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COMPATIBILITY OF CURIUM OXIDE WITH
REFRACTORY METALS AT 1650°C AND 1850°C

J. R. DiStefano
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ISOTOPES DEVELOPMENT CENTER

COMPATIBILITY OF CURIUM OXIDE WITH REFRACTORY METALS
AT 1650°C AND 1850°C

J. R. DiStefano

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APRIL 1972

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COMPATIBILITY OF CURIUM OXIDE WITH REFRACTORY METALS AT 1650°C AND 1850°C

J. R. DiStefano and K. H. Lin

ABSTRACT

The power density of $^{244}\text{Cm}_2\text{O}_3$ makes it an attractive fuel form for a variety of radioisotopic applications. To evaluate the compatibility of $^{244}\text{Cm}_2\text{O}_3$ with various refractory metals for high-temperature applications, we tested Ta, Ta-10% W, T-111, Mo, TZM, W, and W-26% Re at 1650 and 1850°C for times up to 10,000 hr.

Serious reactions between $^{244}\text{Cm}_2\text{O}_3$ and Ta-10% W and T-111 were found at 1650°C. With Mo, TZM, W, and W-26% Re only limited attack occurred, mainly in the form of intergranular subsurface voids.

At 1850°C there was evidence of dissolution of tantalum and the tantalum alloys by $^{244}\text{Cm}_2\text{O}_3$. After 5,000 and 10,000 hr tantalum had transferred from one portion of the capsule to another, and tantalum particles were found in the fuel. Less extensive mass transfer was noted with the other materials, although significant amounts of tungsten from the unalloyed tungsten and W-26% Re tests were found in the fuel.

We concluded that W-26% Re, TZM, and molybdenum exhibited the best compatibility with $^{244}\text{Cm}_2\text{O}_3$ under the test conditions. The influence of temperature gradients on mass transport reactions and greatly increased $^{244}\text{Cm}_2\text{O}_3$ -to-metal surface area or weight ratios should be investigated in future tests.

INTRODUCTION

Electrical power requirements in orbiting satellites, remote weather stations, ocean buoys, etc. have given rise to a need for compact, reliable power supplies capable of long-term operation.^{1,2} Radioisotopes are a source of energy that can be coupled with thermoelectric, thermionic, or mechanical conversion systems to provide the desired characteristics. If the fuel source and its container are compatible, the useful life of a system will depend upon the half-life of the radioisotope and the reliability of the power conversion elements.

The safe and efficient use of radioisotopes as heat sources requires suitable isotopic compounds of known physical and chemical properties.^{3,4} Some important characteristics of several radioisotopes that have been considered for use in the above applications are shown in Table 1.

Table 1. Radionuclides for Isotopic Power Generator Applications

Radio-nuclide	Principal Type of Activity	Half-Life (years)	Fuel Form	Active Isotope in Fuel (%)	Power of Fuel Form (W/g)	Power Density of Fuel Form (W/cm ³)
²¹⁰ Po	Alpha	0.38	Metal	95	134	1210
²³⁸ Pu	Alpha	87.4	PuO ₂	70	0.39	3.9
²⁴² Cm	Alpha, neutron	0.45	Cm ₂ O ₃	82	98	882
²⁴⁴ Cm	Alpha, neutron	18.1	Cm ₂ O ₃	86	2.45	27.0
⁶⁰ Co	Beta, gamma	5.2	Metal	10	1.74	15.8
⁹⁰ Sr	Beta	28	SrTiO ₃	23	0.22	1.01
¹³⁷ Cs	Beta, gamma	30	CsCl	28	0.12	0.38
¹⁴⁴ Ce	Beta, gamma	0.78	Ce ₂ O ₃	3.8	1.0	6.2
¹⁴⁷ Pm	Beta	2.6	Pm ₂ O ₃	82	0.27	1.8

Curium-244 is of particular interest in thermionic systems because it can be made into a chemically stable, high-melting fuel form, ²⁴⁴Cm₂O₃, that has a relatively high power density (~27 W/cm³). Although ²⁴⁴Cm has not yet been produced on a large scale, nuclear reactors at Savannah River Laboratory and Oak Ridge National Laboratory have provided sufficient material for experimental use. Furthermore, the stockpile of ²⁴⁴Cm will naturally increase in coming years as a by-product of reprocessing reactor fuels.

To contain ²⁴⁴Cm₂O₃ at thermionic temperatures (greater than 1500°C) requires metals or alloys having relatively high melting temperatures. Several potential container materials and their melting points are shown in Table 2. When different materials are in contact at elevated temperature, there is often a tendency for interaction across the boundary. The type and extent of interaction will vary with the composition of the materials, the temperature, and the time of exposure. During the past several years we have been studying the nature and extent of reactions between the materials in Table 2 and ²⁴⁴Cm₂O₃ at 1650 and 1850°C for times up to 10,000 hr.

Table 2. Melting Points of Some Refractory Metals and Alloys

Refractory Metal or Alloy	Melting Point (°C)
Tantalum	3000
T-111 (Ta-8% W-2% Hf)	2980
Ta-10% W	3035
Molybdenum	2610
TZM (Mo-0.5% Ti-0.08% Zr)	2610
Tungsten	3410
W-26% Re	3170

CURIMUM-244 OXIDE

Source and Analyses

The major supply of source compound (^{244}Cm oxides, presumably $^{244}\text{CmO}_{1.8-2.0}$) for preparation of the $^{244}\text{Cm}_2\text{O}_3$ was received from Savannah River Laboratory (SRL). A smaller amount of $^{244}\text{CmO}_2$ was obtained from the Transuranium Processing Plant at Oak Ridge National Laboratory (ORNL). Typical isotopic compositions are given in Table 3. Shown in Tables 4 and 5 are radiochemical and elemental impurity contents of the same material. The difference in the elemental impurity contents between the SRL product and the ORNL product in part are attributable to the different methods used for the analyses.

Table 3. Typical Isotopic Composition of ^{244}Cm Oxide Products

Isotope	Content (wt % of the curium)	
	SRL Product ^a	ORNL Product ^b
^{242}Cm	0.0426	0.003
^{243}Cm	0.0238	
^{244}Cm	95.08	94.73
^{245}Cm	0.729	1.76
^{246}Cm	4.02	3.43
^{247}Cm	0.0659	0.063
^{248}Cm	0.0381	0.019

^aInformation provided by D. G. Ebenhack, SRL.

^bInformation provided by W. D. Burch, ORNL.

