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SNC-3693-5
RADIOISOTOPES AND RADIATION
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THULIUM OXIDE FUEL CHARACTERIZATION STUDY

PART II

ENVIRONMENTAL BEHAVIOR AND MECHANICAL, THERMAL AND CHEMICAL STABILITY ENHANCEMENT

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U.S. ATOMIC ENERGY COMMISSION

CONTRACT NUMBER: AT-(40-1)-3693

DECEMBER 1970

By

SANDERS NUCLEAR CORPORATION
Nashua, New Hampshire

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TABLE OF CONTENTS

Abstract

viii

SECTION 1

Introduction

SECTION 2

Summary

SECTION 3

Fundamental Stability Study

<u>Paragraph</u>		<u>Page</u>
3.1	Objective	3-1
3.2	Experimental	3-1
3.3	Results and Discussion	3-3
3.3.1	100% Tm_2O_3 , 80% $Tm_2O_3/20\%$ Yb_2O_3 , 100% Yb_2O_3 Exposed to Air and Dynamic Vacuum at $1450^{\circ}C$ for 5, 24 and 100 hours	3-3
3.3.2	100% Tm_2O_3 , 80% $Tm_2O_3/20\%$ Yb_2O_3 , 100% Yb_2O_3 Exposed to Static and Dynamic Vacuum at $1750^{\circ}C$ for 5, 24 and 100 hours	3-5
3.3.3	100% Tm_2O_3 , 80% $Tm_2O_3/20\%$ Yb_2O_3 and 100% Yb_2O_3 Exposed to Static and Dynamic Vacuum at $2000^{\circ}C$ for 5, 24 and 100 hours	3-9

TABLE OF CONTENTS (Cont)

Section 4

Mechanical, Thermal, Chemical Stability Enhancement

<u>Paragraph</u>		<u>Page</u>
4.1	Bench Marks	4-2
4.2	Process Variable Optimization	4-12
4.2.1	Effects of Varying Chemical Reprocessing of "As Received" Tm_2O_3	4-14
4.2.2	Effects of Sintering - Time/Temperature/ Atmosphere on Tm_2O_3	4-20
4.2.3	Effects of Aging on Mechanical, Chemical and Thermal Stability	4-28
4.3	Metal Oxide Additives - A Means to Product Stability Enhancement	4-75
4.3.1	Experimental	4-76
4.3.2	Results and Discussion	4-76
4.4	An Assessment of Mechanical, Thermal and Chemical Stability Enhancement	4-90

Section 5

Assessment of Tm_2O_3 as a Potential Heat Source Embodiment

Section 6

References

LIST OF ILLUSTRATIONS

<u>Figure</u>		<u>Page</u>
3-1	Air, 1450°C, 17 hours (100X)	3-6
3-2	Air, 1450°C, 100 hours (100X)	3-7
3-3	Dynamic Vacuum, 1450°C, 100 hours (100X)	3-8
3-4	Static Vacuum, 1750°C, 100 Hours (100X)	3-10

LIST OF ILLUSTRATIONS (Cont)

<u>Figure</u>		<u>Page</u>
3-5	Dynamic Vacuum, 1750°C, 100 hours (100X)	3-11
3-6	Vapor Deposited Crystals on Tungsten Capsule	3-13
3-7	Static Vacuum, 2000°C, 5 hours (100X)	3-14
3-8	Static Vacuum, 2000°C, 24 hours (100X)	3-15
3-9	Static Vacuum, 2000°C, 100 hours (100X)	3-16
3-10	Dynamic Vacuum, 2000°C, 5 hours (100X)	3-18
3-11	Dynamic Vacuum, 2000°C, 24 hours (100X)	3-19
3-12	Dynamic Vacuum, 2000°C, 100 hours (100X)	3-20
4-1	Bench Mark Wafers Sintered 1450°C in Air for 17 hours (200X)	4-5
4-2	100% Tm ₂ O ₃ Wafers Sintered 1450°C in Air for 17 hours (100X)	4-6
4-3	Bench Mark Wafers Sintered in Air 1450°C for 17 hours Fractured Surface (100X)	4-7
4-4	Bench Mark Wafers Aged 500 Hours at 1600°C Then 20 Minute Rise to 2000°C and Shut Down (200X)	4-8
4-5	X-ray Composition and Scan of 80% Tm ₂ O ₃ /20% Yb ₂ O ₃ Wafers Aged at 1600°C for 500 Hours (600X)	4-10
4-6	100% Tm ₂ O ₃ Wafer Aged 1600°C for 500 Hours (100X)	4-11
4-7	100% Tm ₂ O ₃ Bench Mark Aged 500 Hours at 1600°C (500X)	4-13
4-8	Tm ₂ O ₃ Powders Calcined at 950°C	4-19
4-9	Urea Process Tm ₂ O ₃ Wafers, Pressed at 4.5 tsi, Sintered 1750°C, Vacuum (As Polished - 70X)	4-29
4-10	Urea Process Tm ₂ O ₃ Wafers, Pressed at 15 tsi Sintered 1750°C, Vacuum (As Polished - 70X)	4-30
4-11	Urea Process Tm ₂ O ₃ Wafers, Pressed at 29 tsi Sintered 1750°C, Vacuum (As Polished - 70X)	4-31
4-12	Urea Process Tm ₂ O ₃ Wafers, Pressed at 4.5 tsi, Sintered 1750°C, Hydrogen (As Polished - 70X)	4-32
4-13	Urea Process Tm ₂ O ₃ Wafers, Pressed at 15 tsi, Sintered 1750°C, Hydrogen (As Polished - 70X)	4-33
4-14	Urea Process Tm ₂ O ₃ Wafers, Pressed at 29 tsi, Sintered 1750°C, Hydrogen (As Polished - 70X)	4-34

LIST OF ILLUSTRATIONS (Cont)

