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FABRICATION AND IRRADIATION BEHAVIOR OF THULIUM SESQUIOXIDE

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ABSTRACT

The results of reactor irradiation of thulium sesquioxide are discussed, along with chemical and physical properties and wafer fabrication. Sintered densities up to 90% of theoretical were obtained in target wafers using oxide reprocessed to obtain readily sinterable powder. Irradiation to about 1.8 w/g did not change the microstructure of the wafers although some wafers broke, probably because of mechanical stresses in target and disassembly.

I. Introduction

Thulium-170 may be a useful heat source for isotopic power generators in certain short-term applications in which its penetrating Bremsstrahlung can be tolerated. Savannah River has studied the feasibility of thulium sesquioxide irradiation in the Savannah River reactors.

To select a reactor target material suitable for irradiation in a form that might be used directly in an isotopic power source, the properties of thulium sesquioxide were evaluated by Smith, Keski, and Angerman,[1] and by Smith.[2] Little technology has been reported on fabrication techniques for thulium sesquioxide; consequently, a procedure for producing dense oxide wafers was required. A similar effort was performed by Eastly and Matson; their results are available only in abstract form.[3] Information on thulium oxide irradiation techniques and behavior was unavailable; therefore, natural thulium oxide wafers were irradiated to assess their behavior under reactor conditions. This paper summarizes results of these investigations.

II. Properties of Thulium Oxide

Thulium-170 is a beta emitter with a half-life of 128 days,[4] which limits its applicability as a heat source fuel to short terms. The decay scheme of ^{170}Tm is shown in Figure 1. The predominant decay mechanism is beta emission to form stable ^{170}Yb; approximately 76% of the beta emissions are 0.967 Mev, and 24% are 0.882 Mev. Bremsstrahlung is the principal contributor to radiation doses.[5]

Candidate materials for use as heat sources in isotopic power generators should (1) have a usable heat generation rate over application lifetimes, (2) require minimum shielding, (3) exhibit physical and chemical stability, and (4) be readily available.

Thulium-170 can be produced with a power level of 2 to 3 w/g by irradiation of natural $^{169}Tm_2O_3$ in reactors operating at fairly high flux.[6] The density of thulia, calculated from the lattice parameters, is 8.884 g/cc. Hence, the specific power available is from 17-26 w/cc; this power is sufficient for thermionic power applications.

In general, some weight penalty must be paid in space applications due to the additional shielding required because of the large Bremsstrahlung contribution to the emitted radiation. Arnold[7] has calculated that the gamma and Bremsstrahlung dose rate expected from an unshielded 1-Kw ^{170}Tm power source would be about 1.5×10^3 rad/hr at a distance of 100 cm from the center of the source. This rate may be decreased to approximately 25 rad/hr with a 1-cm lead shield, and to about 3 rad/hr with a 1-cm uranium shield.

To operate thermoelectric power generators with the heat source material at about 1000°C and thermionic power sources with the fuel at about 1850°C, physical and chemical stability of the oxide must be assessed at these temperatures, particularly with respect to safety during operation. Figure 2, patterned after Foex and Traverse,[8] and Table I indicate the refractory nature of Tm_2O_3 and its decay product Yb_2O_3. The melting point of thulium sesquioxide, measured in a Mendenhall V-vilament furnace, is 2375°C, which is considerably higher than the anticipated maximum temperature during heat source application. In contrast to the lighter rare earth oxides, no phase transformations occur within the expected temperature range of application. The only transformation reported is to a hexagonal structure at 2280°C.[9] The sesquioxide is the only known stable condensed-phase oxide of thulium.

Reaction of containment metals with the isotopic fuel is of great concern because of the radioactivity hazard that would result if the fuel escapes from the container. Thulia has a heat of formation of -451.4 kcal/mole at 298°K;[10] therefore, it is one of the most stable oxides and cannot be reduced by most containment metals.

The vaporization behavior and oxide redistribution rates were estimated using thermodynamic data for other rare earth oxides.[2,11] Because of the high heat of formation and the absence of very stable gaseous molecules, the vapor pressure is very low, approximately 10^{-9} atmosphere at 1725°C.

The linear thermal expansion was taken from a curve of the lattice expansion measured by high-temperature X-ray techniques.[1,12] The behavior is typical of that reported for other rare earth sesquioxides.

III. Experimental Procedure

(1) Fabrication of Thulium Oxide Wafers

Thulium sesquioxide of 99.9% purity, purchased from the Michigan Chemical Corporation, was used. Major impurities were approximately 0.03 wt % of silicon, 0.03 wt % of ytterbium, 0.01 wt % of calcium, and 0.05 wt % of erbium. Vacuum extraction at 1300°C revealed the presence of 4 to 7 cc/g of CO, CO_2, and H_2, which indicated incomplete oxalate decomposition during calcining. Subsequent sintering reduced the gas content of the oxide below 0.01 wt %. Table II lists major impurities found by spark-source mass spectrometry in the as-received powder and in a wafer typical of those irradiated.

Figure 3 illustrates the procedure followed in fabricating thulia wafers. This procedure is a standard approach for obtaining high-density ceramic products. As-received powder was reprocessed to obtain a large surface area for sintering as follows. 1) The powder was dissolved in 5M nitric acid at

75-80°C, digested for 1 hr, and then cooled to room temperature. 2) Thulium hydroxide was then precipitated by adding 5M sodium hydroxide. The hydroxide first precipitated at about pH = 3. Stirring was continued for 30 min; then the precipitate was filtered and washed. 3) The dried precipitate was then calcined in air for 1 hr at 750°C to obtain the oxide.

