C.

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