<u>Figure</u>		<u>Page</u>
4-15	Urea Process Tm_2O_3 Wafers, Pressed at 4.5 tsi Sintered 1750°C, Vacuum (Fractograph 100X)	4-35
4-16	Urea Process Tm_2O_3 Wafers, Pressed at 15 tsi, Sintered 1750°C, Vacuum (Fractograph 100X)	4-36
4-17	Urea Process Tm_2O_3 Wafers, Pressed at 29 tsi, Sintered 1750°C, Vacuum (Fractograph 100X)	4-37
4-18	Urea Process Tm_2O_3 Wafers, Pressed at 4.5 tsi, Sintered 1750°C, Hydrogen (Fractograph 100X)	4-38
4-19	Urea Process Tm_2O_3 Wafers, Pressed at 15 tsi, Sintered 1750°C, Hydrogen (Fractograph 100X)	4-39
4-20	Urea Process Tm_2O_3 Wafers, Pressed at 29 tsi, Sintered 1750°C, Hydrogen (Fractograph 100X)	4-40
4-21	Ammonium Oxalate Process Tm_2O_3 Wafers, Pressed at 4.5 tsi, Sintered 1750°C, Hydrogen (As Polished - 70X)	4-41
4-22	Ammonium Oxalate Process Tm_2O_3 Wafers, Pressed at 15 tsi, Sintered 1750°C, Hydrogen (As Polished - 70X)	4-42
4-23	Ammonium Oxalate Process Tm_2O_3 Wafers, Pressed at 29 tsi, Sintered 1750°C, Hydrogen (As Polished - 70X)	4-43
4-24	Ammonium Oxalate Process Tm_2O_3 Wafers, Pressed at 15 tsi, Sintered 1750°C, Vacuum (As Polished - 70X)	4-44
4-25	Ammonium Oxalate Process Tm_2O_3 Wafers, Pressed at 29 tsi, Sintered 1750°C, Vacuum (As Polished - 70X)	4-45
4-26	Ammonium Oxalate Process Tm_2O_3 Wafers, Pressed at 4.5 tsi, Sintered 1750°C, Vacuum (Fractograph 100X)	4-46
4-27	Ammonium Oxalate Process Tm_2O_3 Wafers, Pressed at 15 tsi, Sintered 1750°C, Vacuum (Fractograph 100X)	4-47
4-28	Ammonium Oxalate Process Tm_2O_3 Wafers, Pressed at 29 tsi, Sintered 1750°C, Vacuum (Fractograph 100X)	4-48
4-29	Ammonium Oxalate Process Tm_2O_3 Wafers, Pressed at 4.5 tsi, Sintered 1750°C, Hydrogen (Fractograph 100X)	4-49

LIST OF ILLUSTRATIONS (Cont)

<u>Figure</u>		<u>Page</u>
4-30	Ammonium Oxalate Process Tm_2O_3 Wafers, Pressed at 15 tsi, Sintered $1750^{\circ}C$, Hydrogen (Fractograph - 100X)	4-50
4-31	Ammonium Oxalate Process Tm_2O_3 Wafers, Pressed at 29 tsi, Sintered $1750^{\circ}C$, Hydrogen (Fractograph - 100X)	4-51
4-32	100% Tm_2O_3 , Pressed at 4.5 tsi, Sintered $1750^{\circ}C$ 8 Hours Vacuum, Aged 500 Hours, $1600^{\circ}C$ (100X)	4-54
4-33	80% Tm_2O_3 /20% Yb_2O_3 , Pressed at 4.5 tsi, Sintered $1750^{\circ}C$, 8 Hours Vacuum, Aged 500 Hours, $1600^{\circ}C$ (100X)	4-55
4-34	100% Tm_2O_3 , Pressed at 4.5 tsi, Sintered $1750^{\circ}C$ 4 Hours, Vacuum, Aged 500 Hours, $1600^{\circ}C$ (100X)	4-56
4-35	100% Tm_2O_3 , Pressed at 29 tsi, Sintered $1750^{\circ}C$ 8 Hours, Vacuum, Aged 500 Hours, $1600^{\circ}C$ (100X)	4-57
4-36	100% Tm_2O_3 , Pressed at 15 tsi, Sintered $1750^{\circ}C$ 6 Hours, Hydrogen, Aged 500 Hours, $1600^{\circ}C$ (100X)	4-58
4-37	100% Tm_2O_3 , Pressed at 29 tsi, Sintered $1750^{\circ}C$ 6 Hours, Hydrogen, Aged 500 Hours, $1600^{\circ}C$ (100X)	4-59
4-38	80% Tm_2O_3 /20% Yb_2O_3 , Pressed at 29 tsi, Sintered $1750^{\circ}C$, 6 Hours, Hydrogen, Aged 500 Hours, $1600^{\circ}C$, (100X)	4-60
4-39	100% Tm_2O_3 , Pressed at 4.5 tsi, Sintered $1750^{\circ}C$, Vacuum, 8 Hours, Aged 500 Hours, $1600^{\circ}C$ (70X)	4-63
4-40	80% Tm_2O_3 /20% Yb_2O_3 Wafers, Pressed at 4.5 tsi, Sintered $1750^{\circ}C$, 8 Hours, Vacuum, Aged 500 Hours $1600^{\circ}C$ (70X)	4-64
4-41	100% Tm_2O_3 , Pressed at 4.5 tsi, Sintered at $1750^{\circ}C$ 4 Hours Vacuum, Aged 500 Hours, $1600^{\circ}C$ (70X)	4-65
4-42	100% Tm_2O_3 , Pressed at 29 tsi, Sintered $1750^{\circ}C$ 8 Hours Vacuum, Aged 500 Hours, $1600^{\circ}C$ (70X)	4-66
4-43	100% Tm_2O_3 , Pressed at 15 tsi, Sintered at $1750^{\circ}C$, 6 Hours Hydrogen, Aged 500 Hours, $1600^{\circ}C$, (20 min) Rise to $2000^{\circ}C$ (70X)	4-67
4-44	100% Tm_2O_3 , Pressed at 29 tsi, Sintered $1750^{\circ}C$, 6 Hours Hydrogen, Aged 500 Hours, $1600^{\circ}C$ (70X)	4-68
4-45	80% Tm_2O_3 /20% Yb_2O_3 Wafers, Pressed at 29 tsi, Sintered $1750^{\circ}C$, 6 Hours Hydrogen, Aged 500 Hours, $1600^{\circ}C$ (70X)	4-69

LIST OF ILLUSTRATIONS (Cont)

<u>Figure</u>		<u>Page</u>
4-46	80% Tm_2O_3 /20% Yb_2O_3 Wafers Aged for 500 Hours at 1600°C Followed by 20 Minute Rise to 2000°C	4-71
4-47	Pressing Pressure vs. % Fines-Sub 10 Micon. Wafers Aged in T-111, TZM and Tungsten for 500 Hours at 1600°C.	4-72
4-48	Tm_2O_3 / Yb_2O_3 + 1% Additive, Melt Samples (300X)	4-78
4-49	Tm_2O_3 and 80% Tm_2O_3 /20% Yb_2O_3 + 1% Additive. Wafers Aged 500 Hours in Tungsten Capsules at 1600°C.	4-79
4-50	100% Tm_2O_3 + 1% Additive Sintered at 1450°C in Air for 17 Hours (100X)	4-80
4-51	Tm_2O_3 Melt Sample Electron Microprobe Composition and Sweep (300X)	4-82
4-52	Tm_2O_3 and 80% Tm_2O_3 /20% Yb_2O_3 + 1% Additive. Wafers Sintered in Air at 1450°C, 17 Hours	4-83