Table 4. Radiochemical Impurities in Typical ^{244}Cm Oxide Products from SRL and ORNL^a

Radio-nuclide	Concentration	
	SRL Product (Ci/g ^{244}Cm)	ORNL Product
	$\times 10^{-5}$	
^{103}Ru	<1	Trace
^{106}Ru	7	
^{134}Cs	<1	
^{137}Cs	<1	Not detectable
^{144}Ce	48	
^{144}Pr	<48	
^{95}Zr	<2	
^{95}Nb	<0.5	Not detectable
^{154}Eu	<2	
^{243}Am	75	
^{252}Cf	10	$\leq 6.7 \times 10^{-5}$ Ci/Ci ^{244}Cm
		0.1 neutron/ ^{244}Cm neutrons

^aInformation from D. G. Ebenhack, SRL, and W. D. Burch, ORNL.

Table 5. Elemental Impurities in Typical ^{244}Cm Oxide Products from SRL and ORNL^a

Element	Concentration (ppm)		Element	Concentration (ppm)	
	SRL Product	ORNL Product		SRL Product	ORNL Product
Li	<50	<500	Cd	60	
Na	230	<500	B	30	<3,000
K	280	<500	Ag	40	
Si	25		Cu	20	
Zn	<250		Mg	10	
Fe	550	<800	Mo	<10	
Cr	240	<1,500	Mn	40	<1,500
Ni	90	<1,500	Co	<50	
Am	9,070	12,500	Pb	70	<15,000
Zr	4,500	<500	Ta	600	
Ca	15	3,800	Sr		2,800
Al	<25	<1,500	Ti		<300
Sn	250	<15,000			

^aInformation from D. G. Ebenhack, SRL, and W. D. Burch, ORNL.

Particle-Size Distribution

Representative samples of ^{244}Cm oxide from SRL had the average particle-size distribution shown in Table 6. Approximately one-half the material was larger than 300 μm . Particles smaller than about 50 μm formed agglomerates of larger sizes, and this behavior persisted even when large particles were pulverized. The particle-size distribution did not change appreciably as the as-received oxide was converted to $^{244}\text{Cm}_2\text{O}_3$.

Table 6. Particle-Size Distribution of ^{244}Cm Oxide from SRL^a

Particle-Size Range (μm)	Fraction (wt %)
10-20	1.9
20-30	1.4
30-45	3.6
45-60	10
60-90	13.3
90-200	12.2
200-300	9.3
>300	48.3

^aInformation from P. Angelini, Isotopes Division, ORNL.

Melting Point

The melting point of $^{244}\text{Cm}_2\text{O}_3$ varies with its purity. Production quality $^{244}\text{Cm}_2\text{O}_3$ has been reported⁵ to melt at 2170 to 2250°C, while the melting point of highly purified material ranges from 2255 to 2277°C. The melting point of most of the $^{244}\text{Cm}_2\text{O}_3$ material used in these studies averaged 2170°C.

Stoichiometry, Crystal Structure, and Phase Transformation

Compounds of ^{244}Cm and oxygen can have several different stoichiometries. The oxides $^{244}\text{CmO}_2$ and $^{244}\text{Cm}_2\text{O}_3$ have been identified by x-ray analysis⁶ and thermogravimetric techniques.⁷ Posey *et al.*⁷ and Chikalla and Eyring⁸ also established evidence for two intermediate phases of composition $^{244}\text{CmO}_{1.71}$ and $^{244}\text{CmO}_{1.83}$. Oxidation states lower than $^{244}\text{Cm}_2\text{O}_3$ have not been reported.

The sesquioxide, $^{244}\text{Cm}_2\text{O}_3$, assumes three different crystal structures, as reported by Mosley,⁹ Wallman,¹⁰ and Haug.¹¹ The A-type $^{244}\text{Cm}_2\text{O}_3$ is a hexagonal structure that was identified^{10,12} in the product of self-radiation of C-type $^{244}\text{Cm}_2\text{O}_3$ (body-centered cubic). The B-type (monoclinic) structure can be obtained by heating the C-type above 850°C. A reversible transformation from the B-type to A-type $^{244}\text{Cm}_2\text{O}_3$ takes place above 1600°C. Self-radiation from alpha decay of ^{244}Cm in the C-type $^{244}\text{Cm}_2\text{O}_3$ induces not only the phase transformation but also lattice swelling that is approximately one-half that observed¹² in $^{244}\text{CmO}_2$. No swelling has been observed in the monoclinic B-type $^{244}\text{Cm}_2\text{O}_3$, which is quite stable under alpha irradiation and is considered to be the most desirable radiation heat source form. The $^{244}\text{Cm}_2\text{O}_3$ samples used in the present study were prepared in such a way that the B-type of structure was obtained.

Density

The theoretical values of density computed from lattice parameters are 11.4 g/cm³ at 1640°C for the A-type $^{244}\text{Cm}_2\text{O}_3$, 11.7 g/cm³ at room temperature for the B-type, and 10.7 g/cm³ at room temperature for the C-type. The hot-pressed $^{244}\text{Cm}_2\text{O}_3$ pellets had densities in excess of 90% of the theoretical value for the B-type.

Radioactivity

The radioactivity of the production-grade $^{244}\text{Cm}_2\text{O}_3$ is summarized in Table 7. Gamma radiations originate from decay of the ^{244}Cm , spontaneous fissions, fission products, and impurities. A typical $^{244}\text{Cm}_2\text{O}_3$ pellet used in the compatibility study weighed approximately 250 mg. At a distance of 2 in. from the outer capsule, when doubly encapsulated, such a pellet (with 0.014 in. total wall thickness) exhibited the following radiation levels: gamma, 40; fast neutron, 120; and intermediate neutron, 20 mR/hr.

Table 7. Radioactivity of $^{244}\text{Cm}_2\text{O}_3$ (Production Grade)^a

Energy (MeV)	Intensity (particles, neutrons, or photons/W·sec)
<u>Alpha Particles</u>	
5.801	8.25×10^{13}
5.759	2.52×10^{13}
<u>Neutrons</u>	
Spontaneous fission spectrum	4.6×10^6
<u>X Ray</u>	
0.017	1.7×10^{11}
<u>Total Gamma</u>	
0-0.5	3×10^8
0.5-1.0	2×10^7
1.0-2.0	4.9×10^6
2.0-3.0	1.6×10^6
3.0-4.0	1.9×10^5
4.0-5.0	6.4×10^4
5.0-6.0	3.3×10^4
6.0-7.0	5.6×10^3

^aAbstracted from S. J. Rimshaw and E. E. Ketchen, *Curium Data Sheets*, ORNL-4357, Oak Ridge National Laboratory (January 1969).

EXPERIMENTAL DESIGN AND PROCEDURE

Capsule Test System Design

The test system used for investigating the compatibility of $^{244}\text{Cm}_2\text{O}_3$ is shown in Fig. 1. It consists of a capsule body, top and bottom end plugs, refractory metal specimen, and a $^{244}\text{Cm}_2\text{O}_3$ pellet. An outer protective capsule of either TZM or Ta-10% W was used as additional precaution against contaminating the furnace if a ^{244}Cm leak occurred in the primary capsule during test operation.