Thermogravimetric analysis of 50 mg of thulium hydroxide indicated that $Tm(OH)_3$ had completely decomposed to form sesquioxide at 700°C. Ten-gram amounts of hydroxide were calcined at several temperatures up to 800°C. 750°C was chosen for all subsequent calcining operations because maximum sintered densities were obtained in wafers from material calcined at this temperature.

The surface area of powder calcined at 750°C was determined to be 22.5 m^2/g using the BET adsorption technique with krypton. If the particles are assumed spherical, the area measured corresponds to particles with an average diameter of 300 A. This powder was agglomerated, but the clusters were broken during pressing.

Five weight percent of a solution of 0.2 wt % of "Carbowax 4000"* in water was added to the calcined oxide as a pressing aid. Specimens of 0.31-in. diameter by 0.1 in. thick were pressed at 10,000 psi in a steel die. Laminations formed in the wafers at pressures >20,000 psi. Pressed wafers were placed on -40 mesh thulium oxide particles on a 99.7 wt % alumina plate for sintering.

The wafers were sintered in either a platinum-rhodium or molybdenum element resistance furnace at 1700°C for 2 hr. Bulk and apparent densities of sintered wafers were determined by using toluene, as an impregnating agent and displacement fluid to determine apparent volumes.

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* Trademark of Union Carbide Corp. for a polyethylene glycol.

(2) Determination of Impurity Effects

Interaction between thulia and aluminum was assessed to establish the temperature limit for the interface between the Tm_2O_3 wafers and the aluminum components of the irradiation assembly. Mixed thulia and aluminum powders were studied by differential thermal analysis up to 1100°C in helium, using a Du Pont 900 DTA instrument. X-ray diffraction analysis was used to identify the reaction products.

The effect of impurities and stoichiometry on the behavior of unirradiated wafers was determined by heating thulia with tantalum. Wafers were heated to 1900°C for 1 hr in contact with an open tantalum support in a flowing helium atmosphere and to 1925°C for 24 hr under helium in a closed tantalum container. Following heating, the impurity content of the test wafers was determined by spark source mass spectrometry. Metallographic and X-ray techniques were used to identify reaction products and the degree of interaction.

(3) Irradiation of Wafers

Thulium-169 sesquioxide wafers were irradiated in Savannah River reactors to produce ^{170}Tm. Wafers of about 0.7-in. diameter and 0.1 in. thick were placed in six aluminum target holders, and irradiated in control rod positions to a power level of about 2 w/g of thulium at discharge. 54 wafers, each weighing approximately 5.5 g, were irradiated.

Thulium sesquioxide wafers were examined before and after irradiation to determine any physical changes. Before irradiation, diameter, thickness, and weight of all wafers were measured, and photomicrographs were made near the center and edges of about 15% of the wafers to determine typical microstructures. The tests were repeated on one-half of the wafers after irradiation.

IV. RESULTS AND DISCUSSION

(1) Fabrication Studies

Thulium sesquioxide was fabricated to densities of 97% of theoretical by reprocessing commercial powders to obtain a readily sinterable powder. Wafers with densities of only 70 to 75% of theoretical were produced by sintering the as-received oxide powder because this powder consisted of large agglomerates that densified slowly. Figure 4 contrasts the highly clustered as-received powder particles with those obtained in reprocessed material calcined at 800°C for 1 hr. Clusters are still apparent in the reprocessed material but these clusters were very friable. The volume occupied by the reprocessed oxide was about five times that of the as-received powders. Particles as small as 100 A were found in the reprocessed material.

Figure 5 shows the effect of calcining temperature upon the final density obtained by sintering pressed wafers for 2 hr at 1700°C. Maximum densities were obtained from material calcined at 750°C. Below 750°C, densities in sintered wafers were low apparently because decomposition was incomplete during sintering. At 800°C, densities were a little lower than at 750°C because increased grain growth and agglomeration subsequently trapped porosity during sintering.

High-density wafers were obtained with reprocessed oxide and sintering temperatures of about 3/4 of the melting temperature. Densities of 95 to 97% of theoretical were obtained on 0.3/in. diameter by 0.1-in. thick wafers sintered in air at 1700°C for 2 hr, but only 90 to 95% of theoretical density was reached at 1650°C for 2 hr. One-in.-diameter wafers were also sintered to 95 to 96% of theoretical at 1725°C for 1 hr.

Typical sintered wafers showed a fine-grained microstructure with an average grain diameter of 5 to 10 microns (Fig. 6). Some wafers, however, did have extensive grain growth during sintering.

This grain growth is believed to be associated with sodium impurities remaining from the reprocessing operation, although this was not shown conclusively.

Silicon was found by spark source mass spectrometric analysis of sintered samples to be present in amounts up to 2 wt % after sintering. This impurity was reduced to about 0.1 wt % by using polyethylene beakers rather than glassware during reprocessing.