LIST OF TABLES

<u>Table</u>		<u>Page</u>
3-1	Test Matrix for Fundamental Stability Study and Product Post Environmental Exposure Analyses (Matrix Applies to Tm_2O_3 , Tm_2O_3 + 20% Yb_2O_3 , and Yb_2O_3)	3-2
3-2	Experimental Data Summary - Fundamental Study	3-4
3-3	Increase/Decrease (%) in Thickness of 100% Tm_2O_3 , 80% Tm_2O_3 /20% Yb_2O_3 and 100% Yb_2O_3 as a Result of Environmental Exposure	3-22
4-1	Summary of Bench Mark Experimental Data	4-3
4-2	Summary of Conditions for Reprocessing "As Received" Tm_2O_3	4-14
4-3	Conversion Efficiency of Chemical Reprocessing - $Tm_2O_3 \rightarrow Tm_2O_3$ (%)	4-15
4-4	Impurity Levels (ppm) of Iron, Magnesium, Aluminum and Silicon in "As Received", PreCalcined, Calcined 750°C and Calcined 950°C Powders	4-17

LIST OF TABLES (Cont)

<u>Table</u>		<u>Page</u>
4-5	Surface Area of Tm_2O_3 Powders Calcined at $950^{\circ}C$ Determined by BET Nitrogen Absorption Method	4-18
4-6	Bulk - Sintered Densities (gm/cc)	4-18
4-7	Test Matrix to Optimize Production Process Variables as Means to Tm_2O_3 Fuel Form Stability Enhancement	4-22
4-8	Experimental Data Summary - Effects of Sintering - Time/Temperature/Atmosphere on Tm_2O_3	4-23
4-9	Process Conditions Selected for Preparing Wafers for Studying "Effects of Aging on Tm_2O_3 "	4-28
4-10	Experimental Data Summary - Effects of Aging on Mechanical, Thermal and Chemical Stability	4-53
4-11	Grain Size of 100% Tm_2O_3 - 80% Tm_2O_3 /20% Yb_2O_3 Wafers aged in T-111, TZM and Tungsten for 500 hours at $1600^{\circ}C$ followed by 20 minute rise to $2000^{\circ}C$ and Shut Down	4-62
4-12	Melting Points, Valence State of Cations and Atomic Size Relative to Thulium of 3 Metal Oxide Additives	4-75
4-13	Metal Oxide Additives - Experimental Data	4-77
4-14	Net Changes in Levels (ppm) of Aluminum, Iron and Magnesium in 100% Tm_2O_3 and 80% Tm_2O_3 /20% Yb_2O_3 Wafers as a Consequence of Aging for 500 hours at $1600^{\circ}C$ in a Tungsten Capsule	4-87
4-15	Comparison of Bench Mark and Additive Data for Pre and Post Aged 100% Tm_2O_3	4-89

ABSTRACT

A study was performed to develop an understanding of the correlation between fuel form stability and exposure environment (temperature and atmosphere). 100% Tm_2O_3 , 80% Tm_2O_3 /20% Yb_2O_3 and 100% Yb_2O_3 wafers were subjected to air, dynamic vacuum and static vacuum at temperatures to 2000°C for times to 100 hours. Results of these experiments showed the Tm_2O_3 / Yb_2O_3 cubic structure to be unaffected by elemental levels of iron, aluminum, magnesium and silicon and unaffected by the environmental conditions imposed on the wafers.

A second task emphasised the optimization of the thermal, mechanical and chemical stability of Tm_2O_3 fuel forms. Enhancement was sought through process variable optimization and the addition of metal oxides to Tm_2O_3 . Process variables studied were chemical processing of "as received" Tm_2O_3 , calcining temperature, cold pressing pressure, sintering time/temperature/atmosphere and aging. Properties assessed were physical appearance, microstructure, crystalline structure, grain size, lattice parameter, density, chemical purity as they affect "fines" generation upon impact. Results showed the properties of Tm_2O_3 to be primarily sensitive to temperature. 1750°C was selected as the optimum sintering temperature/time. Enhancement of resistance to fines generation was indicated in post-aged samples.

Three metal oxide additives CaO , TiO_2 and Al_2O_3 were studied with the objective of forming a grain boundary precipitate to control fines generation. The presence of 1% additive was inadequate to depress the melting point of Tm_2O_3 or to change the cubic crystalline

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structure of $\text{Tm}_2\text{O}_3/\text{Yb}_2\text{O}_3$. $\text{Tm}_2\text{O}_3/\text{Yb}_2\text{O}_3$ wafers containing CaO developed a grain boundary phase that improved the resistance to fines generation. The presence of Yb_2O_3 did not appear to measurably influence behavior.

SECTION 1

INTRODUCTION

A fuel should exhibit mechanical, thermal and chemical stability in normal and accidental environments for time periods consistent with compatibility of containment material and mission duration. The safety design requirements of the fuel vary and depend on whether the application is terrestrial or extraterrestrial. The design specifications on fuel stability for space systems are more stringent because the severity of conditions that space missions can encounter during launch, orbit, reentry and impact are greater than those ordinarily encountered in terrestrial applications. In either case, the first line of defense against potential accident is the fuel form.

The object of this phase of study was a continuation of the thulium oxide fuel characterization study. Primary emphasis was placed on optimization of the thermal, mechanical and chemical stability of thulia fuel forms with respect to operational and safety criteria; this included developing an understanding of the thulium-ytterbium-additive-oxygen systems. Three specific tasks were established to perform the study.

- Material Compatibility Testing
- Fundamental Stability
- Mechanical, Thermal and Chemical Stability Study

Results of the materials compatibility testing portion performed under this phase have been included with the prior materials compatibility data and may be found in Part I of this report.

The object of the fundamental study was the development of an understanding of the correlation between fuel form stability and exposure environment (temperature and atmosphere). Samples with compositions of 100% Tm_2O_3 , 80% Tm_2O_3 /20% Yb_2O_3 and 100% Yb_2O_3 were subjected to three different environments (air, dynamic vacuum and static vacuum) at three temperatures (1450, 1750 and 2000°C) for times to 100 hours. An assessment of stability was obtained from analyses of x-ray diffraction data, microscopic examination of wafers and chemical analysis of selected samples. The chemical analysis also served as a measure of impurity control.

