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ORNL ISOTOPIC POWER FUELS
QUARTERLY REPORT FOR
PERIOD ENDING SEPTEMBER 30, 1972

Eugene Lamb

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ISOTOPES DEVELOPMENT CENTER

ORNL ISOTOPIC POWER FUELS QUARTERLY REPORT
FOR PERIOD ENDING SEPTEMBER 30, 1972

NOVEMBER 1972

Eugene Lamb

Isotopes Division

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CONTENTS

	<u>Page</u>
SUMMARY	1
CURIUM-244 FUEL DEVELOPMENT	1
Curium-244 Oxide Fuel Development and Properties	1
$^{244}\text{Cm}_2\text{O}_3$ Compatibility Program	1
Volatile Transport of Cm_2O_3	3
X-Ray Diffraction Unit	4
Curium Heat Source	5
Impact Testing of Heat Source Materials	5
Sabot Heaters	5
Particle Size Distribution	6
REFERENCE	6

LIST OF FIGURES

Fig. 1. New Heater Mandrel and Impact Cup Design	6
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LIST OF TABLES

Table 1. Summary of Conditions for $^{244}\text{Cm}_2\text{O}_3$ Compatibility Tests	2
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SUMMARY

A number of materials have been selected for evaluation as a container for $^{244}\text{Cm}_2\text{O}_3$ in radioisotopic power generator applications from 900 to 1400°C. Ceramic materials may be desirable as either primary encapsulants or as liners in the assembled curium sources. ThO_2 was chosen as a ceramic material to be included in compatibility tests. Interaction of BeO and $^{244}\text{Cm}_2\text{O}_3$ was studied experimentally, and results from this study eliminated BeO from the test materials. A mixture of $\text{SiC-Cm}_2\text{O}_3$ will be studied experimentally to determine the suitability of SiC as a material for further compatibility tests.

The volatile transport of Cm_2O_3 in vented heat sources is being studied. A high-temperature furnace equipped with a quadrupole mass spectrometer is being used to obtain the equilibrium vapor pressure of $^{244}\text{Cm}_2\text{O}_3$ in the temperature range 900-1527°C and for identification of the volatile species over $^{244}\text{Cm}_2\text{O}_3$ in the temperature range 900-2300°C.

An x-ray diffraction unit for radioactive materials is being readied for characterization of ^{244}Cm materials. Work was resumed on recovery of the Cm_2O_3 fuel from the tungsten fuel block. The capsule has been stored under argon atmosphere in a sealed container.

The loss of structural properties of sabot materials at test conditions resulted in a redesign of the sabot heater units. The diameter of the impact cup was reduced sufficiently to prevent the swaging heater walls from trapping the cup.

CURIUM-244 FUEL DEVELOPMENT

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

Curium-244 Oxide Fuel Development and Properties

$^{244}\text{Cm}_2\text{O}_3$ Compatibility Program

A number of materials have been selected for evaluation as a container for $^{244}\text{Cm}_2\text{O}_3$ in radioisotopic power generator applications from 900 to 1400°C. An outline of the test conditions is shown in Table 1. Taking into account current systems designs, we have included venting the capsules to helium or to vacuum as a requirement of our compatibility test design. The effect of

using graphite as an impact-resistant material surrounding the fuel capsule will also be determined. Tests are scheduled to run for 2500-5000 hr, and evaluation will consist of chemical analyses, metallography, autoradiography, and electron-beam microprobe analysis.

Table 1. Summary of Conditions for $^{244}\text{Cm}_2\text{O}_3$ Compatibility Tests

Time (hr)	Materials		
	Temperature ($^{\circ}\text{C}$)		
	900 ^a	1100 ^b	1400 ^b
2500		Iridium Platinum Pt-2608M Pt ₃ Ir Graphite	Iridium Graphite ThO ₂ SiC or ZrO ₂
5000	Iridium Platinum Pt-20% Rh Pt-2608 Hafnialloy Haynes 25 Haynes 188 Hastelloy C-276 Graphite		Tantalum T-111 Molybdenum Mo-Re Tungsten W-26% Re

^aCapsules vented to helium only. One group of tests will have graphite capsule surrounding an inner capsule; the other will not.

^bFour test variables at 1100 and 1400 $^{\circ}$: capsules vented to either helium or dynamic vacuum and, in each case, one will have graphite intermediate capsule and one will not.

The materials to be tested with $^{244}\text{Cm}_2\text{O}_3$ are being procured. Orders have been placed with Thermo Electron Corporation for 56 inner capsule assemblies (9 different materials), 35 intermediate capsule assemblies (graphite), 16 capsule holders (Al₂O₃ and BeO), and 15 outer container assemblies (tantalum and Hastelloy X). We expect to receive the inner and intermediate capsule assemblies by November 1, 1972, and the remaining components by December 15, 1972. Five inner capsule assemblies of Hafnialloy were received from TRW on October 3, 1972. Precious metals melting stock for inner capsule fabrication has not been obtained.