One of the considerations in the capsule design was the pressure increase resulting from helium generated by ^{244}Cm decay. Since both inner and outer capsules were sealed in argon at 1 atm, the net pressure in the inner capsule was assumed to be determined by the release of helium from the $^{244}\text{Cm}_2\text{O}_3$ pellet. To avoid premature creep rupture of the inner capsule as a result of this pressure buildup, a suitable volume was determined by the equations derived in the Appendix.

Fig. 1. Curium-Refractory Metal Compatibility Test System.

Capsule Fabrication and Inspection

Capsule bodies, end plugs, and specimens were machined from hot-rolled arc-melted bar stock by the Refractory Metals Division of Thermoelectron Corporation. Each part was inspected by a fluorescent penetrant technique to reveal surface defects. An example of the type of defect that led to the rejection of several tungsten capsule bodies is shown in Fig. 2. The capsule bodies were subsequently inspected by ultrasonic techniques and compared against a standard defect 0.0025 in. deep by 0.125 in. long. Only those capsule bodies that had defects less than the standard were used in the test program. All of the refractory metal specimens were metallographically polished before testing to provide a smooth surface. This allowed greater surface area contact between the $^{244}\text{Cm}_2\text{O}_3$ and refractory metal, as well as a constant basis against which to compare the posttest samples. The entire capsule assembly was then annealed 2 hr at 1650°C in vacuum to provide a recrystallized microstructure. This microstructure afforded a more "readable" pattern for evaluating grain boundary reactions within the metal than does the cold-worked microstructure. Figure 3 shows the microstructure of typical before-test specimens sectioned along their longitudinal axes. Note the very smooth appearance of the surface in each case and the relatively large grain size produced in Ta, Ta-10% W, Mo, and W by the pretest anneal.

Fig. 2. Typical Defects in Rejected Tungsten Capsule Bodies.

Fig. 3. Appearance of Compatibility Specimens Before Test, Annealed 2 hr at 1650°C.

Preparation of $^{244}\text{Cm}_2\text{O}_3$ and Fabrication of Pellets

The compound $^{244}\text{Cm}_2\text{O}_3$ was prepared by calcining the oxides (mostly $^{244}\text{CmO}_{1.8-2.0}$) at 1335°C for 30 min. The furnace was located in an inert gas (argon) hot cell, in which the oxygen concentration was maintained at about 20 ppm, and was purged with a continuous flow of argon during calcination. The $^{244}\text{Cm}_2\text{O}_3$ powder thus obtained was transferred to a graphite die in a hot-press (Fig. 4), and the inside space of the press was evacuated to approximately 200 torr. The material in the press was gradually heated to 1445°C , and then a pressure of 4000 psi was applied and maintained for 1 hr. The press was allowed to cool for 30 min at 200 torr after the hot-pressing operation before it was cooled further in an argon gas stream for 1 hr.

Fig. 4. Equipment for Hot-Pressing $^{244}\text{Cm}_2\text{O}_3$ Pellets.

The $^{244}\text{Cm}_2\text{O}_3$ pellets were removed from the press and placed in a tube furnace to burn off any graphite adhering to the surface. This was accomplished by introducing an argon gas stream containing approximately 500 ppm O_2 into the furnace at 1000°C for 3 hr. Surfaces of the pellets were then polished with a diamond wheel (1200 grit). A finished $^{244}\text{Cm}_2\text{O}_3$ pellet weighed about 250 mg and measured about 4.57 mm in diameter by 1.52 mm thick.

Test Assembly

Shown in Fig. 5 is the facility that was employed in the assembly of the compatibility couples. It consists of four glove box compartments containing the hot-press, the welding equipment, the inspection accessories, and the bag-out facility. This hot-press, which is much smaller than the one in Fig. 4, was used to prepare $^{244}\text{Cm}_2\text{O}_3$ pellets for the 1000-hr compatibility experiments only. Most of the pellets were made in the hot-press shown in Fig. 4 and then transferred to the alpha glove box facility. The capsule test system was assembled in the box with the welding equipment shown.

Two methods were used to weld the end closures on the capsules. Electron-beam welding was used to make the bottom end plug weld, and gas tungsten-arc welding was used to make the top end plug weld after the $^{244}\text{Cm}_2\text{O}_3$

Fig. 5. Glove Box Facility for Assembly of Compatibility Couples.

pellet had been loaded into the capsule. Welding parameters for each technique were developed in preliminary studies on each material, and the parameters used are shown in Table 8. Examples of welds produced by each technique are shown in Fig. 6. Electron-beam welds were made in vacuum ($<1 \times 10^{-4}$ torr), and the gas tungsten-arc welding was carried out in an argon atmosphere that contained <100 ppm O_2 (<50 ppm generally). In the case of gas tungsten-arc welding, additional protection from contamination was provided by argon (<5 ppm O_2) flowing through the welding torch.

An inspection for defects using a dye penetrant was made after welding. Each capsule was then enclosed in a TZM or Ta-10% W outer capsule for additional protection. Similar welding and inspection techniques, as described above, were employed for the outer containers. The capsules that passed the examination were removed through the bag-out facility.

Table 8. Welding Parameters for Electron-Beam and Gas Tungsten-Arc Sealing of Refractory Metal Capsules

Capsule Material	Welding Current (A)	
	Electron Beam ^a	Gas Tungsten Arc ^b
Tantalum	100	90
T-111	90	90
Ta-10% W	105	90
Molybdenum	120	110
TZM	120	85
Tungsten	125	190
W-26% Re	120	

^aEB weld atmosphere: vacuum ($<1 \times 10^{-4}$ torr);
speed: 6 in./min.

^bGTA weld atmosphere: argon (<100 ppm O_2);
speed: 8 in./min.

Capsule Disassembly

Since the principal method of evaluating the exposure was by metallographic examination, it was essential to preserve the integrity of the after-test interface between the refractory metal specimen and the $^{244}\text{Cm}_2\text{O}_3$ pellet. First, we maintained the capsule in a vertical position at all times following loading. After removal from the furnace the capsules were transferred to the High Radiation Level Examination Laboratory (HRLEL) to be prepared for metallographic examination. There the outer protective containers were removed by making a transverse cut through the capsule wall using an Al_2O_3 resinoid-reinforced cutoff wheel. A similar transverse cut was made to remove the top end plug of the inner capsule, and then an epoxy material was poured into the inner capsule to immobilize the specimen and pellet. Each capsule was mounted and then polished longitudinally until its approximate midplane was reached. At this point the capsule was photographed at $\sim 6\times$, and an autoradiograph¹³ was made to

(a)

(b)

(c)

Fig. 6. End Plug Welds. (a) Typical electron-beam welded TBM. (b) Gas-tungsten-arc-welded tungsten. (c) Gas-tungsten-arc-welded Ta-10% W.

show the ^{244}Cm distribution in the capsule. Finally the capsule wall and specimen and fuel surfaces were examined metallographically to determine any changes in microstructure that occurred. No facilities for chemical analyses of the test samples were available at the beginning of the program. Subsequently, equipment for electron microprobe and x-ray diffraction analysis was acquired and used to obtain added useful data.

