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AEC RESEARCH AND DEVELOPMENT REPORT

INTERACTIONS OF THULIUM OXIDE WITH CONTAINER METALS

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J. R. KESKI

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INTERACTIONS OF THULIUM OXIDE WITH CONTAINER METALS

by

P. Kent Smith and James R. Keski

Approved by

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Nuclear Materials Division

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ABSTRACT

The properties of Tm_2O_3 make it an attractive fuel form for ^{170}Tm heat sources. To establish specifications for a reactor target to produce ^{170}Tm in a form suitable for direct use in isotopic heat sources after irradiation, possible interactions between Tm_2O_3 and candidate container metals were evaluated at temperatures up to 2000°C.

Reaction between Tm_2O_3 and aluminum, the cladding material for target assemblies during irradiation, was observed only above 590°C, considerably higher than projected temperatures of irradiation. After 1000 hours at 1000°C, no significant reaction was observed between Tm_2O_3 and tungsten, tantalum, molybdenum, "Inconel" 600, or "Haynes" 25. Short-term tests of Tm_2O_3 in sealed tantalum capsules were made to verify the thermodynamic predictions of the compatibility of Tm_2O_3 with refractory metals. Reaction of Tm_2O_3 with Ta to form $TmTaO_4$ occurred in unsealed capsules, which allowed escape of the product Tm (or TmO) gas. Reaction between silica in the Tm_2O_3 and Ta to form Ta_5Si demonstrated the need for control of impurities in the target Tm_2O_3.

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INTRODUCTION

As part of a program to explore the feasibility of large-scale production of heat-producing radioisotopes, test irradiations of ^{169}Tm were made in Savannah River reactors to develop technology for production of ^{170}Tm for isotopic heat sources. Thulium-170, a beta-emitter with a half-life of 128 days, may be a suitable substitute for polonium-210 (an alpha-emitter with a half-life of 138 days) in some applications in which the more penetrating ^{170}Tm radiation can be tolerated.

Thulium-169 oxide (Tm_2O_3) has been irradiated in Savannah River reactors to specific powers in the range of 2 to 3 watts/gram (18-27 watts/cc), which may be a sufficient power density for use in heat sources operating at up to 1500-2000°C.(1,2) Thulium oxide has been demonstrated to be a very refractory and inert fuel material.(3,4)

To provide specifications for a target form for reactor irradiation that would be suitable for direct use in a heat source after irradiation, an evaluation of the properties and high-temperature behavior of Tm_2O_3 was made.(3,4) This report summarizes results of a preliminary survey of potential interactions of the oxide with candidate container metals to which the oxide would be exposed in the course of reactor irradiation, postirradiation handling, and heat source application.

SUMMARY

To aid in specification of suitable target materials for production of ^{170}Tm in Savannah River Plant reactors, an analysis was made of possible reactions between thulium sesquioxide and potential container metals to which the target would be exposed during irradiation processing and final application.

Thulium oxide can be irradiated in aluminum metal up to interface temperatures of 590°C, above which reaction occurs at the interface to form Al_2O_3 and Tm-Al alloys.

Wafers of Tm_2O_3 were heated in contact with tantalum, molybdenum, tungsten, "Inconel"* 600, and "Haynes"** 25 for 100 and 1000 hours, at 1000°C. No evidence of reaction was observed metallographically.

Because Tm_2O_3 is among the most stable of all oxides, we predict that it cannot be reduced by candidate encapsulating metals, tungsten, molybdenum, rhenium, and tantalum, to form their oxides, particularly since thulium does not form alloys with tungsten, molybdenum, or tantalum. Although $TmRe_2$ probably exists, experiments with other rare earth oxides indicate rhenium will not reduce Tm_2O_3. Eutectic melting between thulia and refractory metals probably occurs above 2000°C. Compounds do not exist in binary systems involving Tm_2O_3 and the encapsulating metals. Ytterbium-170, the stable decay product formed in solid solution with Tm_2O_3, is another rare earth element whose oxide stability and compatibility potential should be nearly identical with that of Tm_2O_3.