While thulia and alumina do react,[13] thulia could be sintered on alumina at temperatures below 1750°C because the reaction is kinetically hindered. High concentrations of aluminum were introduced in wafers sintered directly upon 99.7% alumina setter plates. By placing coarse thulia particles between the wafers and the substrate, the aluminum concentration is kept below approximately 0.01 wt %.

As previously noted, highly volatile impurities were reduced in concentration during sintering. In general, most other impurities remained at about the same levels throughout the process (Table II). Thulia samples may thus be fabricated with a purity of about 99.5%, although the irradiated wafers in this work contained about 1 wt % silicon.

(2) Interaction of Tm_2O_3 with Aluminum Target Components

Reaction between Tm_2O_3 and Al to form thulium-aluminum alloys and Al_2O_3 can be predicted from thermodynamic considerations and by analogy to behavior of other oxide-aluminum systems.

Differential thermal analysis on mixed thulia and aluminum powders in helium showed the onset of exothermic reaction at 585 ±5°C. Continued heating at 10°/min to 1100°C showed little exothermic character, which indicated the reaction was very slow. Subsequent X-ray diffraction analysis showed that unreacted aluminum and thulia predominated with lesser amounts of Al_2O_3 and $TmAl_3$.

Since during irradiation, the Al-Tm_2O_3 interface in reactor target elements is considerably below 585°C, no reaction is expected. The absence of reaction was confirmed in postirradiation tests.

(3) Influence of Target Impurities and Composition

Appreciable quantities of impurities or nonstoichiometry may be introduced into the thulia during reprocessing and subsequent sintering that could cause reaction between the reactor product and its container. An unirradiated thulia wafer, made according to the process outlined above, reacted with an open tantalum support to form $TmTaO_4$ on the tantalum after 1 hr at 1900°C in a flowing helium atmosphere. The tantalate was identified by comparing its X-ray diffraction pattern with those of other rare earth tantalates. The reaction to form $TmTaO_4$ and Tm(g) may proceed when the thulium vapor is removed by the flowing helium.[14]

However, in a helium atmosphere in a closed tantalum container the Tm_2O_3 per se and tantalum did not react after 24 hr at 1925°C. The reaction is presumably suppressed when the equilibrium partial pressure of Tm(g) is rapidly established in the closed system. However, the silicon impurity in the Tm_2O_3 did react with the tantalum. This reaction product was identified by X-ray analysis as Ta_5Si. Figure 7 shows a photomicrograph of the 0.003-in.-thick layer of Ta_5Si. Spectrographic analysis indicated that the silicon concentration of the wafer was reduced by a factor of 10 and that the tantalum concentration had not changed.

A multitude of very small crystals were deposited in the gap between the tantalum and the wafer after the heating in static helium. These crystals, identified as Tm_2O_3 by X-ray diffraction analysis, appeared as transparent single or bicrystals approximately 0.01 cm in length (Fig. 7).

The thulia wafer was reduced during the heating in static helium. After cooling from 1925°C to room temperature in 30 min, the color of the material had changed from tan in the as-sintered condition to a greyish-black, which was uniform throughout the wafer. Reheating a portion of the wafer in air for 10 hr at 1100°C caused regions near the surface to regain a tan color.

The oxygen content of the reduced wafer was determined by inert gas fusion to be 12.05%, corresponding to a composition $Tm_2O_{2.90}$, while that of the partially reoxidized portion was 12.09%. Metallographic examination of the specimen using both bright-field and dark-field illumination indicated the presence of free metal associated with pores or grain boundaries (Fig. 8).

The cubic lattice parameter of the $Tm_2O_{2.90}$ was determined to be 10.489 A, essentially equivalent to that of stoichiometric oxide. The absence of significant variation in the lattice parameter supports the existence of a two-phase reduced product that is apparently formed by precipitating metal on cooling a substoichiometric oxide.

Little, if any, detrimental interaction at elevated temperatures is therefore expected between thulium oxide and refractory metals or alloys. The irradiated thulia wafers probably can be used directly in heat source applications if impurity concentrations in the oxide have been kept sufficiently low.

(4) Irradiation Behavior

Three of the six aluminum target holders were opened and examined after irradiation. A power level of approximately 1.8 w/g for the wafers at reactor discharge was determined by calorimetry.

Visual examination after irradiation showed a thin deposit of aluminum oxide on the thulia wafer surfaces. However, the deposit was readily removed, and the surface finish was not destroyed on those wafers that had been polished for preirradiation studies. Thus, the chemical interaction between the thulia and the aluminum had not occurred. The aluminum oxide coating is believed to have formed because of local heating of the aluminum adjacent to the thulia wafer during postirradiation handling of the target holders in air.

The diameter or thickness of the wafers did not change after irradiation. Small weight changes in some wafers were attributed to chipping or to pickup of surface contamination from the aluminum holders.

Figure 6 shows the microstructure of one of the thulia wafers before and after irradiation. The grain size was the same at the center and at the edge on both unirradiated and irradiated wafers; irradiation did not change the structure.

About two-thirds of the wafers were found broken into two or more pieces when they were removed from the aluminum holders; however, no evidence of microcracking was found in wafers that remained intact. The cause of the breakage is not known, although either mechanical impact during target assembly and disassembly or thermal stresses during irradiation may have contributed to breakage. The aluminum holders were clad with an aluminum jacket swaged into contact with the holders' surfaces. This jacket was broken open to separate individual holders after irradiation. Either operation may have damaged the wafers because of the close tolerances and impact loading. During irradiation, temperature gradients estimated up to 300°C across the wafers may also have produced stresses that contributed to breakage. For future irradiations, target assembly and handling procedures that are suitable for brittle ceramic material have been developed.