Ceramic materials, due to their resistance to attack by atmospheric environments, may be desirable either as primary encapsulants or as liners in assembled $^{244}\text{Cm}_2\text{O}_3$ sources. Little information is available concerning the reaction of Cm₂O₃ with possible ceramic capsule materials. There are, however, considerable data concerning lanthanide oxides. These data can serve as a guide to the expected behavior of Cm₂O₃. Phase diagrams of mixtures of various lanthanides and BeO, MgO, Al₂O₃, ZrO₂, and ThO₂ were found. In most cases, the minimum melting points of these mixtures were

above 1400°C, the maximum operating temperature of current interest. This characteristic suggests that these materials might be used with Cm_2O_3 without rapid failure. There is, however, a degree of mutual solubility of the solid phases in all cases. The results of these interactions are unknown. The maximum effects might be dimensional changes, a tendency to crack during temperature changes, and the passage of curium through the capsule walls.

Thorium dioxide was selected as one ceramic material for investigation with $^{244}\text{Cm}_2\text{O}_3$. Three rods of ThO_2 were isostatically pressed at 60,000 psi and densified to 97.1% theoretical at 1900°C in the Ceramics Laboratory of the Metals and Ceramics Division. However, attempts to machine the rods were unsuccessful due to the formation of radial and longitudinal cracks. Additional rods were fabricated at a reduced pressure and these specimens are currently being machined.

The interaction of BeO and $^{244}\text{Cm}_2\text{O}_3$ was studied experimentally. A mixture of 67 mole % $^{244}\text{Cm}_2\text{O}_3$ and 23 mole % BeO was ground and cold-pressed to form a pellet. (It was surmised from phase diagrams of actinides and lanthanides with BeO that a eutectic of approximately the above composition will be formed in the system $\text{BeO}-^{244}\text{Cm}_2\text{O}_3$.) The $^{244}\text{Cm}_2\text{O}_3$ -BeO pellet was reacted for 2 hr at temperatures up to 1900°C. Observation of the pellet indicated shrinking at 1500°C, formation of a liquid phase at 1750°C, and melting at 1850°C. These results eliminate BeO from inclusion in the list of test conditions given in Table 1.

SiC- Cm_2O_3 couple tests will be completed during the next quarter to determine the choice of the second ceramic material to be included in Table 1.

Volatile Transport of Cm_2O_3

The data on Cm_2O_3 that are required to define the transport characteristics in the vapor phase are:

1. Determination of equilibrium vapor pressure of $^{244}\text{Cm}_2\text{O}_3$ in the temperature range 900-1527°C.
2. Identification of the volatile species over $^{244}\text{Cm}_2\text{O}_3$ for the temperature range 900-2300°C.

Knudsen cell vaporization rates have been determined previously for a higher temperature range (1527-2327°C) by Smith and Peterson.¹ They did not identify the molecular species in the vapor directly but deduced that the Cm_2O_3 dissociated into CmO and O . The identification of the vapor species and the extension of the temperature range of the vapor pressure data down to 900°C is necessary.

The required additional data will be obtained using a high-temperature furnace which is equipped with a quadrupole mass spectrometer. The vapor species of curium oxide and impurities in the curium oxide product can be identified and quantitized by use of the mass spectrometer.

Although all methods of volatile transport can in theory be calculated from vapor pressure rate data and geometry, in practice these calculations on complex systems may prove unreliable. Several experiments based on models of various vented sources will be tested to determine the reliability of calculated values and to yield empirical data applicable to real systems.

One important factor which must be evaluated is the interaction of material in the source with $^{244}\text{Cm}_2\text{O}_3$. Materials which act as reducing agents would tend to shift the dissociation equilibrium so as to increase the volatility of curium. The reducing materials that could be present are the capsule metals and carbon.

Qualitative information concerning the effect of a temperature excursion will be obtained by suddenly increasing the temperature of the sample to a higher temperature.

The quadrupole mass spectrometer and the associated equipment for these experiments have been completed and installed in a manipulator cell. A refinement made to the quadrupole mass spectrometer was the addition of a beam chopper between the source of the vapor being analyzed and the detector of the mass spectrometer. The beam chopper will eliminate the effect of high signal-to-noise ratio which is encountered at low temperatures (900°C) when the vapor concentrate seen by the detector is low.

To make quantitative determinations of mass transfer using the quadrupole mass spectrometer, it is necessary to calibrate the ionization efficiency and the geometry factor of the mass spectrometer using absolute values of the vapor pressure of $^{244}\text{Cm}_2\text{O}_3$. These values have never been determined in the prime range of interest (900-1400°C) for isotopic power applications. A Knudsen-type vapor pressure apparatus will be used to acquire the vapor pressure data. These data will be used to calibrate the quadrupole mass spectrometer, which can then be used to rapidly determine quantitatively the mass transfer rates of all species of curium vapor under source operating conditions.