In an experimental verification of these predictions, no reaction to form $TmTaO_4$ was observed between Tm_2O_3 and a sealed tantalum container after 24 hours at 1925°C, although the oxide was reduced to $Tm_{2.00}O_{2.90}$ and the tantalum reacted with a silicon impurity in the Tm_2O_3 to form Ta_5Si. The Tm_2O_3 did react with tantalum to form $TmTaO_4$ in flowing helium at 1900°C under conditions where the product Tm(g) or TmO(g) was removed from the reaction site.

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* Trademark of International Nickel Co.

** Trademark of Union Carbide Corp.

DISCUSSION

INTERACTION BETWEEN Tm_2O_3 AND Al

Because of the similarity in neutron absorption between thulium and cobalt, it was convenient to irradiate thulium targets using target shapes, hardware, and fabrication technology developed for cobalt wafers. On this basis, thulia wafers were irradiated in aluminum metal slugs, which caused some concern about a possible interaction between the aluminum and thulium oxide.

As shown in Table I, Tm_2O_3 is one of the most stable oxides in the periodic system. Aluminum cannot reduce Tm_2O_3 to form Al_2O_3 and Tm because of the higher stability of Tm_2O_3. However, the existence of stable $TmAl_2$ and $TmAl_3$, reported by Jones, Norlock, and Boucher,$^{(5)}$ provides sufficient free energy for the following reaction to occur:

$$Tm_2O_3 + 8\ Al = 2\ TmAl_3 + Al_2O_3$$

Reactions between Gd_2O_3 and Al and between CeO_2 and Al to form $GdAl_4$ or $CeAl_4$ and Al_2O_3 have been shown at the Savannah River Laboratory to occur at temperatures below 600°C.$^{(6)}$ These reactions were not very exothermic and were very slow. Powder-compacted cermets that had been heated for several hours at 600°C contained predominantly unreacted starting materials.$^{(6)}$ Similar behavior is expected for the Tm_2O_3-Al reaction.

Differential thermal analysis (DTA) and X-ray diffraction were used to confirm the reaction between Tm_2O_3 and Al and to determine the threshold temperature above which reaction occurs. High purity Tm_2O_3 and Al powders were mixed in proper proportions to form $TmAl_2$ and Al_2O_3. In each of two experiments, about 15 mg of the mixture was heated at 10°C/min in platinum DTA cells (Du Pont Model 900 DTA instrument) under flowing helium.

The thermograms obtained in both experiments (Figure 1) show the onset of the exothermic reaction between Tm_2O_3 and Al at 590 ±5°C. The reaction is severely hindered kinetically as shown by the (1) absence of additional exothermic reaction up to 1100°C, (2) endothermic melting of unreacted aluminum at 660°C, and (3) predominance of unreacted Tm_2O_3 and Al in the product. The Debye-Scherrer pattern of the powdered product showed four phases: a predominance of Tm_2O_3 and Al and a minor amount of Al_2O_3 and $TmAl_3$.

TABLE I

Comparison of Stabilities of Metal Oxides

Oxide(a)	$-\Delta H^{o}_{298^{o}K}$,(b) kcal/gram-atom(c) of oxygen
$Ca + \frac{1}{2} O_2 = CaO$	151.6
$\frac{2}{3} Tm + \frac{1}{2} O_2 = \frac{1}{3} Tm_2O_3$	150.5
$\frac{2}{3} Al + \frac{1}{2} O_2 = \frac{1}{3} Al_2O_3$	133.3
$\frac{1}{2} Hf + \frac{1}{2} O_2 = \frac{1}{2} HfO_2$	133.0
$\frac{1}{2} Zr + \frac{1}{2} O_2 = \frac{1}{2} ZrO_2$	129.8
$\frac{1}{2} U + \frac{1}{2} O_2 = \frac{1}{2} UO_2$	129.5
$Ti + \frac{1}{2} O_2 = TiO$	123.9
$V + \frac{1}{2} O_2 = VO$	103.0
$\frac{2}{5} Ta + \frac{1}{2} O_2 = \frac{1}{5} Ta_2O_5$	97.7
$Nb + \frac{1}{2} O_2 = NbO$	98.5
$\frac{1}{2} Mo + \frac{1}{2} O_2 = \frac{1}{2} MoO_2$	70.0
$\frac{1}{2} W + \frac{1}{2} O_2 = \frac{1}{2} WO_2$	70.5
$\frac{1}{2} Re + \frac{1}{2} O_2 = \frac{1}{2} ReO_2$	50.8

(a) Oxides higher in the table will not be reduced by metals lower in the table.