Stability in this study was understood to mean an absence of change in the properties of the test specimen when compared to the reference samples (bench marks). Changes were measured from analysis of data obtained from atomic absorption analysis, x-ray diffraction and metallographic observations. The process used for preparing the test specimens was selected on the basis of preliminary observations of the process variable optimization study⁽¹⁾. The environments to which the test coupons were exposed were representative of those to be encountered operationally. Although the times and temperatures do not encompass the most extreme conditions envisionable, they were sufficiently broad to induce changes in the Tm_2O_3 wafer. The results and discussion of this work are presented in Section 3.

The object of the mechanical, thermal and chemical stability study task was to assess improvement of mechanical, thermal and chemical stability of Tm_2O_3 through:

- Process Variable Optimization
- Selective Addition of Metal Oxides

In each task, Tm_2O_3 wafers produced were subjected to visual examination, x-ray diffraction, metallography and chemical and fines analysis to obtain the following data points:

- Density
- Purity
- Lattice parameter
- Grain size
- "Fines" generated

These data points were obtained in each study from both "as sintered" and "aged" wafers. The aging process consisted of exposing wafers encapsulated in tungsten, T-111 and TZM to static vacuum at 1600°C for 500 hours. This was followed by a twenty minute rise time to 2000°C and a three hour cool period to room temperature.

Stability enhancement was considered to be an improvement in any of the properties of Tm_2O_3 directly related to the data points obtained, providing that enhancement in one domain did not produce an unacceptable change in another, e.g., that an increase in grain size did not indirectly result in an increase in generation of fines in the respirable range.

The object of the Process Variable Optimization subtask was to observe the effects on wafer stability when varying several process parameters. These parameters were: precipitating agent used in processing "as received" Tm_2O_3 , calcining temperature, surface area of calcined powder, method of binder addition, impurity levels of calcined powder, pressing pressure, sintering time, temperature and atmosphere. Ultimately, 54 sets of process variables were evaluated with 5 sets selected for further testing. Selection of the final process from these five sets was based on "fines" generation only. In light of the test matrix established, this process was considered to produce the most stable Tm_2O_3 wafer and was used to produce 30 specimens for further testing by AEC.

The object of the Metal Oxide Additives task was also to measure enhancement of mechanical, thermal and chemical stability, but through the addition of a metal oxide to Tm_2O_3 powder prior to pressing and sintering, rather than through the variation of

several process parameters. The term mechanical strength in this task was interpreted in a different context, and influenced the experimental design and analysis.

Rather than using metal oxide additives that would be soluble in the $\text{Tm}_2\text{O}_3/\text{Yb}_2\text{O}_3$ matrix and hopefully improve stability by complement, additives were carefully selected whose properties ensured a high degree of insolubility, preferably precipitating at grain boundaries. The presence of a grain boundary phase would provide a means to absorb the energy created by impact of the fuel that would otherwise promote transgranular cracking. In addition, the additive might be instrumental in controlling grain size such that population distribution of fines generated on impact would find the majority of particles equal to or larger than the grain size and fines (particles < 10 microns) much reduced. Such a result would provide a greater safety margin to the designer planning space missions.

Section 4 discusses the basis for selection of additives and the results of the studies.

SECTION 2

SUMMARY

The object of the study was a continuation of the thulium oxide fuel characterization study begun in Phases I and II. Primary emphasis was placed on optimization of the thermal, mechanical, and chemical stability of thulia fuel forms with respect to operational and safety criteria; this included developing an understanding of the thulium - ytterbium - additive - oxygen systems. Three specific tasks were established to perform the study.

- Material Compatibility Testing
- Fundamental Stability
- Mechanical, Thermal and Chemical Stability Study

Results of the materials compatibility testing portion performed under this phase have been included with the prior materials compatibility data and may be found in Phase I of this report.

FUNDAMENTAL STABILITY

100% Tm_2O_3 , 80% Tm_2O_3 /20% Yb_2O_3 and 100% Yb_2O_3 wafers were exposed to air, dynamic vacuum and static vacuum (tungsten capsules) at temperatures to 2000°C for times to 100 hours. The stability of the Tm_2O_3 - Yb_2O_3 cubic structure was unaffected by the elemental levels of iron, aluminum, silicon and magnesium present in the wafers and unaffected by the environmental conditions imposed on the wafers. Vapor phase mass transport was observed in static vacuum tests for all three compositions. Dimensional swelling developed in several wafers including 100% Tm_2O_3 and may be a potential problem because the behavioral pattern is not known.

MECHANICAL, THERMAL AND CHEMICAL STABILITY ENHANCEMENT

Enhancement of the mechanical, thermal and chemical stability of Tm_2O_3 was sought as the end product of

- Process Variable Optimization
- Selective Addition of Metal Oxides

Enhancement was defined as improvement in the properties of the end products of process variable optimization and selective addition of metal oxides when compared with bench mark properties. Properties investigated were:

- Physical Appearance
- Crystalline Structure and Lattice Parameter
- Grain Size
- Microstructural Appearance
- Sintered Density
- Chemical Purity
- Impact Resistance to Fines Generation

Tm_2O_3 was exposed to the following process variables:

- Chemical Processing
- Calcining Temperature
- Pressing Pressure
- Sintering Time/Temperature/Atmosphere
- Aging
- Metal Oxide Additives

Enhancement was assessed from macroscopic, microscopic, x-ray diffraction, electron microprobe, chemical and impact-particle sizing analyses; density, grain size, surface area and lattice parameter measurements.

Process Variable Optimization

Four methods of chemical processing evaluated with respect to conversion efficiency, purity and surface area of product and bulk sintered density of Tm_2O_3 wafers prepared from these powders provided two final chemical processes for continued study. The

two processes selected were: (1) a homogeneous precipitation method utilizing urea as a precipitating agent, and (2) a heterogeneous precipitation method utilizing ammonium oxalate as a precipitating agent. Conversion efficiencies (oxide to oxide) on batches utilizing 500 gm of starting oxide were consistently an acceptable 90% or better. Wafers prepared from powders produced from these two processes achieved sintered densities to 90% theoretical.

54 sets of processing conditions including these two methods of processing "as received" Tm_2O_3 were analyzed with respect to cold pressing of wafers at 4.5, 15 and 29 tsi and sintering at 1450°C and 1750°C for times to 32 hours in air, vacuum and hydrogen. Results showed the cubic Tm_2O_3 crystalline structure to be insensitive to this broad processing matrix, thereby providing flexibility in selection of fabrication conditions.