Test Procedure

One of the three high-vacuum furnaces for providing the desired exposure environment is shown in Fig. 7. Each furnace accommodated up to 14 compatibility capsules, which were held in a molybdenum sample holder (Fig. 8). The furnaces were equipped with automatic safety shutoff switches for both the vacuum and the cooling water systems, and an ammeter-recorder connected to each furnace recorded the time of any accidental shutdown of the furnace system during the exposure. Several thermal cycles occurred as a result of these shutdowns during each 5000- or 10,000-hr test run.

Pressures in the furnace during test were maintained in the range 10^{-5} to 10^{-6} torr. Temperatures were monitored with a brightness optical pyrometer and a two-color optical pyrometer. Correction factors for the temperature range and system geometry were obtained by comparing the known melting temperatures of pure nickel, platinum, and iridium with those measured by the brightness optical pyrometer when these metals were melted in the furnace.

Fig. 7. High-Temperature Vacuum Furnace
Used in Refractory Metal- $^{244}\text{Cm}_2\text{O}_3$ Tests.

Fig. 8. Molybdenum Holder for Refractory Metal Capsules.

The test conditions are summarized in Table 9. Two temperatures were chosen to allow us to treat both temperature and time as variables, and these two temperatures represent those applicable to current thermionic systems. Additional tests were subsequently run at 1250°C for times up to 10,000 hr, but they have not been reported yet.

Table 9. Summary of Conditions for Refractory Metal-
 $^{244}\text{Cm}_2\text{O}_3$ Compatibility Tests

Temperature (°C)	Time (hr)	^{244}Cm Source	Metals and Alloys Tested
1650	1,000	ORNL	All ^{a,b}
	10,000	SRL	All ^a
1850	1,000	ORNL	All ^a
	5,000	SRL	All ^a
	10,000	SRL	All ^a

^aTa, T-111, Ta-10% W, Mo, TZM, W, and W-26% Re.

^bW-26% Re was unavailable at the time tests were conducted.

RESULTS

Tests at 1650°C

The results of 1000-hr tests at 1650°C are shown in Figs. 9 and 10. At the tops of the figures are photomacrographs of a longitudinal cross section of each capsule. Both the refractory metal specimen and the $^{244}\text{Cm}_2\text{O}_3$ pellet are visible. To the right of each photomacrograph is an autoradiograph of the same longitudinal section, showing the ^{244}Cm distribution. High-magnification photomicrographs of the specimen- $^{244}\text{Cm}_2\text{O}_3$ interface area are shown below. In all of these tests the $^{244}\text{Cm}_2\text{O}_3$ pellet remained intact, and very little ^{244}Cm radioactivity was noted outside the pellet itself. However, the $^{244}\text{Cm}_2\text{O}_3$ tested with tantalum did show a reaction zone at the Ta- $^{244}\text{Cm}_2\text{O}_3$ interface, and after etching, the tantalum showed an oriented Widmanstätten precipitate similar in appearance to Ta_2O_5 . Evidence of reaction was also seen for Ta-10% W and T-111 with $^{244}\text{Cm}_2\text{O}_3$. A discontinuous precipitate was evident in the grain boundaries of the T-111 specimen to a depth of about 3 mils, and electron-beam microprobe analysis of the precipitate revealed that it was very high in ^{244}Cm . On the other hand, molybdenum, TZM, and tungsten showed only very shallow reaction zones at the fuel-metal interface, primarily along the grain boundaries of the metal.

Results after 10,000 hr at 1650°C were generally similar to the 1000-hr results, but the extent of reaction was greater in every case. It should be noted that the ^{240}Pu concentration in the Cm_2O_3 was approximately the same in these tests as in the 1000-hr tests. Metallographic results are summarized in Figs. 11 through 17. Note that the $^{244}\text{Cm}_2\text{O}_3$ pellets were

Fig. 9. Tantalum and Tantalum Alloys
Exposed to $^{244}\text{Cm}_2\text{O}_3$ 1000 hr at 1650°C.

Fig. 10. Molybdenum, TZM, and Tungsten
Exposed to $^{244}\text{Cm}_2\text{O}_3$ 1000 hr at 1650°C.

Fig. 11. Tantalum Exposed to $^{244}\text{Cm}_2\text{O}_3$
10,000 hr at 1650°C.

Fig. 12. Ta-10% W Alloy Exposed to $^{244}\text{Cm}_2\text{O}_3$
10,000 hr at 1650°C.

Fig. 13. T-111 Alloy Exposed to $^{244}\text{Cm}_2\text{O}_3$
10,000 hr at 1650°C.

Fig. 14. Molybdenum Exposed to $^{244}\text{Cm}_2\text{O}_3$
10,000 hr at 1650°C.

Fig. 15. TZM Alloy Exposed to $^{244}\text{Cm}_2\text{O}_3$
10,000 hr at 1650°C.

R 53425

Fig. 16. Tungsten Exposed to $^{244}\text{Cm}_2\text{O}_3$
10,000 hr at 1650°C.

R 53147

Fig. 17. W-26% Re Alloy Exposed to $^{244}\text{Cm}_2\text{O}_3$
10,000 hr at 1650°C.

not intact as after 1000 hr. (The capsule outline has been drawn to better identify the location of the $^{244}\text{Cm}_2\text{O}_3$ in the autoradiograph.) In some of the tests the section we examined contained very little $^{244}\text{Cm}_2\text{O}_3$ (e.g., see Fig. 15), which raised a question as to what might have happened to it. Except for the Ta-10% W test there was no evidence of ^{244}Cm outside the inner capsule; however, calculations show that redistribution in the form of a very thin layer (~ 0.001 in.) along the inside wall of the capsule and on the upper end cap could account for most of the $^{244}\text{Cm}_2\text{O}_3$.

Some dissolution of the tantalum was noted, and a peculiar spear-shaped phase (Fig. 11) was found in the capsule wall above the level of the tantalum specimen. Electron-beam microprobe analysis could not distinguish it from pure tantalum; therefore, we speculate that it could be a suboxide of tantalum such as Ta_4O (ref. 14) or Ta_xO (ref. 15) (where $x > 4$).

We expected that hafnium in T-111 might react with $^{244}\text{Cm}_2\text{O}_3$, since HfO_2 has a thermodynamic stability comparable to that of $^{244}\text{Cm}_2\text{O}_3$. In the 1000-hr test with T-111 at 1650°C , ^{244}Cm was identified in the T-111. Considerably deeper attack (up to 25 mils) was noted after 10,000 hr, and both hafnium and ^{244}Cm were identified as components of the gray nonmetallic phase in the T-111 (Fig. 13). In addition, hafnium was identified as a major component of a white phase we observed along some grain boundaries in the capsule.