(b) $\Delta H^{o}_{298^{o}K}$ is in the same order as $\Delta F^{o}_{298^{o}K}$ since $\Delta S^{o}_{298^{o}K}$ is approximately the same for each reaction.

(c) Reference 8

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Reaction probably could be observed at lower temperatures than 590°C if cermets were heated for long times, but the interface temperature between Tm_2O_3 pellets and their aluminum jackets is not expected to be high enough for reaction during reactor irradiation. Tm_2O_3 pellets (95% theoretical density, 0.672-inch diameter, and 0.100-inch thickness) have been irradiated in aluminum rods to a specific activity of 2 watts/gram without reaction between the pellets and the rods.[7]

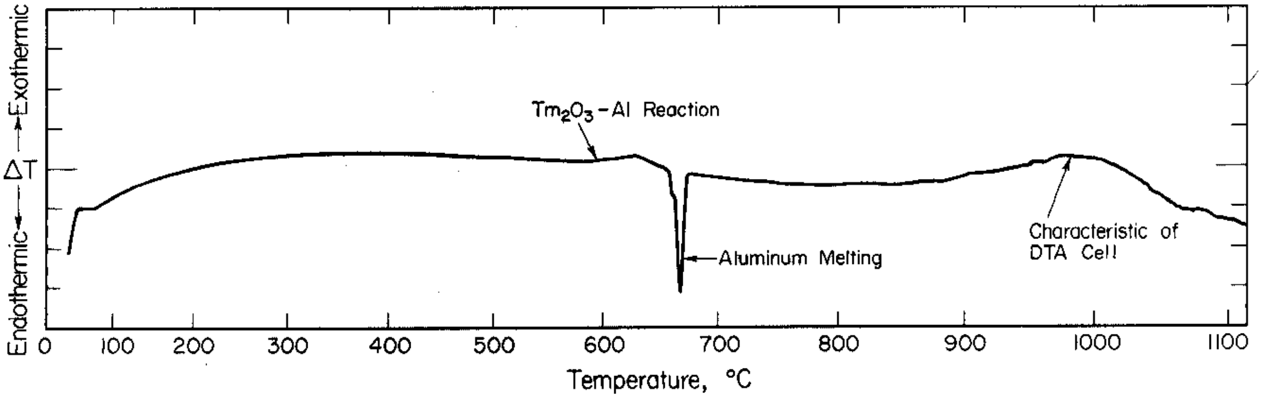

FIG. 1 TYPICAL DIFFERENTIAL THERMAL ANALYSIS OF Tm_2O_3-Al REACTION

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INTERACTION BETWEEN Tm_2O_3 AND METALS AT 1000°C

Screening tests were made to study possible interactions between Tm_2O_3 and tantalum, tungsten, molybdenum, "Inconel" 600, and "Haynes" 25 to establish candidate materials for postirradiation handling operations and to obtain some assurance that Tm_2O_3 wafers could be used directly after irradiation in heat sources operating at relatively low temperatures (1000°C). The concentrations of the principal impurities found in a typical wafer are listed in Table II.