The tensile strength of the oxide was determined from diametral compression tests on a few unirradiated specimens. This limited amount of data indicates a tensile strength of 2500 to 4000 psi for five specimens at sample densities of 75 to 80%

of theoretical. A single sample with a density of 96% had a tensile strength of 6140 psi. Similar tests upon three irradiated specimens with densities of 96% of theoretical yielded tensile strengths of 4,240, 4,950, and 7,140 psi. The data are not sufficient to state whether neutron irradiation did reduce the average strength of the thulia wafers. However, deterioration of strength to a point where wafers may not be handled did not occur.

V. Conclusion

Thulium sesquioxide has been shown to be a promising target material for irradiation to produce ^{170}Tm in a form that is probably suitable for direct use in isotopic power sources, without extensive postirradiation processing. The thulia may be fabricated into target wafers up to 97% of theoretical density, and the purity can be controlled to limit interactions in high-temperature applications. Reactor irradiation had no apparent effect on the dimensions or microstructure of the wafers, although some wafers were broken into a few large pieces, probably because of mechanical stresses in target assembly.

Acknowledgment

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Table I. Properties of Thulium Sesquioxide

Power density, w/g of irradiated Tm_2O_3 (corresponds to 13-19% ^{170}Tm in the irradiated fuel form)	2 - 3
Structure	
To 2280°C: Body-centered cubic	a = 10.482 A
2280°C to melting: Hexagonal	a = 3.78 A (estimated from c/a = 1.60[9]) c = 6.04 A
Density, g/cc	8.884
Melting Point, °C	2375 ±25
Heat of formation, kcal/mole, 298°K	-451.4
Vapor Pressure, atm at 2000°K (estimated)	4.2×10^{-9}
$\log_{10} P_T = 7.37 - 31500/T(°K)$	
Linear Thermal Expansion, %	
At 500°C	0.4
1000°C	0.8
1500°C	1.3

Table II. Major Impurities in Thulium Sesquioxide*

	Concentration, wt %	
Element	As-Received Powder	Fabricated Wafer**
W	1.9×10^{-4}	4.3×10^{-4}
Ta	1.9×10^{-4}	1.8×10^{-4}
Yb	1.8×10^{-3}	6.0×10^{-4}
Er	5.2×10^{-2}	5.2×10^{-2}
Si	2.9×10^{-2}	9.5×10^{-1}
Ca	1.4×10^{-2}	1.4×10^{-2}
Ni	3.1×10^{-4}	1.8×10^{-3}
Co	6.0×10^{-5}	6.0×10^{-5}
Fe	1.9×10^{-2}	2.1×10^{-1}
Mn	1.8×10^{-3}	5.5×10^{-4}
Al	9.0×10^{-3}	9.0×10^{-3}
Na	-	2.4×10^{-5}
B	8.5×10^{-5}	4.6×10^{-3}
Cl	1.6×10^{-1}	4.9×10^{-2}
K	3.1×10^{-4}	1.3×10^{-2}

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* Measurements made by spark-source mass spectrometry. All other impurities noted were present in amounts of less than approximately 3×10^{-3}%.