An autoradiograph of the Ta-10% W capsule (Fig. 12) showed that it had been completely penetrated along grain boundaries by ^{244}Cm (or $^{244}\text{Cm}_2\text{O}_3$), and some evidence of ^{244}Cm was found outside the capsule. (This was the only test in which $^{244}\text{Cm}_2\text{O}_3$ leaked into the outer capsule.) No significantly higher than average concentrations of either tantalum or tungsten were found in any areas of the specimen.

Reactions of $^{244}\text{Cm}_2\text{O}_3$ with Mo, TZM, W, and W-26% Re were more extensive than we had observed previously after 1000-hr exposures, although the surface appearance of the specimens was generally similar after each time period. Each capsule test showed some evidence of metal dissolution by $^{244}\text{Cm}_2\text{O}_3$, as suggested by the roughened surfaces. The line of voids at different but specific depths in all the alloys strongly suggests that they are due to helium bubble formation from alpha particles that penetrated the materials.

In three of the 10,000-hr tests at 1650°C (Ta-10% W, Fig. 12; TZM, Fig. 15; and W-26% Re, Fig. 17), the outer protective capsule was Ta-10% W instead of TZM. We found a nonmetallic-appearing layer along the bottom and sides of the inner capsules in these three cases. Electron-beam microprobe analysis indicated that the tantalum concentration in this phase was approximately the same as in Ta_2O_5 , and only a small amount of tungsten was present. In addition, the capsule material immediately below the layer was preferentially enriched in tantalum. It is interesting that no such reaction occurred at 1850°C , where Ta-10% W was used as the outer container in all the tests. If the compound were of the type Ta_2O_5 , it might be speculated that an activity gradient

of oxygen developed along the capsule axis as a consequence of a temperature gradient along the capsule. However, it is not evident that such gradients existed in our furnaces except during startup or cooldown. The reaction did not occur at 1850°C, possibly because of the lower free energy of formation of Ta_2O_5 at the higher temperature.

Tests at 1850°C

The results of the compatibility tests of tantalum and the tantalum alloys at 1850°C were significantly different from those at 1650°C. Results after 1000 hr are shown in Fig. 18. The $^{244}\text{Cm}_2\text{O}_3$ pellet completely redistributed in these tests, and in each case ^{244}Cm was found in the space between the specimen and wall. The appearance of the $^{244}\text{Cm}_2\text{O}_3$ indicates that it (or a combination of $^{244}\text{Cm}_2\text{O}_3$ plus tantalum) was molten at the test temperature, since it formed a meniscus between the top edge of the disk specimen and capsule wall. Since the melting point of production-grade $^{244}\text{Cm}_2\text{O}_3$ has been reported⁵ to be about 2200°C, we believe that dissolution of tantalum into $^{244}\text{Cm}_2\text{O}_3$ resulted in the formation of a lower melting phase. Although there were some subsurface voids in T-111 and Ta-10% W, we did not find penetration of ^{244}Cm into the alloys as we did after exposure at 1650°C.

Figure 19 shows Mo, TZM, W, and W-26% Re after 1000-hr exposures. Each showed some slight evidence of attack near the specimen-pellet interface. A view of the interfaces between the tungsten specimen and fuel and fuel and bottom end plug at a higher magnification is shown in Fig. 20. The

Fig. 18. Tantalum and Tantalum Alloys
Exposed to $^{244}\text{Cm}_2\text{O}_3$ 1000 hr at 1850°C.

Fig. 19. Molybdenum, TZM, Tungsten, and W-26% Re
Exposed to $^{244}\text{Cm}_2\text{O}_3$ 1000 hr at 1850°C.

Fig. 20. Tungsten Exposed to $^{244}\text{Cm}_2\text{O}_3$
1000 hr at 1850°C.

unevenness of the tungsten specimen surface and the tungsten particles in the fuel suggests that tungsten may have been dissolved by $^{244}\text{Cm}_2\text{O}_3$ and subsequently precipitated upon cooling from the test temperature. Similar results after 1000 hr at 2000°C have also been reported.¹⁶

Typical results after 5000 hr at 1850°C are shown in Figs. 21 through 24. Redistribution of the $^{244}\text{Cm}_2\text{O}_3$ exposed to Ta-10% W and T-111 was similar to that found after 1000 hr. The metallic particles adhering to $^{244}\text{Cm}_2\text{O}_3$ at the bottom of the Ta-10% W capsule were identified as pure tantalum. This also strongly suggests that tantalum was dissolved by $^{244}\text{Cm}_2\text{O}_3$ and subsequently precipitated upon cooling from 1850°C. Mass transfer of metal components of capsule wall and disk specimen was seen in all of the tests but was less severe with W-26% Re, Mo, and TZM.

Results after 10,000 hr at 1850°C are summarized in Figs. 25 through 31. In general, these results are similar to those discussed above. Significant ^{244}Cm redistribution was noted in all of the tests, but it was most severe where $^{244}\text{Cm}_2\text{O}_3$ was exposed to tantalum or a tantalum alloy (Figs. 25-27). Surface roughening and subsurface void formation occurred in all the tests but was significantly greater in molybdenum, TZM, and tungsten (Figs. 28-30). Mass transfer of metal components was greater in tests with the tantalum alloys.

It is significant that none of the capsule materials were breached after 10,000 hr at 1850°C. (This was not the case at 1650°C.) Although some limited reaction was noted in all the tests, no catastrophic effects were found. Metallographic results on all the disk specimens at 1850°C are summarized in Fig. 32.

Fig. 21. Ta-10% W Exposed to $^{244}\text{Cm}_2\text{O}_3$ 5000 hr at 1850°C.

Fig. 22. T-111 Alloy Exposed to $^{244}\text{Cm}_2\text{O}_3$
5000 hr at 1850°C.

Fig. 23. Molybdenum Exposed to $^{244}\text{Cm}_2\text{O}_3$
5000 hr at 1850°C.

R 50981

Fig. 24. Tungsten Exposed to $^{244}\text{Cm}_2\text{O}_3$
5000 at 1850°C.

R 53429

Fig. 25. Tantalum Exposed to $^{244}\text{Cm}_2\text{O}_3$
10,000 hr at 1850°C.

Fig. 26. Ta-10% W Alloy Exposed to $^{244}\text{Cm}_2\text{O}_3$
10,000 hr at 1850°C.

Fig. 27. T-111 Alloy Exposed to $^{244}\text{Cm}_2\text{O}_3$
10,000 hr at 1850°C.

Fig. 28. Molybdenum Exposed to $^{244}\text{Cm}_2\text{O}_3$
10,000 hr at 1850°C.