TABLE II

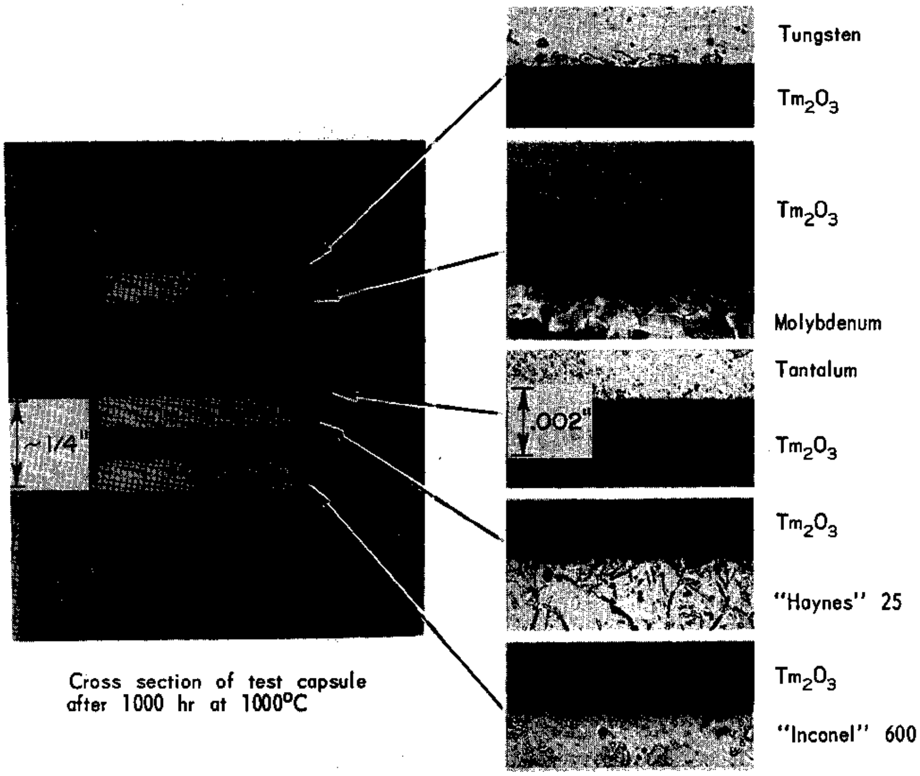
Major Impurities in Tm_2O_3 Pellet Used in 1925°C Test

	Concentration, wt %(a)	
Element	Before	After
W	4.3×10^{-4}	3.4×10^{-4}
Ta	1.8×10^{-4}	9.0×10^{-4}
Yb	6.0×10^{-4}	2.0×10^{-4}
Er	5.2×10^{-2}	5.2×10^{-2}
Si	9.5×10^{-1}	9.5×10^{-2}
Ca	1.4×10^{-2}	1.4×10^{-2}
Ni	1.8×10^{-3}	1.8×10^{-3}
Co	6.0×10^{-5}	6.0×10^{-5}
Fe	2.1×10^{-1}	6.0×10^{-2}
Mn	5.5×10^{-4}	5.5×10^{-4}
Al	9.0×10^{-3}	9.0×10^{-3}
Na	2.4×10^{-5}	2.4×10^{-5}
B	4.6×10^{-3}	1.4×10^{-3}
Cl	4.9×10^{-2}	4.9×10^{-2}
K	1.3×10^{-2}	1.3×10^{-2}

(a) All other impurities noted were present in amounts less than ~3×10^{-3} mole %. Total measured impurity content was ~1.3 wt %. Impurity concentrations, determined by spark source mass spectrometry, are believed within a factor of 3 for absolute values and within a factor of 2 for comparative values.

No evidence of reaction between thulium oxide and candidate container materials was obtained from two tests conducted at 1000°C. In the first experiment, sintered Tm_2O_3 wafers in contact with tantalum, tungsten, "Inconel" 600, and "Haynes" 25 were heated in a sealed type 304 stainless steel capsule containing helium. After 100 hours at 1000°C, no indication of reaction between the Tm_2O_3 and the metals was noted metallographically.

The experiment was repeated to include molybdenum and was extended to 1000 hours at 1000°C. After this test period, no reaction was noted metallographically between the Tm_2O_3 and tantalum, tungsten, molybdenum, "Inconel" 600, and "Haynes" 25. Figure 2 shows the cross-sectional configuration of the capsule and the Tm_2O_3-metal interfaces at the conclusion of the experiment. Differences in thermal expansion of the various materials in the test led to some cracking and subsequent pullouts at the oxide-metal interfaces during metallographic preparation of the stacked specimens. However, no evidence of interaction was observed for any oxide-metal couple.