Chemical processing, pressing pressure, sintering, atmosphere and time were a secondary influence on levels of impurity, sintered density, grain size and "fines" generation. The major influence on these properties was temperature. 1750°C was selected as the optimum temperature for sintering Tm_2O_3 wafers. At this temperature, bulk sintered densities of 95% of theoretical or better were achievable with many sets of process conditions and populations of particles of less than 149 microns in size were as low as 0.2% of total weight. Five sets of process conditions representing the optimum with respect to sintered density and small particle generation were selected from several possible sets for studying the effects of aging. The processes were:

- Ammonium oxalate - $*1750^\circ\text{C}$, 29 tsi, 6 hours, hydrogen
- Ammonium oxalate - 1750°C , 29 tsi, 8 hours, vacuum
- Ammonium oxalate - 1750°C , 15 tsi, 6 hours, hydrogen
- Ammonium oxalate - 1750°C , 4.5 tsi, 4 hours, vacuum
- Urea - $*1750^\circ\text{C}$, 4.5 tsi, 8 hours, vacuum

*Selected for preparing 80% Tm_2O_3 /20% Yb_2O_3 wafers.

Wafers prepared by these processes were encapsulated in TZM, T-111 and tungsten, aged for 500 hours at 1600°C and given a thermal

spike to 2000°C over a 20 minute period. Evidence of vapor phase mass transport was observed in all capsules. The absence of infused elements related to the metal matrix and of evidence of chemical reaction with the encapsulant support the excellent chemical stability of Tm_2O_3 . Impact resistance of aged wafers as measured by fines generated was superior to preaged wafers. Within the test matrix, particles of < 10 micron size were as low as 0.04% of total weight. Populations of particles in this size range were observed to correlate with initial pressing pressure. It was concluded that $\text{Tm}_2\text{O}_3/\text{Yb}_2\text{O}_3$ has excellent thermal, chemical and mechanical stability when exposed to nominal operational mission conditions and that resistance to fines generation was enhanced by the aging process.

Metal Oxide Additives - A Means To Product Stability Enhancement

Stability enhancement was interpreted in this study as an enhancement of resistance to fines generation through the use of additives. Criteria for selection of metal oxide additives were established to provide the greatest potential for grain boundary precipitation of the additive thereby encouraging fracture to follow grain boundaries rather than propagating through the grains. Atomic size, valence state of cation, melting point, additive concentration and radiation contribution were the criteria evaluated. Calcium oxide (CaO), aluminum oxide (Al_2O_3) and titanium dioxide (TiO_2) were selected.

The behavior of three additive metal oxides suggest the correctness of the original selection criteria as each additive proved to be insoluble in the $\text{Tm}_2\text{O}_3/\text{Yb}_2\text{O}_3$ matrix and did not effect the crystalline structure or melting point of $\text{Tm}_2\text{O}_3/\text{Yb}_2\text{O}_3$. The original rationale, the presence of a grain boundary phase that would provide an alternate means of dissipating the kinetic energy of impact so as to reduce transgranular cracking, was also successfully achieved by means of CaO addition. This additive produced a grain boundary phase that reduced the particle population in the 10 - 149 μ range and proved to be a sintering aid as well.

Comparison of additives with bench marks suggested that mechanical stability was improved to some degree with additives and

offered potentially greater enhancement in the case of calcium oxide. The presence of Yb_2O_3 did not appear to influence behavior in any measurable way.

Tm_2O_3 possesses excellent thermal, chemical and mechanical stability by virtue of the insensitivity of the cubic structure to environmental conditions, process variables, compatibility couples and the presence of Yb_2O_3 . Availability of raw material, ease and reproducibility of fabrication, and activation provide a means to achieve a relatively low cost fuel. Excellent containment, characteristics chemical inertness and thermal stability provide a high margin of safety for operational applications and recommend Tm_2O_3 as the fuel form of choice for short term mission applications.

SECTION 3

FUNDAMENTAL STABILITY STUDY

3.1 OBJECTIVE

The objective of the fundamental stability study was to develop an understanding of the correlation between fuel form stability and exposure environment (temperature and atmosphere). Samples were prepared and analyzed to determine the possible loss of oxygen as a function of time, temperature and atmosphere (air, static vacuum and dynamic vacuum) and to assess the effects of such oxygen loss on the structure of $\text{Tm}_2\text{O}_3 - \text{Yb}_2\text{O}_3$. Controls were used to establish reference properties. The test matrix appears in Table 3-1.

The impurity contents of samples were measured before and after testing to determine the effects of impurity content and to measure possible contamination during test. Impurity contents were determined by atomic absorption spectrophotometry techniques. Specifically, iron, aluminum, magnesium and silicon levels and changes thereof were determined.

The oxygen content of the samples was to be measured before and after testing by means of an inert gas analyzer. The possible effects of oxygen loss on the structure of the $\text{Tm}_2\text{O}_3\text{-Yb}_2\text{O}_3$ were determined by x-ray diffraction. Metallographic analyses were used to determine the morphology of possible new phases and other effects such as porosity and microcracking.

3.2 EXPERIMENTAL

Samples consisted of wafers approximately 0.6 inch in diameter and approximately 0.06 inch thick. Wafers were fabricated from

TABLE 3-1.

TEST MATRIX FOR FUNDAMENTAL STABILITY STUDY AND PRODUCT
POST ENVIRONMENTAL EXPOSURE ANALYSES

(MATRIX APPLIES TO Tm_2O_3 , $\text{Tm}_2\text{O}_3 + 20\% \text{Yb}_2\text{O}_3$, and Yb_2O_3)

	1450°C			1750°C			2000°C			
	5 hr	24 hr	100 hr	5 hr	24 hr	100 hr	5 hr	24 hr	100 hr	Control
<u>Testing Atmosphere</u>										
Air	x*	x	x							
Dynamic Vacuum	x	x	x	x	x	x	x	x	x	
Static Vacuum				x	x	x	x	x	x	
<u>Analyses</u>										
1. Purity (Emission Spectroscopy or AA)			x	x		x	x		x	x
2. Metal/Oxygen Ratio	x	x	x	x	x	x	x	x	x	x
3. Phase Determination, morphology, porosity and micro-structure										
a. X-ray diffraction			x			x	x	x	x	x
b. Metallography			x			x	x	x	x	x

*x-indicates samples exposed and/or analysed under conditions specified

"as received" Tm_2O_3 and Yb_2O_3 powder reprocessed using the urea precipitation method developed in another phase of this work (see Section 4.2 of this report) and subsequently calcined at 950°C . Mixed oxide powder was prepared by mixing appropriate amounts of Tm_2O_3 and Yb_2O_3 prior to the addition of 4% Carbowax 4000* as binder. Powders were pressed at 29 tsi and sintered in air at 1450°C for 17 hours subsequent to binder burn off treatment at 325°C . Bulk sintered densities were obtained by weighing each sample and calculating the volume from micrometer measurements. A control representative of each composition was retained for reference.