Fig. 29. TZM Alloy Exposed to $^{244}\text{Cm}_2\text{O}_3$
10,000 hr at 1850°C.

Fig. 30. Tungsten Exposed to $^{244}\text{Cm}_2\text{O}_3$
10,000 hr at 1850°C.

Fig. 31. W-26% Re Alloy Exposed to $^{244}\text{Cm}_2\text{O}_3$
10,000 hr at 1850°C.

Fig. 32. Refractory Metals Exposed to $^{244}\text{Cm}_2\text{O}_3$ at 1850°C .

Effects on $^{244}\text{Cm}_2\text{O}_3$

The $^{244}\text{Cm}_2\text{O}_3$ in these tests was hot-pressed at 4000 psi and 1445°C (see p. 9). At this temperature the crystal structure of the $^{244}\text{Cm}_2\text{O}_3$ is the monoclinic B-type. When heated above 1600°C , it transforms reversibly to hexagonal A-type $^{244}\text{Cm}_2\text{O}_3$. The reverse reaction is reported⁹ to be very rapid, and, after heating above 1600°C , a highly twinned microstructure, characteristic of materials undergoing a phase transformation during cooling, is generally observed. The microstructures of several of the $^{244}\text{Cm}_2\text{O}_3$ pellets exposed to different refractory metals at 1650 and 1850°C are shown in Fig. 33. Typical structures as reported in the literature can be seen in the $^{244}\text{Cm}_2\text{O}_3$ tested at 1650°C . The $^{244}\text{Cm}_2\text{O}_3$ exposed to Ta-10% W had smaller grains than that exposed to either molybdenum or tungsten. This indicates that the addition of an element or elements to the $^{244}\text{Cm}_2\text{O}_3$ apparently restricted grain growth.

The microstructure of the $^{244}\text{Cm}_2\text{O}_3$ was significantly changed by the 1850°C exposure, especially in tests with Ta-10% W. The grain structure is not well-defined, although we can still see a number of twins in the $^{244}\text{Cm}_2\text{O}_3$ exposed to molybdenum or tungsten. Metallic particles of either tantalum, molybdenum, or tungsten were identified in the Cm_2O_3 , and, in the $^{244}\text{Cm}_2\text{O}_3$ exposed to Ta-10% W, there was evidence of a second phase, which reinforces the view that tantalum had been dissolved by the $^{244}\text{Cm}_2\text{O}_3$.

Fig. 33. Microstructure of $^{244}\text{Cm}_2\text{O}_3$ Exposed to Refractory Metals.

DISCUSSION AND CONCLUSIONS

Fundamental Considerations

Before discussing the test results, let us first consider some of the possible interactions among the chemical species that were present in the compatibility couple. Major chemical species of importance were, of course, $^{244}\text{Cm}_2\text{O}_3$, the capsule material (refractory metals or alloys), and ^{240}Pu , which is the main decay product of ^{244}Cm . The contributions to compatibility reactions by impurities present in the original curium oxide (see Tables 4 and 5, pp. 3-4) will not be treated, since the quantities involved were small. Americium and zirconium represent the major impurities in the curium oxide obtained from SRL. However, these elements form oxides about as stable as the oxides of curium and plutonium, based on free-energy data.

Curium-244 Oxides and Decay Product

Curium oxide compositions range from CmO_2 to Cm_2O_3 . Curium dioxide is thermally stable in an inert gas atmosphere up to 400°C , but it decomposes to lower oxides when heated higher.⁸ That is,

As the calcining temperature is increased to about 1300°C, the B-type (monoclinic) Cm_2O_3 is obtained (p. 5). Near 2000°C Cm_2O_3 vaporizes congruently and presumably dissociates into CmO and atomic oxygen in the gas phase,¹⁷ as in:

The $\text{CmO}_{1.8-2.0}$ starting material contained some $^{240}\text{PuO}_2$ from the radioactive decay of ^{244}Cm to ^{240}Pu , which has a half-life of 6760 years. When the oxide was calcined to curium sesquioxide at 1335°C and hot-pressed into pellets at 1445°C in a graphite die (see pp. 9-10), the $^{240}\text{PuO}_2$ present (estimated to vary from 3 to 7 mole %) should not have been significantly reduced.¹⁸ After conversion to a $^{244}\text{Cm}_2\text{O}_3$ fuel pellet, further decay of ^{244}Cm should result in the formation of Pu_2O_3 . Formation of PuO_2 or PuO in this step would be unlikely because the free energies of formation indicate that Cm_2O_3 will neither oxidize nor reduce Pu_2O_3 . In addition, if oxygen in the atmosphere inside the compatibility capsule completely reacted to form PuO_2 , no more than about 2×10^{-8} moles of PuO_2 could come from this source. In comparison, a curium oxide pellet contained approximately 4×10^{-4} moles of $^{244}\text{Cm}_2\text{O}_3$ initially.

Although the Pu_2O_3 content of the curium oxides is insignificant shortly after its processing from the reactor target, it is not negligible as the time after processing is extended. For $^{244}\text{Cm}_2\text{O}_3$ samples used in the present study, we estimate that the total ^{240}Pu content could range from about 4 to 12 mole % at the conclusion of the compatibility exposure runs, of which 3 to 7% is PuO_2 . Theory¹⁹ predicts that Cm_2O_3 and Pu_2O_3 should form solid solutions in all proportions, and miscibility up to 10 mole % Cm_2O_3 has been verified experimentally.²⁰ Furthermore, Pu_2O_3 vaporizes and dissociates²¹ at temperatures approaching 2000°C:

However, the equilibrium concentrations of $\text{PuO}(g)$ and $\text{PuO}_2(s)$ are relatively small in the temperature range of interest.

Direct Oxidation-Reduction Involving Cm_2O_3 or Pu_2O_3

Listed in Table 10 are the estimated values of free energy of formation (ΔG) at different temperatures for oxides of various metallic elements encountered in the compatibility study (compare with Table 2), and which might be formed by reactions such as

Table 10. Estimated Free Energy of Formation (ΔG) of Various Oxides

Oxide	$-\Delta G$ of Formation (kcal/g-atom O_2)		
	1850°C	1650°C	27°C
ReO ₂	15	16	44
ReO ₄	15	16	33
ReO ₃	26	27	42
MoO ₃	28	29	54
WO ₃	30	31	64
WO ₂	33	34	62
Nb ₂ O ₅	53	54	85
NbO ₂	56	57	87
Ta ₂ O ₅	56	58	92
NbO	58	60	90
TiO ₂	70	72	106
Ti ₃ O ₅	77	78	111
Ti ₂ O ₃	79	80	114
ZrO ₂	86	88	124
HfO ₂	88	89	125
Pu ₂ O ₃	91	93	123
R ₂ O ₃ ^a	99-100	100-103	136-138

^aR represents rare earth, including Nd, Sm, La, Ce, and Pr.