Cross section of test capsule after 1000 hr at 1000°C

Interfaces between Tm_2O_3 and indicated metals

FIG. 2 INTERACTION BETWEEN Tm_2O_3 AND CONTAINER METALS AT 1000°C

INTERACTION BETWEEN Tm_2O_3 AND REFRACTORY METALS ABOVE 1000°C

To obtain preliminary assurance of direct applicability of Tm_2O_3 target wafers in high-temperature (1700°C) heat sources, thermodynamic analyses, a literature search, and screening tests were performed to establish possible interactions between Tm_2O_3 wafers and refractory container metals. Effects of impurities and oxide composition in as-processed target material were of particular interest in the screening tests.

Reduction by Refractory Metals

As shown in Table I,(8) Tm_2O_3 is considerably more stable than are the refractory metal oxides. Thulia should not react with tungsten, molybdenum, and rhenium, or their alloys, even above the thulia melting temperature of 2375°C, to form thulium metal and refractory metal oxides.

Reduction of Tm_2O_3 by tantalum, molybdenum, or tungsten to form binary alloys and refractory metal oxides probably will not occur because thulium does not form binary compounds or extensive solid solutions with any of these refractory metals. Moriarity and Baenziger(9) found no intermediate compounds and only limited mutual solubility between tungsten, molybdenum, or tantalum and gadolinium or dysprosium. Daane and Spedding(10) reported less than 0.2 wt % molybdenum is soluble in cerium or lanthanum at 1300°C, and found no intermediate phases. Daane and Spedding(9) found that no tantalum-thulium compounds exist and that thulium dissolved 1.5 wt % tantalum to raise the melting point by 135° above that of pure thulium to 1680°C.

Reaction of Tm_2O_3 with rhenium to form $TmRe_2$ is possible if $TmRe_2$ is sufficiently stable. Existence of $TmRe_2$ seems certain since Lundin(9) has identified YRe_2, which melts at 2520°C. However, Föex and Traverse(11) melted Tm_2O_3 on rhenium filaments in high temperature X-ray experiments with no visual reaction or unexpected changes observed in X-ray patterns.

Eutectic Melting

Eutectic melting is not expected to limit the usefulness of Tm_2O_3 as a heat source. Melting of a eutectic composition formed between Tm_2O_3 and the refractory metal container would increase surface contact, enhance diffusion, and lead to fuel redistribution. However, eutectic temperatures for Tm_2O_3 and pure refractory metal systems are expected to be over 2000°C. For example, the eutectic temperature for Y_2O_3-W is about 2135°C,(14) 285° less than the melting point of Y_2O_3. No eutectic melting was observed at 2000°C between tungsten and Dy_2O_3, Sm_2O_3, or Eu_2O_3 (with melting points of 2340°C, 2325°C, and 2050°C, respectively) according to Hoyt, Cummings, Zimmerman, and Perrine.(12) Eutectic temperatures between refractory metal alloys and Tm_2O_3 will be lower than for the corresponding pure metal systems, but are expected to be near 2025°C.

Formation of Ternary Compounds

Reactions of Tm_2O_3 with refractory metals and alloys to form ternary compounds or extensive solid solutions probably do not occur. No ternary oxides whose composition can be represented by a stoichiometric combination of Tm_2O_3 and refractory metal are known to exist. Some ternary compounds do exist, e.g., tungstates, molybdates, and tantalates, but they are oxygen-rich compared to the system Tm_2O_3-metal.

Walsh, Goldstein, and White(13) found that La_2O_3 and Nd_2O_3 react appreciably with tantalum crucibles above 1725°C, according to the reaction $3\ RE_2O_3 + Ta = 5\ REO(g) + RETaO_4$, to produce vapor pressures of $LaO(g)$ or $NdO(g)$ comparable to the vapor pressure observed at temperatures 200 to 300° higher in inert crucibles. In a closed capsule with no temperature gradients, tantalum would not be expected to reduce Tm_2O_3 to form $TmTaO_4$, even above the melting point of Tm_2O_3, since achievement of the equilibrium pressure of $TmO(g)$ would prevent the reaction from continuing. Experimental confirmation of this hypothesis is discussed on page 14.