** Total measured impurity content was approximately 1.3%.

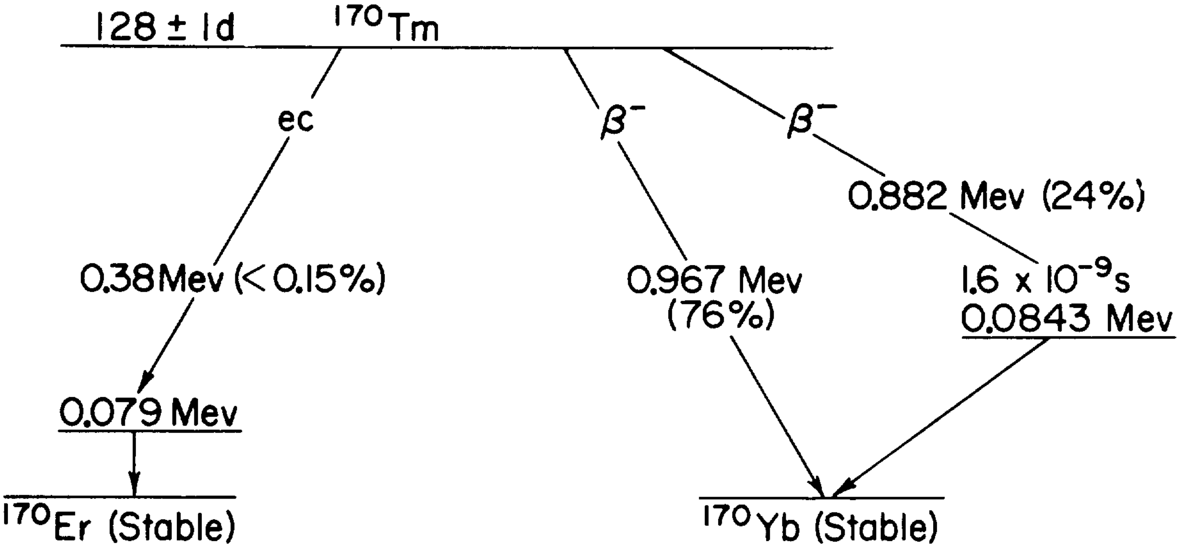


FIG. 1 DECAY SCHEME FOR ^{170}Tm

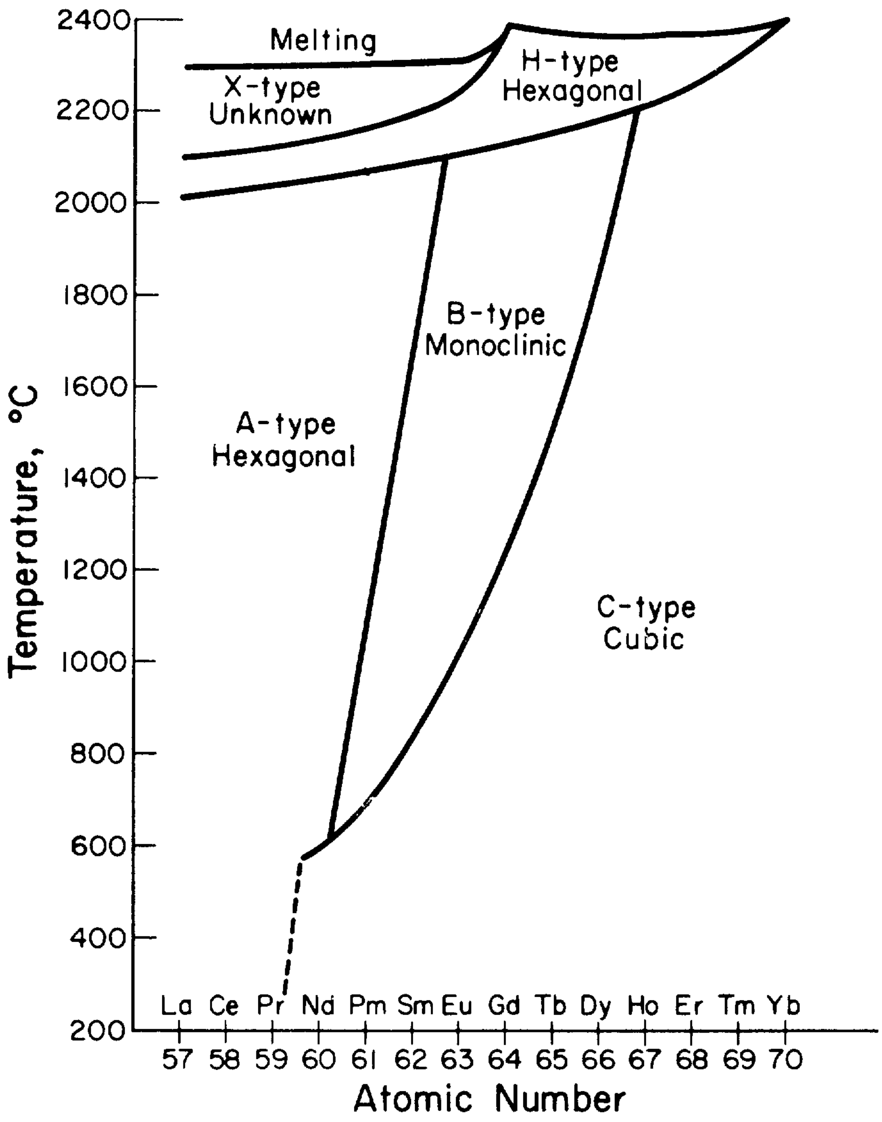


FIG. 2 CRYSTAL STRUCTURE OF RARE EARTH SESQUIOXIDES
(After Föex and Traverse[5])