These values are a guide in determining the relative stability of various oxides in the temperature range of interest. Thus, a large negative value of ΔG for an oxide generally implies that the metallic element is more readily oxidized than one having a small negative free energy of oxide formation.

As noted in Table 10, values of ΔG for oxides of tungsten, rhenium, and molybdenum in the temperature range of interest are considerably less negative than those for rare-earth oxides and Pu₂O₃. The free energy of formation of Cm₂O₃ is expected to be approximately the same as those of the rare-earth oxides. Hence, the large difference mentioned above would suggest that capsules made of tungsten, rhenium, molybdenum, or their alloys should not form oxides by direct reduction of either Cm₂O₃ or Pu₂O₃. A similar statement is probably applicable to tantalum and niobium, although the difference in ΔG values is smaller. However,

the values of ΔG for titanium, zirconium, and hafnium oxides are so close to those for Cm_2O_3 and Pu_2O_3 that the possibility of interaction cannot be ruled out. Theoretically, this implies that refractory alloys T-111 (Ta-8% W-2% Hf) and TZM (Mo-0.5% Ti-0.1% Zr) might reduce Cm_2O_3 and Pu_2O_3 , and the test results for T-111 did suggest that hafnium was associated with the corrosion product at 1650°C.

Oxygen-Metal Interactions

In the $^{244}\text{Cm}_2\text{O}_3$ -refractory metal compatibility couple, metal-oxygen solutions or metal oxides may be formed by reactions other than the type discussed above. For example, atomic oxygen produced in the vaporization of Cm_2O_3 at elevated temperatures [Eq. (2)] could oxidize tantalum and the tantalum alloys according to:

where $(\text{O}_x)_\text{M}$ stands for oxygen dissolved in the metal phase. However, the data suggest that reactions of this type would be limited, since no oxide lower than Cm_2O_3 was reported¹⁷ after hydrogen reduction at 2000°C, and the partial pressures of atomic oxygen from Eq. (2) would be approximately 2.3×10^{-7} and 8.5×10^{-9} atm, respectively, at 1850 and 1650°C. The worst case would occur when the residual O_2 (present in the argon atmosphere at the time of welding) in the compatibility capsule (up to about 2×10^{-5} atm partial pressure at room temperature) is completely consumed in internally oxidizing the metal or in forming oxide films on the inside walls of the capsule. In the case of the tantalum capsules, this corresponds to an oxygen concentration less than 1 ppm or an equivalent thickness of Ta_2O_5 film less than 3 Å.

Another possible type of refractory metal oxide formation is the interaction of PuO_2 present at the time of encapsulation or PuO_2 formed in Eq. (3) with a refractory metal (e.g., tantalum) according to:

Andelin and Watrous²² have discussed reactions of this type for several refractory metals (Mo, W, Re, Ta), and they indicate that (assuming unit activities for each phase) PuO_2 will be reduced to PuO_{2-x} (where x depends on the particular refractory metal).

Any refractory metal oxide formed either by Eq. (6) or through oxidation by atomic oxygen released from Cm_2O_3 could be reduced to metal on cooling because of the high stability of both Cm_2O_3 and Pu_2O_3 at low temperatures (except in cases involving titanium, zirconium, and hafnium).

Other Interactions

Other possible interactions between Cm_2O_3 (or Pu_2O_3) and refractory metal include dissolution of the metal or its oxide into Cm_2O_3 (or Pu_2O_3), and the shift in phase transformation (melting point, crystal structure, etc.) of Cm_2O_3 resulting from the solubility relationship among the compounds involved. Solubility of refractory metals in Cm_2O_3 and any resulting changes in phase transformation have not been reported, but some degree of solubility of tantalum in PuO_2 at high temperatures was suggested by Batey *et al.*²³ and Selle *et al.*²⁴ Also Pu_2O_3 forms complex oxides¹⁹ with Ta_2O_5 or Nb_2O_5 as in:

Discussion of Test Results

Except for the extensive penetration of T-111 and Ta-10% W at 1650°C, the results of these compatibility tests were generally encouraging. As noted in Fig. 32, the most consistent microstructural feature in the refractory metals was the subsurface voids in areas exposed to $^{244}\text{Cm}_2\text{O}_3$. These voids were of two types. One type was rather large, appeared to occur where there was surface roughening, and in some cases contained a gray phase identified to be high in ^{244}Cm by microprobe analysis. These are probably diffusion or Kirkendall voids associated with chemical interactions between the refractory metal and $^{244}\text{Cm}_2\text{O}_3$ fuel. (Several possible reactions were discussed on pp. 31-33.) In addition, we also noted some much smaller voids at discrete levels below the surface and usually confined to a depth of 1 to 3 mils. Since the depth of these voids was essentially independent of exposure time, they may have been formed by the coalescence into bubbles of helium atoms injected into the metal from the decay of ^{244}Cm .

The mechanism of attack of T-111 and Ta-10% W at 1650°C is not clear. Tantalum and tungsten are common ingredients of both alloys, but similar reactions were not observed in either pure tantalum or tungsten. The dissolution of Cm_2O_3 by the refractory metal was not considered to be likely. Reactions such as those suggested in Eqs. (4), (6), or (7) could have occurred. However, our analysis did not determine the composition of the ^{244}Cm -containing phases that were found.

Attack of the Ta-10% W and T-111 alloys at 1650°C in each case was associated with grain boundary reaction. In the case of T-111, the reaction involved hafnium and would appear to be of the type discussed in conjunction with Eq. (4). The mechanism of attack of Ta-10% W is less easy to explain, since similar reactions were not observed in either pure tantalum or tungsten. Adding tungsten to tantalum markedly lowers the solid solubility of oxygen in the alloy. From this fact, one can speculate that in the course of these tests higher oxygen activities were reached in the grain boundaries of Ta-10% W than in the pure tantalum. This follows if one assumes a comparable grain boundary diffusion rate for oxygen in the

two materials and that the pure tantalum grains afford a greater sink for oxygen. The higher oxygen activity in the Ta-10% W (if indeed it occurred) could lead to formation of tantalum oxides in the grain boundaries or to compounds involving tantalum, curium, and oxygen.