Vapor Transport Reactions

Formation of small amounts of oxide gas by limited reaction between thulia and container metals at high temperatures presents the possibility of vapor transport erosion of the capsule metal in a temperature gradient. This mechanism has been evaluated for tantalum transport because tantalum is the refractory metal most likely to show such an effect.

Temperature gradients in a capsule should not cause a tantalum capsule to be eroded from the inside even though $TaO(g)$ is fairly stable and has a fairly high vapor pressure at temperatures over 1700°C. Possible transport processes involving $TaO(g)$ are all endothermic and would transport tantalum only to cold surfaces. Failure of a capsule because of vapor transport in temperature gradients is even less probable for molybdenum, tungsten, and rhenium since their gaseous oxides are less stable than $TaO(g)$.

Experimental Confirmation of Noninteraction of Tm_2O_3 with Refractory Metals

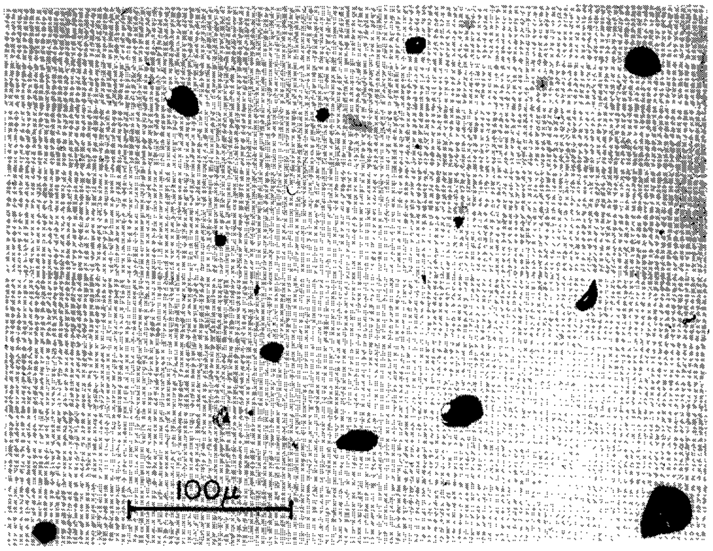
Short-term compatibility of Tm_2O_3 and other rare earth sesquioxides with tantalum, niobium, tungsten, molybdenum, and rhenium has been demonstrated in experiments at the Savannah River Laboratory and by several other investigators.

Capsule Heating Tests

A thulia wafer was heated in a welded tantalum container at 1925°C for 24 hours in a test at Savannah River. No reaction between Tm_2O_3 and Ta was observed by metallographic or X-ray diffraction analyses. In this experiment, a sintered wafer of Tm_2O_3 was heated in a closed tantalum capsule containing helium. The tantalum capsule, with 0.005% C and 0.0046% O_2 as principal impurities, was approximately 7/8 inch in diameter by 1/2 inch high with a wall thickness of 1/16 inch. Reaction to form $TmTaO_4$ should not proceed, if thulium vapor was not removed. After 24 hours at 1925°C, the Tm_2O_3 pellet was intact, even after the thermal shock of cooling from 1925°C to room temperature in about 30 minutes. No evidence of $TmTaO_4$ formation was found, confirming the thermodynamic predictions.

Analysis of the Tm_2O_3 pellet showed an oxygen concentration of 12.05% (determined by vacuum fusion) corresponding to $Tm_{2.00}O_{2.90}$, demonstrating that the pellet had lost oxygen during the high-temperature test. The Tm_2O_3 pellet, uniformly gray after heating at 1925°C, was broken and one portion was reheated in air for 10 hours at 1125°C to determine whether reoxidation would occur. The color returned to light yellow, but the oxygen content increased by only 0.04%. Reoxidation occurred by a diffusion-controlled reaction.