X-Ray Diffraction Unit

An x-ray diffraction unit for radioactive materials is being readied for characterization of ^{244}Cm materials. The unit has a vertical-type goniometer contained in an inert-gas glove box with a furnace attachment to heat samples to 2000°C. X-ray diffraction data will facilitate the characterization of $^{244}\text{Cm}_2\text{O}_3$ for application in aerospace isotopic power generators operating for long periods at temperatures to 1400°C and having the possibility of excursions to approximately 2000°C for short time periods such as atmospheric reentry. Specific applications for the x-ray unit in our experiments are: (1) study of the $^{244}\text{Cm}_2\text{O}_3$ - $^{240}\text{PuO}_{2-x}$ (decay product of $^{244}\text{Cm}_2\text{O}_3$) phase system to determine lattice parameters, density, and phase transitions; (2) compatibility of Cm_2O_3 with ceramic materials such as BeO and SiC; (3) characterization of Cm_2O_3 -metal systems to assist in evaluating compatibility data; and (4) identification of volatile species in product-grade $^{244}\text{Cm}_2\text{O}_3$ and residual effects on the lattice structure of the remaining $^{244}\text{Cm}_2\text{O}_3$.

Curium Heat Source

Work was completed on recovery of the Cm_2O_3 fuel from the tungsten fuel block. Attempts to recover one or more whole Cm_2O_3 pellets or large chunks of the fuel from the heat source proved unsuccessful. Tooling was installed in the cell to remove the fuel by drilling through the columns of pellets in each channel of the fuel block.

The remainder of the $^{244}\text{Cm}_2\text{O}_3$ fuel was removed from the tungsten capsule by drilling. All seven of the fuel cavities were drilled with a 0.4375-in.-diam end mill, and five of the cavities were then drilled with a 0.5312-in.-diam end mill. The inside diameter of each fuel cavity is 0.540 in. Two of the fuel cavities were not drilled with the larger end mill in order to preserve the fuel-capsule interface for metallographic examination. The capsule has been welded into a stainless-steel shipping can for transfer to HRLEL for sectioning and metallographic examination. It is estimated that 10 W(th) (4 g) of material remains in the capsule.

Impact Testing of Heat Source Materials

Sabot Heaters

The loss of structural properties of the sabot materials when heated to test conditions has resulted in a redesign of the sabot heater units. In test findings of the heated units, two problems were encountered. One was that the clearance between the impact cup and the cavity of the sabot heater was too small to allow free flight of the impact cup from the heater cavity. When the heater impacts on the dividing wall of the catcher box, the heater cavity walls deform and swage around the impact cup, thus reducing the impact velocity. Another problem has been the removal of the threaded end cap at the impact cup. Only one end cap of those tested could be removed.

Three samples of Mo- ThO_2 cermet were impacted at a temperature of 800°C. The desired impact velocity of each of the samples was 300 ft/sec. The impact velocity of the first sample was 273.2 ft/sec. The impact cup which contained the sample was 1-in. OD with a 1/8-in. radial clearance between the impact cup and the heater cavity. Examination of the impact cup and heater after firing showed that the heated cavity walls were swaging around the impact cup and reducing the impact velocity. A second sample was fired in which a 3/16-in.-high ring was tack-welded onto the sabot impacting surface in the catcher box on the assumption that this additional distance would allow the impact cup to clear the heater cavity before the cavity swaged around it. An old impact cup with only 0.015 in. of radial clearance between cup and heater cavity was used. This clearance was insufficient, and the impact cup lodged in the heater cavity. Approximately 7/32 in. of the cup exited the cavity before the cavity walls swaged around it.

To achieve free flight of the impact cup, the heater mandrel wall thickness was increased and the maximum outside diameter of the impact cup was decreased to 1 in. (Fig. 1). One of the redesigned units was fired with an impact velocity of 295 ft/sec, which is within the limits of the gun calibration. Examination of the impact cup after this shot showed that the cup cleared the heater cavity and that the impact was centered and at right angles to the granite block. In all of the three test shots the sample of the Mo-ThO₂ cermet did not fracture upon impact, and no particles were generated. These samples were 73 wt % molybdenum and were impacted at a temperature of 800°C.

ORNL DWG. 72-12635

Fig. 1. New Heater Mandrel and Impact Cup Design.

Recalibration of the timer for the impact device has been accomplished using a Strobotac and a rotating wire. The timer was in excellent agreement with the calibrating device.

Particle Size Distribution

A sample of gadolinium sesquioxide (Gd₂O₃) particles generated from the impact of a Gd₂O₃ sphere was shipped to Millipore. The sample contained 638.3 mg of particles that were $\leq 125 \mu\text{m}$ in size. The sample of particles will be analyzed with Millipore's πMC particle size analyzer and a particle size distribution will be obtained. A control sample of the particles was also taken for analysis by the πMC when the machine has been delivered to ORNL.

REFERENCE

1. P. K. Smith and D. E. Peterson, "High Temperature Evaporation and Thermodynamic Properties of Cm₂O₃," *J. Chem. Phys.* 52, 4963-72 (1970).

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