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HIGH TEMPERATURE STABILITY OF ^{244}Cm AND ^{170}Tm OXIDE

by

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SUMMARY

Curium and thulium sesquioxide are attractive candidate fuel materials for isotopic heat sources to power thermionic diodes.

The vaporization rate of Cm_2O_3 is sufficiently high that significant fuel redistribution will occur during thermionic operation, but sufficiently low that helium venting may be possible. CmO_2 loses oxygen preferentially on heating through two ordered intermediate oxides to form Cm_2O_3 . Cm_2O_3 exhibits body-centered-cubic (bcc), monoclinic, and hexagonal symmetry up to its melting point of 1950°C . Cm_2O_3 vaporizes congruently in vacuum with $\Delta H_{2000^\circ\text{K}}^\circ(\text{vap}) = 133.0 \pm 2.7$ kcal/mole of gas and $\Delta S_{2000^\circ\text{K}}^\circ(\text{vap}) = 33.5 \pm 1.2$ cal/(deg)(mole) of gas. $\log P_{\text{E}}(\text{atm}) = 7.32(\pm 0.26) - 29,050(\pm 590)T^{-1}(\text{K})$. The extrapolated boiling point is $3970 \pm 200^\circ\text{K}$.

Tm_2O_3 is an excellent fuel material for isotopic thermionic power because of its high melting point and low vaporization rate. Tm_2O_3 has cubic symmetry to 2280°C , hexagonal symmetry above 2280°C , and melts at $2375 \pm 25^\circ\text{C}$. The oxide vaporizes congruently in vacuum primarily to form gaseous atoms. $\Delta H_{298^\circ\text{K}}^\circ(\text{vap}) = 748.3$ kcal/mole and $\Delta S_{298^\circ\text{K}}^\circ(\text{vap}) = 169 \pm 5$ eu. $\log P_{\text{T}}(\text{atm}) = 7.37 - 31,500 T^{-1}(\text{K})$. The extrapolated boiling point is $4400 \pm 300^\circ\text{K}$.

INTRODUCTION

A variety of radioisotopes are presently being developed as fuels for heat sources in space or terrestrial power sources.^{1,2} Many of these isotopes, such as ^{238}Pu , ^{244}Cm , ^{210}Po , ^{60}Co , and ^{170}Tm , can be made as the primary products of production reactors. A pilot quantity of

about 5 kg of ^{244}Cm has been made recently at the Savannah River Plant.^{3,4} Ninety-five percent dense thulium oxide wafers have been made with power densities typically 2 watts thermal per gram.^{5,6,7}

The state of the art for thermionic diodes is well advanced and considerable effort has been devoted to reactor-powered thermionic devices. However, little technology exists for isotope-powered thermionic devices largely because of insufficient data on the fuel materials. Considerable information on the properties of curium oxides has been accumulated in programs underway at Savannah River and Oak Ridge National Laboratories to develop production and heat source technology for ^{244}Cm . The properties of thulium oxide were assessed at Savannah River to select a reactor target material to make ^{170}Tm in a form suitable for direct use at reactor discharge.⁵ Those high temperature properties that relate to $^{244}\text{Cm}_2\text{O}_3$ or $^{170}\text{Tm}_2\text{O}_3$ fuel behavior at thermionic temperatures are described in this paper to stimulate consideration of these fuels for thermionic devices.

Curium-244 is primarily an alpha emitter with a half-life of 18.1 years and a specific power of 2.42 watts thermal per gram of oxide, or 28.2 watts thermal per cubic centimeter.⁸ The containment or venting of the helium decay product and the radiation from fission neutrons are two potential problems with ^{244}Cm heat sources.

Thulium-170 is a beta emitter with a relatively short half-life of 128 days and a power density in the range 2 to 3 watts thermal per gram of oxide, or

18 to 27 watts thermal per cubic centimeter.⁵ Decay of ^{170}Tm produces no permanent gas, but the bremsstrahlung radiation associated with beta decay must be shielded.

Both ^{244}Cm and ^{170}Tm have sufficient power densities for efficient thermionic operation.

Stringent requirements are placed on the isotopic fuels to meet operational and aerospace safety requirements. Fuel forms should be high melting, fully oxidized, have low vapor pressure, and have no deleterious phase transformations or decomposition products. The potential appears excellent for $^{244}\text{Cm}_2\text{O}_3$ and $^{170}\text{Tm}_2\text{O}_3$ to meet these requirements at thermionic temperature. The phase stability, interactions in various atmospheres, melting points, vaporization processes and rates, boiling points, and phase transition temperatures for Cm_2O_3 and Tm_2O_3 are described below. An assessment is made of rates of fuel transport within the capsule, caused by temperature gradients, and an estimate is made of possible rates of loss through defective welds or through helium vents.