Metallographic examination of the Tm_2O_3 specimen showed free metal, presumably thulium, associated with pores in the oxide wafer (Figure 3). Lattice parameter variation before and after the test was less than 1 part in 10^5. Spark source mass spectrometry of the oxide revealed only 15 ppm atom pickup of tantalum during the test. These data suggest that the Tm_2O_3 had been reduced to a substoichiometric oxide at 1925°C and that thulium metal had precipitated during cooling from the high test temperature. Small single crystals of Tm_2O_3 were formed by vapor transport and deposited on tantalum surfaces near the thulia wafer (Figure 4). These crystals were transparent, and up to ~0.1 mm long.



Gray background is Tm_2O_3; black regions are pores; white spots are metal

FIG. 3 METALLIC PRECIPITATES IN THULIUM OXIDE (Structure of thulium oxide after heating in tantalum capsule at 1925°C in helium)

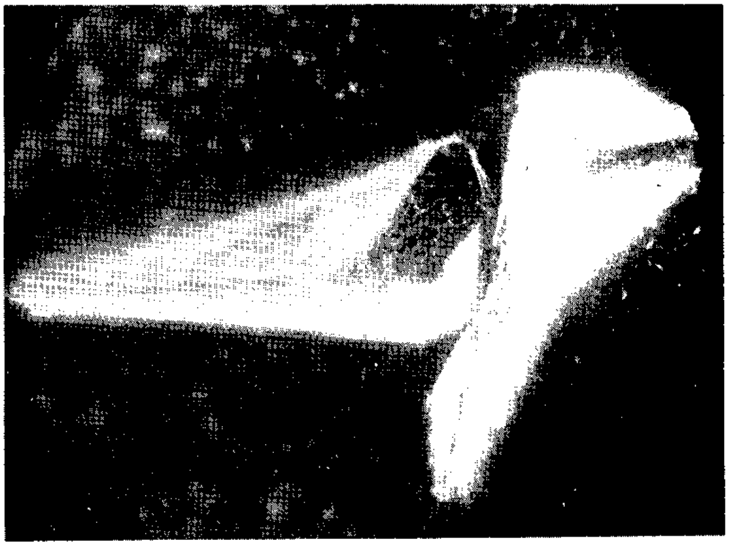


FIG. 4 Tm_2O_3 CRYSTALS FORMED DURING Tm_2O_3-Ta INTERACTION TEST Tm_2O_3 heated in sealed tantalum capsule for 24 hours at 1925°C; crystals approximately 150 microns long

A reaction was observed between tantalum and silicon impurity in the thulia to form Ta_5Si, indicating that impurity levels of target materials charged to the reactor must be known and controlled. A reaction layer, identified by X-ray diffraction as Ta_5Si, had formed on the inside bottom of the tantalum capsule and 3/16 inch up the side (Figure 5). The Ta_5Si layer varied up to 5 microns in thickness. The silicide formation was due to 0.95% silicon impurity in the oxide.

Spark source mass spectrometry revealed that the silicon content of the Tm_2O_3 was lowered by a factor of 10 during heating to 1925°C because of reaction with tantalum and/or direct vaporization. Table II lists the major impurities found in the specimen before testing and indicates the reduction of the silicon content following the high-temperature test.

As predicted, reaction between tantalum and a Tm_2O_3 wafer to form $TmTaO_4$ was observed in only 1 hour at 1900°C under conditions where Tm(g) or TmO(g) was removed by flowing helium. A layer of reaction product, identified by X-ray analysis as $TmTaO_4$, was formed on the tantalum (Figure 6).

Filament Heating Tests

In high-temperature X-ray diffraction experiments at Savannah River to measure the thermal expansion of Tm_2O_3, powdered thulium oxide and an internal standard of molybdenum powder were heated 6 to 8 hours at 1850°C on a tungsten filament in an atmosphere of 4% hydrogen in helium. No reaction was observed either visually or by unexpected changes in X-ray pattern.

In similar experiments, thulia has been heated to 2275°C for several hours on tungsten and rhenium filaments by Föex and Traverse,(11) who reported no changes in X-ray diffraction characteristics indicative of reaction.