Prior to environmental exposure, wafers to experience a static vacuum environment were placed in tungsten capsules and sealed by electron beam welding. All capsules were leaked checked for integrity of the weldment prior to test.

The oxygen content of wafers was measured by inert gas analyser techniques. The data obtained on test specimens as well as that on the standards were not reproducible and therefore were not included in this study.

3.3 RESULTS AND DISCUSSION

A summary of the experimental data may be found in Table 3.2. A simple numerical code was used to denote the degree of change in appearance of the samples; the key is given below.

1. No change
2. Minor change
3. Major change

3.3.1 100% Tm_2O_3 , 80% Tm_2O_3 /20% Yb_2O_3 , 100% Yb_2O_3 EXPOSED TO AIR AND DYNAMIC VACUUM AT 1450°C FOR 5, 24 and 100 HOURS

Wafers of both compositions exposed to air were off-white in color. 100% Tm_2O_3 and 80% Tm_2O_3 /20% Yb_2O_3 in vacuum were pale green. Vacuum treated wafers exhibited somewhat more shrinkage, primarily diametric shrinkage than those exposed to air and as a result, the

*Carbowax 4000 is a registered trademark of the Union Carbide Corporation.

Table 3-2
Experimental Data Summary - Fundamental Study

EXPOSURE TIME 5 HOURS				24 HOURS				100 HOURS				CONTROL				100 HOURS							
Env. Cond/Composition	Lattice param. (Å)	Elemental Level (ppm)				Lattice param (Å)		Lattice param (Å)	Elemental Level (ppm)				Lattice param (Å)	Elemental Level (ppm)				Density	Color Change		Cracking	Transparency	
		Fe	Al	Si	Mg				Fe	Al	Si	Mg		Fe	Al	Si	Mg						
Control																							
Tm ₂ O ₃								10.48	23	33	230	1.6	7.8 ± 0.1	1				2			1		
Tm ₂ O ₃ + 20% Yb ₂ O ₃								10.46	25	33	200	2.0	7.8 ± 0.2	1				2			1		
Yb ₂ O ₃								10.42	45	25	200	2.0	8.3 ± 0.1	1				2			1		
1450°C (air)																							
Tm ₂ O ₃								10.47	31	33	220	3.7							1		2		1
Tm ₂ O ₃ + 20% Yb ₂ O ₃								10.46	47	48	70	2.2							1		2		1
Yb ₂ O ₃								10.42	55	40	200	3.1							1		2		1
1450°C (dynamic vac).																							
Tm ₂ O ₃								10.48	33	40	240	2.4							2		2		1
Tm ₂ O ₃ + 20% Yb ₂ O ₃								10.46	31	55	390	1.8							2		2		1
Yb ₂ O ₃								10.42	27	33	230	1.9							1		2		1
1750°C (dynamic vac).																							
Tm ₂ O ₃		44	40	140	1.4			10.48	33	33	120	0.9							2		2		2
Tm ₂ O ₃ + 20% Yb ₂ O ₃		26	33	390	1.5			10.47	16	40	370	1.3							2		2		2
Yb ₂ O ₃		27	48	40	2.2			10.41	10	28	90	1.1							1		2		2
1750°C (static vac)																							
Tm ₂ O ₃		31	28	240	1.9			10.47	28	52	60	2.7							2		2		2
Tm ₂ O ₃ + 20% Yb ₂ O ₃		29	78	390	4.0			10.46	26	60	390	3.0							2		2		2
Yb ₂ O ₃		44	48	250	2.2			10.42	16	33	260	4.7							1		2		1
2000°C (dyanmic vac).																							
Tm ₂ O ₃	10.48	24	33	170	1.1	10.47		10.47	32	44	260	1.7							2		1		1
Tm ₂ O ₃ + 20% Yb ₂ O ₃	10.48	26	83	520	0.15	10.47		10.47	14	38	260	2.1							2		2		2
Yb ₂ O ₃	10.43	10	28	120	1.2	10.42																	
2000°C (static vac)																							
Tm ₂ O ₃	10.47	16	60	230	2.0	10.47		10.47	17	39	210	2.4							2		2		2
Tm ₂ O ₃ + 20% Yb ₂ O ₃	10.46	15	28	300	4.3	10.46		10.47	20	39	160	4.9							3		2		2
Yb ₂ O ₃	10.43	15	40	350	3.0	10.41		10.43	16	18	160	4.1							3		3		2

final bulk sintered densities were slightly higher for comparable test times. The impurity levels after the 100 hours exposure were not significantly different from the controls except a slight decrease in iron level in the 100% Yb_2O_3 sample treated in vacuum. The silicon levels throughout these experiments were many times higher (by two orders of magnitude) than the controls levels and very erratic. This was attributed to the method of sample preparation required to dissolve the sample; it was necessary to grind extensively and subsequently treat with strong nitric acid for many hours. For this reason, silicon data points would not be considered meaningful although silicon levels might be a factor.

X-ray diffraction patterns were typically those of the controls; no change in the lattice parameters as calculated from these patterns was observed.

Metallographic examination of the 100 hour exposure test specimens showed varying degrees of cracking that was typical of high pressure - cold pressing methods. The micro-structure appeared similar to the controls, with the exception of the 100% Yb_2O_3 sample exposed in air, in which a different porosity behavior was noted from the control. All samples appeared to have a fine grained texture. Figures 3-1, 3-2 and 3-3 are micrographs of the controls and 1450°C treated specimens.

3.3.2 100% Tm_2O_3 , 80% Tm_2O_3 /20% Yb_2O_3 , 100% Yb_2O_3 EXPOSED TO STATIC AND DYNAMIC VACUUM AT 1750°C FOR 5, 24 and 100 HOURS

Static Vacuum

100% Tm_2O_3 and 80% Tm_2O_3 /20% Yb_2O_3 wafers treated in a static environment were pale green, while 100% Yb_2O_3 wafers were white. Some areas of enhanced translucency were observed primarily at edges and cracks. No bonding of the ceramic to the encapsulant was observed, however, a very small amount of vapor deposited crystals on the tungsten surface was noted in each composition. The wafers were all intact, but laminations were present at the edges.