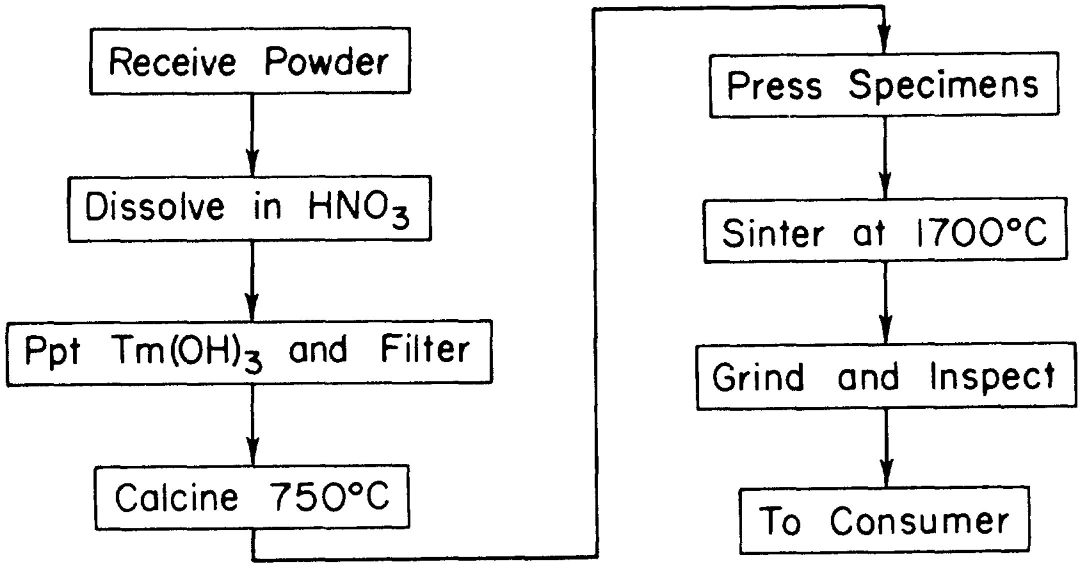
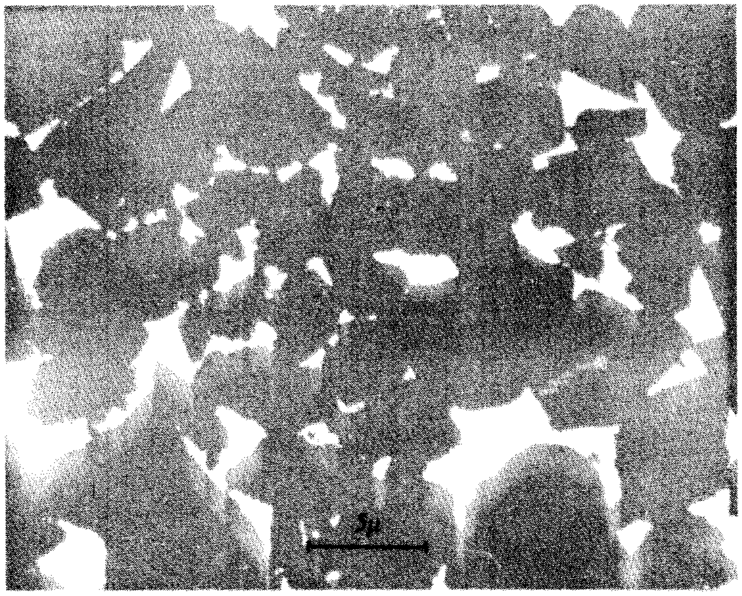
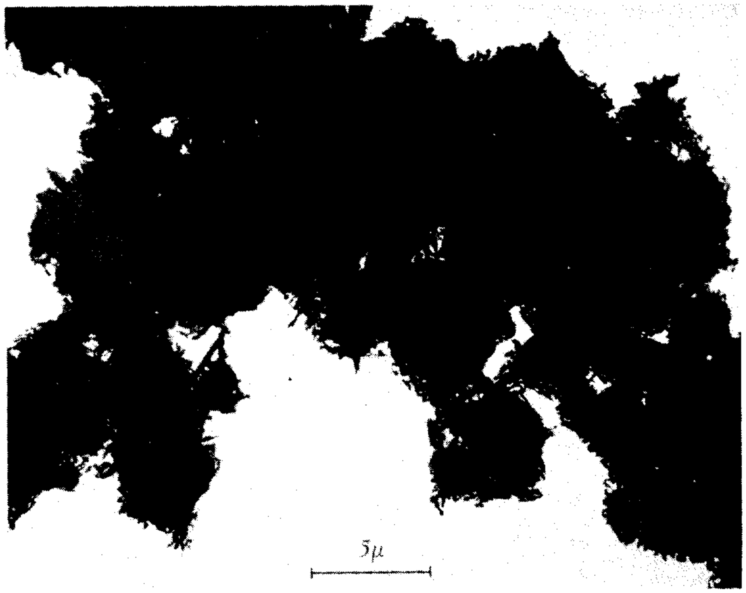


FIG. 3 FLOW CHART FOR THULIUM OXIDE WAFER FABRICATION



As-received Tm_2O_3



Reprocessed and Calcined at 800°C for 1 hr.