Interaction Between Other Rare Earth Oxides and Refractory Metals

Other rare earth sesquioxides do not react with refractory metals. Grossman(14) cycled yttrium sesquioxide in a tungsten crucible through the melting point of Y_2O_3 and observed only small solubility effects of W in Y_2O_3 and vice versa. Several researchers(13,15,16,17) used tungsten effusion cells to study vaporization behavior of RE_2O_3, including Tm_2O_3, and found no reaction with tungsten. Hoyt, et al.(12) studied the reaction

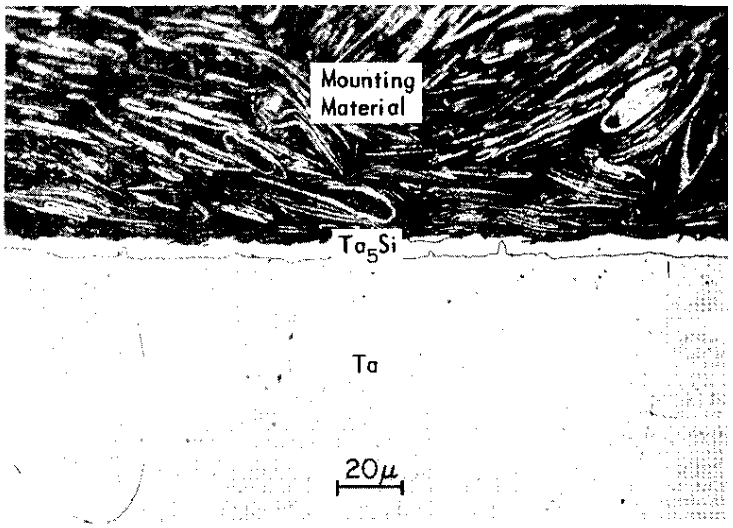


FIG. 5 Ta_5Si FORMED ON TANTALUM
Tm_2O_3 heated in sealed tantalum capsule for 24 hr at 1925°C

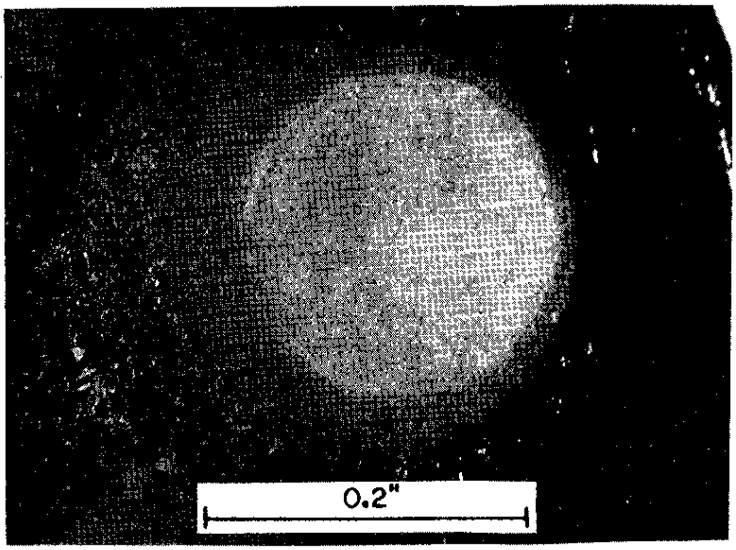


FIG. 6 $TmTaO_4$ FORMED ON TANTALUM
Tm_2O_3 heated on tantalum plate for 1 hr at 1900°C in flowing helium

[redacted]

of Dy_2O_3, Sm_2O_3, and Eu_2O_3 with molybdenum, tungsten, and niobium by heating powdered materials in vacuum for 2 hours at 1800-2000°C and subsequently examining the product metallographically; no signs of reaction were observed between any pair of oxide and metal.

Influence of Ytterbium Decay Product

Thulia forms a stable decay product, ^{170}Yb, whose oxide is almost identical in refractory character, composition, and structure with the parent oxide matrix. ^{170}Yb should form a solid solution with Tm_2O_3 as $Tm_{2-x}Yb_xO_3$; the high temperature behavior and stability of this solid solution should be nearly identical to that of Tm_2O_3.

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