X-ray diffraction patterns were again typically those of the controls; the same being true for lattice parameters calculated for the x-ray data. The iron content increased for 100% Tm_2O_3 but

A. 100% Tm_2O_3

B. 80% Tm_2O_3 /20% Yb_2O_3

C. 100% Yb_2O_3

Figure 3-1 Air, 1450°C , 17 Hours (100X).

A. 100% Tm_2O_3

B. 80% Tm_2O_3 /20% Yb_2O_3

C. 100% Yb_2O_3

Figure 3-2 Air, 1450°C, 100 Hours (100X).

A. 100% Tm_2O_3

B. 80% Tm_2O_3 /20% Yb_2O_3

C. 100% Yb_2O_3

Figure 3-3 Dynamic Vacuum, 1450°C , 100 Hours (100X).

decreased for 100% Yb_2O_3 in each comparative time frame. Net changes in magnesium and aluminum content were generally small and erratic.

Figures 3-4 a, b, and c show the microstructure of wafers treated for 100 hours. Appearance of individual grains, in all compositions, attested to additional grain growth at this time-temperature condition over that observed at 1450°C . 80% Tm_2O_3 /20% Yb_2O_3 and 100% Yb_2O_3 wafers contained large voids that caused some swelling, otherwise, high degree of density was observed. The surfaces were irregular and showed evidence of behavior of selective surfaces vaporization. Enhanced translucency at surface and laminar crack areas was again observed. Laminations were extensive in 100% Yb_2O_3 wafers. No insoluble phases were observed.

Dynamic Vacuum

The observations noted above for static vacuum apply equally well to the dynamic vacuum environment with some exceptions. The microstructure did not exhibit the same population of individual transparent grains observed in the static vacuum environment (Figure 3-5 a, b, and c). 100% Tm_2O_3 (Figure 3-5 a) shows very few of these grains, but yet the material appears very dense. No insoluble phases were observed and the diffraction patterns were the same as the controls.

The surface of the 100% Yb_2O_3 wafer was very irregular and characteristic of vaporization. The thickness had been reduced and after 100 hours, approximately a 30% weight reduction had resulted.

3.3.3 100% Tm_2O_3 , 80% Tm_2O_3 /20% Yb_2O_3 AND 100% Yb_2O_3 EXPOSED TO STATIC AND DYNAMIC VACUUM AT 2000°C FOR 5, 24 AND 100 HOURS

Static Vacuum

Wafers exposed in a static vacuum environment were not broken during test, nor did the ceramic bond to the metal capsule. Three had changed color; the 100% Tm_2O_3 wafer was black after 5 hours exposure and the 80% Tm_2O_3 /20% Yb_2O_3 and 100% Yb_2O_3 wafers were purple after 100 hours. Vapor deposited crystals were observed

A. 100% Tm_2O_3

B. 80% Tm_2O_3 /20% Yb_2O_3

C. 100% Yb_2O_3

Figure 3-4 Static Vacuum, 1750°C , 100 Hours (100X).

Figure 3-5 Dynamic Vacuum, 1750 C, 100 Hours (100X).

in each specimen capsule at 100 hours increasing in quantity with ytterbium content. The 100% Yb_2O_3 wafer gave up approximately 50% of its mass in this manner (Figure 3-6). Laminations were observed in all wafers, but were more severe for the 100% Yb_2O_3 .

Elemental levels of iron decreased with differences in loss being a function of increasing ytterbium content. Changes in levels of aluminum and magnesium were insensitive to environment. X-ray diffraction patterns obtained on wafers were typical of the controls. Lattice parameters calculated from the patterns were also in good agreement with control values. In the case of 100% Yb_2O_3 , the x-ray pattern of the crystals deposited on the tungsten was not that of Yb_2O_3 and was not identified. X-ray patterns of crystals deposited in the 100% Tm_2O_3 and 80% Tm_2O_3 /20% Yb_2O_3 cases were not obtained because of insufficient material.

The microstructures of wafer specimens are shown in Figures 3-7 to 3-9. Considerable increase in grain size was observed at 2000°C with some grain boundary definition appearing. Particularly, large growth was observed in the 80% Tm_2O_3 /20% Yb_2O_3 wafer where some grains were 700 microns in size after 100 hours. Translucency was generally enhanced throughout, the bodies becoming transparent in many areas. The bodies appeared to be quite dense. No insoluble phases were observed. The surface of the 100% Yb_2O_3 sample (Figure 3-9) shows the effect of selective vaporization.

Dynamic Vacuum

Wafers exposed to dynamic vacuum for 5, 24 and 100 hours did not change color. Laminations could be observed macroscopically particularly with the 100% Yb_2O_3 wafers. The wafers were intact with the exception of the 100 hour - 100% Yb_2O_3 wafer which had completely vaporized. The surfaces were irregular and swelling was again observed in wafers containing Yb_2O_3 at 5 and 24 hours. (See Table 3-3).

Iron levels were essentially the same as those reported for 1750°C dynamic vacuum and had the same behavioral pattern. The net changes for aluminum and magnesium were again without apparent

Figure 3-6 Vapor Deposited Crystals on Tungsten Capsules From
100% Tm_2O_3 Wafer.

A. 100% Tm_2O_3

B. 80% Tm_2O_3 /20% Yb_2O_3

C. 100% Yb_2O_3

Figure 3-7 Static Vacuum, 2000°C, 5 Hours (100X).

A. 100% Tm_2O_3

B. 80% Tm_2O_3 /20% Yb_2O_3

C. 100% Yb_2O_3

Figure 3-8 Static Vacuum, 2000°C , 24 Hours (100X).

A. 100% Tm_2O_3

B. 80% Tm_2O_3 /20% Yb_2O_3

C. 100% Yb_2O_3

Figure 3-9 Static Vacuum, 2000°C, 100 Hours (100X).

pattern. X-ray diffraction patterns were obtained on all but the missing wafer. Patterns were typical of controls except for a new line appearing in the 100% Tm_2O_3 samples exposed for 5 and 24 hours. No change in lattice parameter was found in those samples analyzed.

Microscopically, the grain sizes in these samples were smaller than those observed in static vacuum, but larger than their 1750°C analogs. No insoluble phases were observed. Again, clear evidence of vaporization can be seen from the surfaces of the wafers particularly at 5, 24 and 100 hours (Figures 3-10 to 3-12). Samples are quite translucent overall, with some areas being quite transparent.