FIG. 4 ELECTRON MICROGRAPHS OF THULIUM SESQUIOXIDE POWDERS

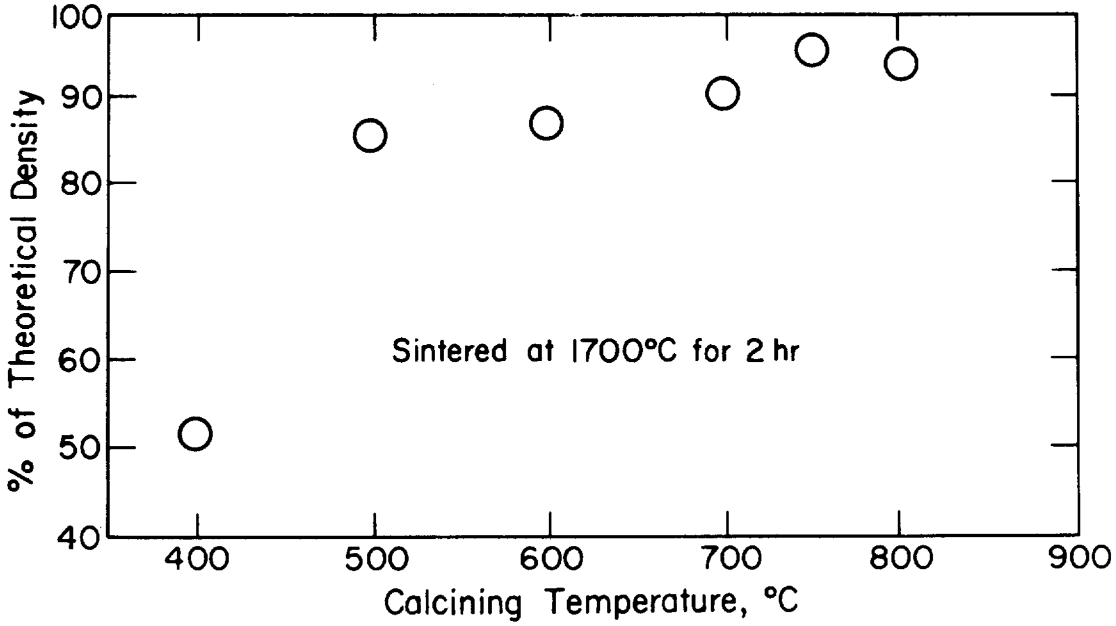
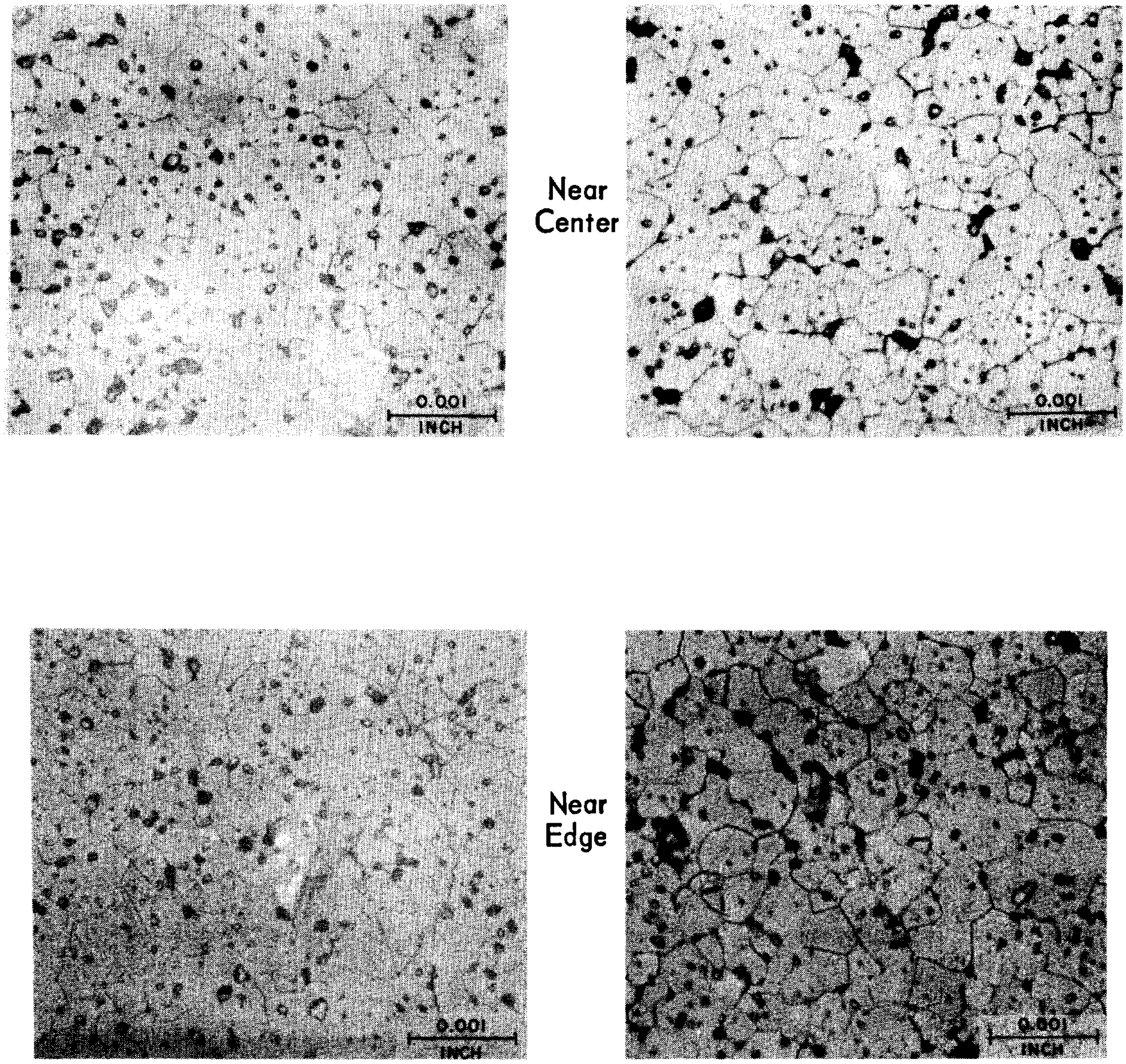