PROPERTIES OF CURIUM OXIDES AT HIGH TEMPERATURES

Phase Behavior

Thermogravimetric analyses at Oak Ridge and Savannah River have shown that the curium-oxygen system is complicated by several oxide compositions between CmO_2 and Cm_2O_3 .⁹⁻¹⁷ On heating in air, CmO_2 decomposes to $\text{CmO}_{1.85}$ at 400°C ; $\text{CmO}_{1.85}$ decomposes to $\text{CmO}_{1.73}$ at 450°C ; $\text{CmO}_{1.73}$ decomposes above 700°C to a phase with composition between $\text{CmO}_{1.68}$ and $\text{CmO}_{1.54}$; and $\text{CmO}_{1.54}$ decomposes to $\text{CmO}_{1.50}$ above 900°C . No oxides lower than Cm_2O_3 were observed when Cm_2O_3 was heated in hydrogen. The most suitable compound for high temperature service, then, is Cm_2O_3 rather than CmO_2 , as was first suggested by analogy to the refractory oxides ThO_2 , UO_2 , and PuO_2 .

The phase behavior in the Cm_2O_3 region is still being explored. Three

structures have been observed by X-ray diffraction in different temperature ranges: body-centered-cubic (bcc), monoclinic, and hexagonal.¹⁰ This behavior is entirely predictable when actinide sesquioxide behavior is compared with that of the rare-earth sesquioxides.¹⁸ All three structures occur among the rare-earth sesquioxides and the temperature range over which a particular structure exists is dependent on the size of the +3 metal ion. The parallel ionic size-temperature relation among the structures of the actinide sesquioxides is indicated by observation of hexagonal Np_2O_3 ,¹⁹ cubic and hexagonal Pu_2O_3 ,²⁰ cubic and monoclinic Am_2O_3 ,²¹⁻²³ cubic Bk_2O_3 , and monoclinic and cubic Cf_2O_3 .²⁴ For a Cm^{+3} radius between that of Sm^{+3} and Fm^{+3} , Cm_2O_3 should exist as bcc up to $700\text{--}800^\circ\text{C}$, monoclinic to about 1500°C , and hexagonal above 1500°C . High-temperature X-ray diffraction analyses substantiate this, showing the sluggish, irreversible transition from bcc to monoclinic between 800 and 1300°C , and a completely reversible transition between monoclinic and hexagonal symmetry at 1600°C . Thermogravimetric and X-ray diffraction evidence, in addition to related information among rare-earth oxides, suggest that the bcc form of Cm_2O_3 may be oxygen-rich.

Monoclinic or hexagonal Cm_2O_3 are the desired curium oxides for high temperature application. The large density change (9%) in bcc-to-monoclinic transition would be deleterious to fabricated fuel forms. The density change in monoclinic-to-hexagonal transition (2.5%) is considerably less severe.

The melting point of Cm_2O_3 has been reported by Oak Ridge National Laboratory as 1950°C .²⁵

Vaporization Rates

The vaporization behavior and vaporization rate of Cm_2O_3 have been determined at Savannah River by the Knudsen technique, using a tungsten effusion cell in a vacuum of 10^{-7} mm Hg. Thermionic fuel should vaporize without significant change in composition of the solid. The invariant vaporization was

shown when monoclinic and hexagonal structures were observed in both the vapor deposits and residues after up to 85% of the Cm_2O_3 had been vaporized. This invariance is demonstrated by the linear plot of $\log P_E$ versus $1/T$ in Fig. 1. Experimental points ranged between 1800 and 2600°K, through the transition temperature and melting point.

The vapor pressure cannot be established because the vapor species are not known. Consequently, P_E is the calculated pressure of a fictitious Cm_2O_3 molecule. Several vaporization processes are possible to form combinations of gaseous Cm, O, O_2 , CmO, and CmO_2 . Precedent for these vapor species has been set by the observation of similar species over other actinide oxides. Depending on the particular vaporization process, total pressures calculated from the measured vaporization rates would be greater than P_E by factors between 1.4 and 1.9.

The low vaporization rate of Cm_2O_3 further indicates the suitability of Cm_2O_3 for thermionic operation. The vapor pressure of Cm_2O_3 is one-fourth that of PuO_2 and only 30 times that of ThO_2 , one of the most refractory oxides.

Table I summarizes the available thermochemical information on Cm_2O_3 . The heat of formation was estimated from related data on other actinide oxides.

The temperature dependence of vapor pressure and rate of weight loss on vaporization are expressed. The boiling point of Cm_2O_3 was determined to be $3970 \pm 200^\circ\text{K}$ by extrapolating the $\log P_E$ versus $1/T$ curve to $P_E = 1 \text{ atm}$.