At 1850°C it seems likely that with tantalum, and possibly with tungsten, the results we observed were caused by reactions that lead to the formation of low-melting curium fuel*-Ta(W) phases. [See Eqs. (4) or (7) in the previous section.] Reactions of this type have been reported between PuO_2 , UO_2 , or $\text{U}_x\text{Pu}_y\text{O}_z$ and these metals.^{16,23,25,26} With UO_2 tantalum has been reported to form a double oxide or a tantalate with the formula $\text{U}(\text{TaO}_3)_4$. Either reaction is thought to first involve the formation of Ta_2O_5 by reduction of UO_2 to UO_{2-x} . Although oxides lower than $\text{CmO}_{1.5}$ have not been reported, the close resemblance of our results with those of tantalum exposed to PuO_2 at 1440°C and $\text{UO}_{0.85}\text{Pu}_{0.15}\text{O}_2$ at 1740°C leads us to believe that the reaction mechanisms are probably similar. Another similarity between the results of UO_2 compared with Cm_2O_3 was that tungsten was penetrated by UO_2 along its grain boundaries, and tungsten particles were sometimes identified in the UO_2 . In addition, molybdenum and rhenium were reported to have better compatibility than tantalum and tungsten with UO_2 , although UO_2 was found in molybdenum grain boundaries in some cases. In our tests W-26% Re appeared to have the best compatibility with $^{244}\text{Cm}_2\text{O}_3$, and where we did see evidence of reaction (Fig. 34), tungsten seemed to be involved rather than rhenium. The ^{240}Pu concentration in the $^{244}\text{Cm}_2\text{O}_3$ varied from 4 to 12%, but we did not note any relation between it and the depth or type of attack. If the similarity between our results with $^{244}\text{Cm}_2\text{O}_3$ and those reported previously for PuO_2 were related to the ingrowth of ^{240}Pu , we would have expected to notice some trend with the final concentration of plutonium.

Another observation that we noted in the 1850°C tests was the mass transport of metallic elements from one point in the capsule to another. For example, in tungsten exposed for 5000 hr (Fig. 24) and Ta-10% W exposed for 10,000 hr (Fig. 26), the capsule and specimen were joined together at some points because of this mass transfer. Although solubility of the refractory metals in $^{244}\text{Cm}_2\text{O}_3$ could explain the mass transport of these metals, the amount of material transported and its disposition in the tantalum and tungsten systems lead us to postulate chemical transport reactions. These are reactions in which the solid (tantalum) reacts with a gas [CmO or O from Eqs. (1) or (2)] to form a vapor-phase reaction product, and then the reverse reaction occurs at a different place in the system, resulting in the reformation of the solid (tantalum). For such a reaction to occur, an activity gradient must exist. An activity gradient could result from a temperature gradient, pressure change, or energy changes resulting from geometrical considerations. Since the system is closed, there is no way to postulate a pressure difference in the capsule. There should have been no temperature difference within the same capsule, but it is possible, since the capsules were heated and cooled several times, that significant

*Curium fuel includes $^{244}\text{Cm}_2\text{O}_3$, decay products PuO_2 and Pu_2O_3 , and other impurities present in the system.

(a)

(b)

(c)

Fig. 34. Tungsten Embedded in $^{244}\text{Cm}_2\text{O}_3$ After Exposure of W-26% Re to Cm_2O_3 for 5000 hr. The field of view shown is 0.0027 in. high. (a) Optical micrograph. (b) X-ray image showing tungsten. (c) X-ray image showing curium. White in (b) and (c) shows the element distribution.

temperature gradients may have occurred during these periods. It may also be significant that mass transfer often resulted in the removal of material from the corner of a disk specimen (as in Fig. 28) — a high energy area. Reactions of this type have been reported²² for tungsten and rhenium exposed to PuO_2 .

SUMMARY AND RECOMMENDATIONS

Based on these test results, several materials appear suitable for containing $^{244}\text{Cm}_2\text{O}_3$ up to 1850°C . The alloy W-26% Re showed the least interaction with $^{244}\text{Cm}_2\text{O}_3$, but molybdenum, TZM, and tungsten also showed acceptable behavior and looked especially promising at 1650°C . Except for tantalum alloys, the interactions encountered with the metals and alloys investigated were not extremely serious. However, because of the dissolution effects noted in most of the systems, very careful consideration should be given to the effect of temperature gradients on mass transport reactions. Likewise, a greatly increased $^{244}\text{Cm}_2\text{O}_3$ -to-metal surface area or weight ratio could also be an important factor affecting dissolution. In view of our excellent results with W-26% Re, future high-temperature tests should also include pure rhenium.

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APPENDIX

Calculation of Capsule Volume Required for
Release of Helium From Decay of ^{244}Cm

If we assume that the capsule design in Fig. 1 can be treated as a thin-wall cylinder, the instantaneous tangential stress can be shown to be:

$$\sigma = \frac{2RT}{h_0 \pi} \frac{N}{D_0 X_0} \quad (1)$$

and

$$\frac{d\sigma}{dt} = \dot{\sigma} = \frac{2RT}{\pi h_0 D_0 X_0} \left(\frac{dN}{dt} \right), \quad (2)$$

where

σ = stress,

N = number of moles of helium,

h_0 = effective initial height of capsule,

D_0 = initial internal diameter of capsule,

X_0 = initial wall thickness of the capsule,

R = gas content,

T = temperature,

$\dot{\sigma}$ = stress buildup rate.

From a model developed by McCoy²⁷ for using creep data under constant stress to predict creep behavior under a linearly increasing stress, we find that

$$\left(\frac{d\sigma}{dt} \right)^n \frac{(t_\epsilon)^{n+1}}{n+1} = A^n, \quad (3)$$

where t_ϵ is the time to a particular strain and A and n are constants for the particular materials.

Combining Eqs. (2) and (3) we can arrive at

$$\log t_\epsilon = \frac{\log(n+1)}{n+1} + \frac{n}{n+1} \log A - \frac{n}{n+1} \frac{2RT}{\pi h_0 D_0 X_0} \left(\frac{dN}{dt} \right). \quad (4)$$

If we assume complete release of helium into the capsule from each $^{244}\text{Cm}_2\text{O}_3$ pellet of known activity, we can use Eq. (4) and constant-load creep data for the materials²⁸⁻³¹ to calculate the time required to reach a particular strain for a set of values of D_0 , X_0 , and h_0 . We chose to fix the maximum allowable stress as that which would produce rupture at 1.5 times the test duration. By adjusting the values of h_0 and X_0 , we used capsules with the same internal diameter in each case. No creep failures occurred in any of the tests at either 1650 or 1850°C, indicating the adequacy of our assumptions. A more complete discussion of predicting the performance of tungsten under similar conditions has been presented by Swindeman.³²

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Fig. 12. Ta-10% W Alloy Exposed to $^{244}\text{Cm}_2\text{O}_3$
10,000 hr at 1650°C.

Fig. 13. T-111 Alloy Exposed to $^{244}\text{Cm}_2\text{O}_3$
10,000 hr at 1650°C.

Fig. 12. Ta-10% W Alloy Exposed to $^{244}\text{Cm}_2\text{O}_3$
10,000 hr at 1650°C.

Fig. 13. T-111 Alloy Exposed to $^{244}\text{Cm}_2\text{O}_3$
10,000 hr at 1650°C.