FIG. 5 EFFECT OF CALCINING TEMPERATURE ON SINTERED DENSITY OF THULIUM SESQUIOXIDE



Unirradiated Irradiated

FIG. 6 MICROSTRUCTURE OF Tm_2O_3 SAMPLE

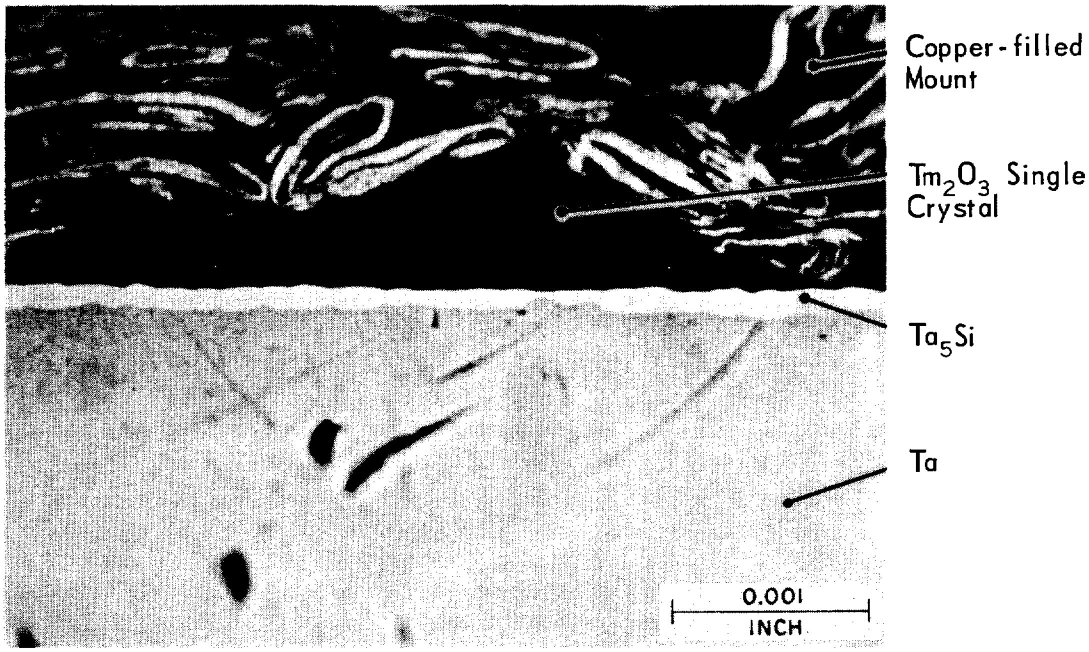
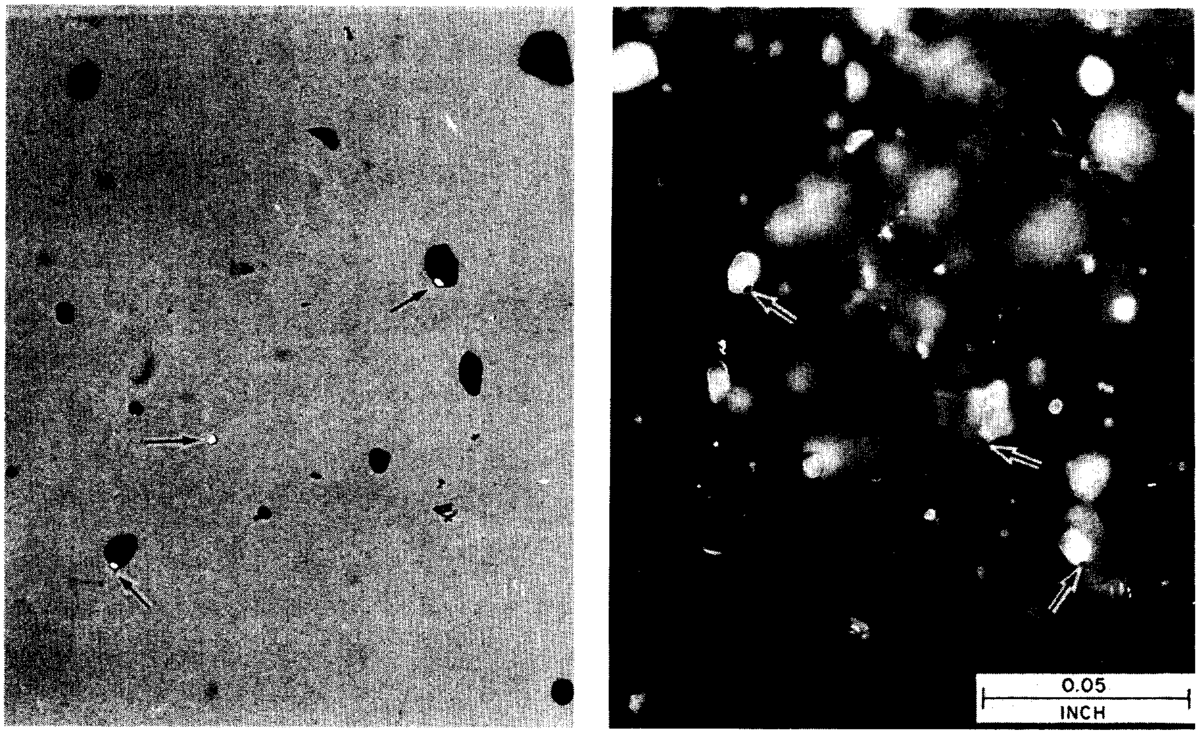


FIG. 7 Ta_5Si LAYER FORMED IN THULIA WAFER



BRIGHT FIELD ILLUMINATION

DARK FIELD ILLUMINATION

FIG. 8 MICROSTRUCTURE OF THULIA WAFER SHOWING FREE METAL AFTER HEATING IN CLOSED TANTALUM CONTAINER