TABLE I

Thermodynamic Properties of Cm_2O_3

Heat of Formation:

$$\Delta H_{298^\circ\text{K}}^\circ = (-415 \pm 30 \text{ kcal/mole})$$

Melting Point:

$$T_f = 1950 \pm 25^\circ\text{C}$$

Vapor Pressure:

$$\log P_E(\text{atm}) = 7.32(\pm 0.26) - \frac{29050(\pm 590)}{T(^{\circ}\text{K})}$$

Vaporization Rate:

$$\log \frac{W}{\text{at}} \left(\frac{\text{g}}{\text{sec cm}^2} \right) = 10.33(\pm 0.26) - \frac{29050(\pm 590)}{T(^{\circ}\text{K})} - 1/2 \log T(^{\circ}\text{K})$$

Boiling Point:

$$T_b = 3700 \pm 200^\circ\text{C}$$

Heat of Vaporization:

$$\Delta H_{2000^\circ\text{K}}^\circ = 133.0 \pm 2.7 \text{ kcal/mole of gas}$$

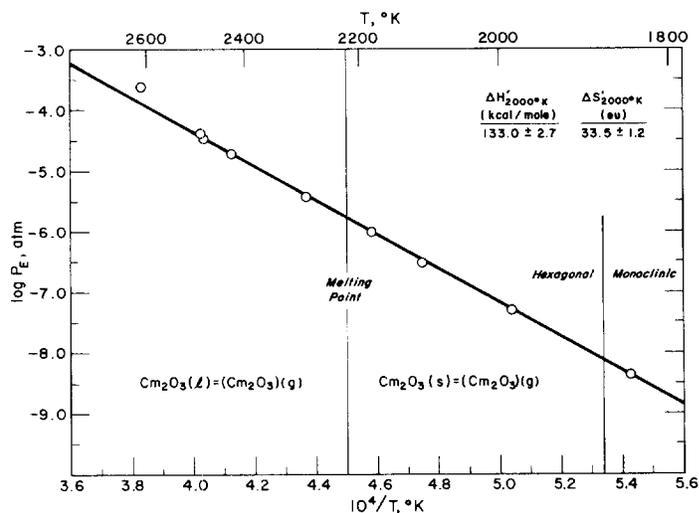


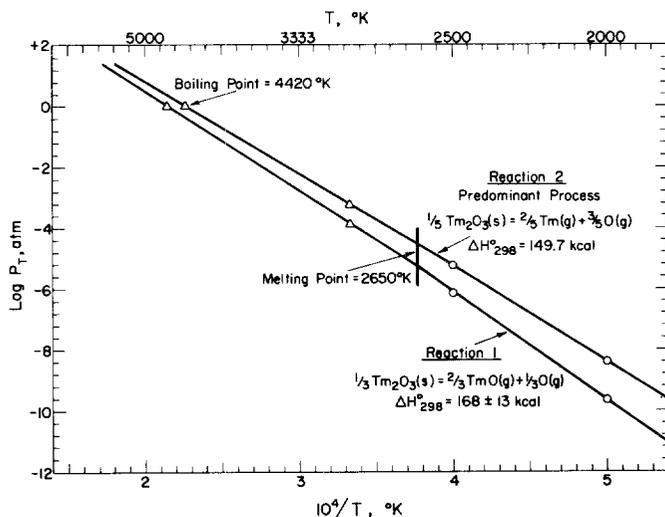
Fig. 1 Vaporization of Curium Sesquioxide

PROPERTIES OF THULIUM OXIDE
AT HIGH TEMPERATURE

The thulium-oxygen phase diagram is simple. Only one oxide of thulium exists, Tm_2O_3 , even on heating in oxygen or hydrogen.⁵ It is essentially a "line compound" with a cubic structure (density = 8.884 g/cc) up to 2280°C, where it transforms to hexagonal structure. The melting point was determined at Savannah River as 2375 ± 25°C. It has a very high heat of formation ($\Delta H_{298}^{\circ} = -451.4$ kcal/mole), making it one of the most stable oxides known.^{2,6}

The vaporization process and vapor pressures were established by thermodynamic arguments based on limited data on Tm_2O_3 , and extensive data on other related rare-earth oxides.^{2,7} Thulia vaporizes at constant composition in vacuum predominantly to form gaseous atoms. Competing with vaporization to the elements is vaporization to $TmO(g)$ and oxygen. Because of the uncertainty in the dissociation energy of $TmO(g)$, the relative importance of $TmO(g)$ compared with $Tm(g)$ cannot be established thermodynamically. However, mass spectrometric studies by Panish^{2,8} show that $Tm(g)$ is a factor of 10 more important than $TmO(g)$ in equilibrium with $Tm_2O_3(s)$.

Calculated curves for $\log P_T$ versus $1/T$ for both vaporization processes are shown in Fig. 2. Tm_2O_3 has about the



same vapor pressure as ThO_2 and is 30 times less volatile than is Cm_2O_3 .

The thermodynamic properties of Tm_2O_3 are summarized in Table II. Expressions for the temperature coefficient of vapor pressure and vaporization rate are derived that apply below and above the melting point. The boiling point was established by extrapolating the curve in Fig. 2 to a vapor pressure of 1 atmosphere.

TABLE II

Thermodynamic Properties of Tm_2O_3

Heat of Formation:

$$\Delta H_{298}^{\circ} = -451.4 \text{ kcal/mole}$$

Melting Point:

$$T_f = 2375 \pm 25^{\circ}C$$

Vapor Pressure:

$$\log P_T(\text{atm}) = 7.37 - \frac{31500}{T(^{\circ}K)} (0-2650^{\circ}K)$$

$$\log P_T(\text{atm}) = 6.81 - \frac{30100}{T(^{\circ}K)} (2650-4400^{\circ}K)$$

Vaporization Rate:

$$\log \frac{W}{\text{at}} \left(\frac{\text{g}}{\text{sec cm}^2} \right) = 10.02 - \frac{31500}{T(^{\circ}K)} - 1/2 \log T(^{\circ}K) (0-2650^{\circ}K)$$

Boiling Point:

$$T_b = 4150 \pm 300^{\circ}C$$

Heat of Vaporization:

$$\Delta H_{298}^{\circ} = 748.3 \text{ kcal/mole}$$

Fig. 2 Total Pressure for Congruent Vaporization of Tm_2O_3

FUEL TRANSPORT RATES

Even though vapor pressures are low, possible fuel transport within and from a thermionic heat source must be evaluated for operation and safety. Vaporization rates of Cm_2O_3 and Tm_2O_3 at various temperatures are listed in Table III. These rates are sufficiently high that a considerable radiological hazard would occur if a capsule of either isotope were to break open and continue to maintain a fuel temperature of the order of 1850°C .

TABLE III

Temp, $^\circ\text{C}$	Vaporization Rate, $\text{g}/(\text{cm}^2)(\text{sec})$	
	Cm_2O_3	Tm_2O_3
1000	9.2×10^{-15}	5.0×10^{-17}
1500	2.1×10^{-8}	4.3×10^{-10}
1850	9.7×10^{-6}	3.3×10^{-7}
2000	7.5×10^{-5}	2.8×10^{-6}

On the other hand, suppose that a capsule operating at 1850°C contains a cracked weld that can be represented by a hole 0.001 in. in diameter by 0.200 in. long. If molecular flow were limiting, about 125 μg of Cm_2O_3 and 4 μg of Tm_2O_3 would enter the leak in one month and about 1/100th of that would escape. These rates represent the worst condition, because fuel escape by transpiration in vented helium gas saturated with Cm_2O_3 or Tm_2O_3 vapor, or escape by diffusion in a helium atmosphere, would both be lower by factors of 100. Such a leak rate may represent a tolerable radiological hazard. The fairly low loss rate of $^{244}\text{Cm}_2\text{O}_3$ through small holes suggests it may be possible to design a ^{244}Cm -fueled capsule that vents the helium decay product directly, which would eliminate thick-walled capsules and the need for void volume, and would increase power efficiency.

Vapor transport rates for Cm_2O_3 are sufficiently high at thermionic temperatures that fuel will redistribute in a

few days over the void volume of a capsule to form an isothermal fuel-void interface. Table IV shows the net transport rates per unit area down temperature gradients that might be experienced initially in fuel capsules. In a ten-degree gradient, curium oxide will redistribute at $\sim 10 \text{ g}/(\text{month})(\text{cm}^2)$ of vaporizing surface). The rates increase 3-fold and 5-fold for gradients of 50 and 100°C , respectively. Again the rates are for the worst case of molecular flow. An inert gas blanket and a decreasing gradient with fuel redistribution would lengthen the time required to generate an isothermal fuel surface. Even so, the relatively high rate of Cm_2O_3 redistribution suggests that high-density oxide forms such as microspheres, discs, or annular rings may not be appropriate; or, alternatively, primary encapsulation in a cermet form permeable to helium will be desired to fix the fuel.

TABLE IV

Vaporization Rates of Cm_2O_3 and Tm_2O_3
in Thermal Gradients

Temperature Gradient, $^\circ\text{C}$	Net Transport Rate, $\text{g}/(\text{cm}^2)(\text{sec})$	
	Cm_2O_3	Tm_2O_3
1850 to 1840	14×10^{-7}	0.5×10^{-7}
1850 to 1800	41×10^{-7}	1.9×10^{-7}
1850 to 1750	76×10^{-7}	2.7×10^{-7}

The redistribution rate for Tm_2O_3 is 1/30th that of Cm_2O_3 . Because of lower redistribution rate and absence of a gaseous decay product, $^{170}\text{Tm}_2\text{O}_3$ may be encapsulated as a high-density form without planned void volume.

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