Conclusions

Initial powders were obtained by a homogeneous precipitation process that provides some purification of the "as received" Tm_2O_3 and Yb_2O_3 . The changes in levels of the four principle elements were measured against control specimens sintered in air at 1450°C for 17 hours. Only iron changed with any degree of order. Increases in iron in 100% Tm_2O_3 were seen in all but the 2000°C static vacuum exposure. In comparative time frames, the absolute iron level decreased as ytterbium concentration increased. The significance of this behavior and the possible implications that the presence of iron may have was not known. However, the Tm_2O_3 - Yb_2O_3 cubic structure was stable where these levels of "impurity" were present.

The laminations frequently observed were also present in the control wafers and were due to the high pressure - cold pressing conditions used in preparing the test specimens. In several instances, particularly at the higher temperatures, these laminations had begun to heal.

X-ray diffraction patterns were typical of the controls except in the 100% Tm_2O_3 wafers exposed to a static vacuum at 2000°C for 5 and 24 hours. A new line observed in the diffraction pattern of this sample suggested the presence of some other

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A. Tm_2O_3

B. 80% Tm_2O_3 /20% Yb_2O_3

C. 100% Yb_2O_3

Figure 3-10 Dynamic Vacuum, 2000°C , 5 Hours (100X).

A. 100% Tm_2O_3

B. 80% Tm_2O_3 /20% Yb_2O_3

C. 100% Yb_2O_3

Figure 3-11 Dynamic Vacuum, 2000°C , 24 Hours (100X).

A. 100% Tm_2O_3

B. 80% Tm_2O_3 /20% Yb_2O_3

Figure 3-12 Dynamic Vacuum, 2000°C , 100 Hours (100X).

crystalline phase. A similar occurrence was reported for the tungsten - Tm_2O_3 compatibility couple after 500 hours at 2000°C ⁽²⁾.

The 100% Yb_2O_3 wafer exposed in a similar environment had a normal diffraction pattern but the pattern obtained from the vapor deposited crystals was not that of Yb_2O_3 . The different behavior was not understood. It does suggest, however, that designers with applications requiring tungsten encapsulated Tm_2O_3 beyond 500 hours at 2000°C should conduct additional compatibility tests. Lattice parameters as calculated from the diffraction patterns obtained were all in good agreement with the control values.

Mass transport was evident in all samples encapsulated and exposed at 1750°C and above. The degree of transport was temperature, time and ytterbium concentration dependent, the latter probably having the greatest influence because of the higher vapor pressure of Yb_2O_3 . Mass transport behavior would not be significant, capsule failure notwithstanding, as containment has been demonstrated for times to 10,000 hours. In a dynamic vacuum, mass loss was observed to be primarily a function of temperature and time for a given composition.

Dimensional swelling was noted for several environmental conditions (Table 3-3). Swelling became more observable with increasing ytterbium concentration. Swelling increased with increasing temperature to 2000°C . At 2000°C , the dimensional thickness was observed to decrease; the decrease was greater as ytterbium concentration increased. The swelling behavior suggests some dedensification process, possible the formation of a lower density phase. The temperature at which this behavior might be initiated was not known nor could long time exposure effects be postulated from the sparse data available. The decrease in thickness at higher temperatures suggested that vapor pressure was the predominant factor operating. Attributing these effects to one or the other factor, however, was not possible within the confines of the experiment. In addition, the $\text{Tm}_2\text{O}_3/\text{Yb}_2\text{O}_3$ used herein was processed by one method and because no other process wafers had experienced this set of

TABLE 3-3

INCREASE/DECREASE (%) IN THICKNESS OF 100% Tm_2O_3 , 80% Tm_2O_3 /20% Yb_2O_3
AND 100% Yb_2O_3 AS A RESULT OF ENVIRONMENT EXPOSURE

TEMPERATURE/ATMOSPHERE	TIME	INCREASE/DECREASE (%)		
		100% Tm_2O_3	80% Tm_2O_3 /20% Yb_2O_3	100% Yb_2O_3
1450°C/air	100 hrs	7	14	23 to 32
1450°C/dynamic vacuum	100 hrs	0	0	-6.5
1750°C/static vacuum	100 hrs	7	13	26
1750°C/dynamic vacuum	100 hrs	0	0 to 10	0 to 14
2000°C/static vacuum	5 hrs	0	13	23
2000°C/dynamic vacuum	5 hrs	0	7	7 to 14
2000°C/static vacuum	24 hrs	0	10	14
2000°C/dynamic vacuum	24 hrs	-7	10 to 13	-90
2000°C/static vacuum	100 hrs	10	-3	-25 to -35
2000°C/dynamic vacuum	100 hrs	-58	-58	-100

conditions, the possibility of a third factor, a process factor could not be eliminated.

The data obtained in this study indicate that the crystalline structure of $\text{Tm}_2\text{O}_3\text{-Yb}_2\text{O}_3$ is stable in air, dynamic vacuum and static vacuum for periods to 100 hours at 2000°C .

SUMMARY

100% Tm_2O_3 , 80% $\text{Tm}_2\text{O}_3/20\%$ Yb_2O_3 and 100% Yb_2O_3 wafers were exposed to air, dynamic vacuum and static vacuum (tungsten capsules) at temperatures to 2000°C for times to 100 hours. The stability of the $\text{Tm}_2\text{O}_3\text{-Yb}_2\text{O}_3$ cubic structure was unaffected by the elemental levels of iron, aluminum, silicon and magnesium present in the wafers and unaffected by the environmental conditions imposed on the wafers. Dimensional swelling developed in several wafers including 100% Tm_2O_3 and may be a potential problem because the behavioral pattern is not known.

SECTION 4

MECHANICAL, THERMAL, CHEMICAL STABILITY ENHANCEMENT

The goal of this task was to assess enhancement of mechanical, thermal, chemical stability of Tm_2O_3 . Possible enhancement was to emerge as the end product of:

- Process Variable Optimization
- Selective Addition of Metal Oxides

Enhancement was defined when properties of the end products of process variable optimization and selective addition of metal oxides were improved when compared to bench marks. Mechanical integrity was assessed from macroscopic, microscopic and impact - particle sizing analyses; thermal influences were determined from density measurements, grain size and x-ray diffraction analyses; chemical influence from changes in impurity levels of aluminum, silicon, magnesium and iron, lattice parameter data, macro-microscopic evaluation and electron microprobe analysis. It was understood that all of these major categories were heavily interrelated. The experimentation proceeded according to the general format.

- Characterization of starting materials,
- Processing under controlled conditions into sintered product,
- Characterization of sintered product,
- Controlled aging,
- Characterization of aged product.

The sequence of accomplishment of the three task elements was:

- Bench mark testing,
- Process variable optimization testing,
- Metal oxide additives testing.

4.1 BENCH MARKS

Starting powder was obtained by processing "as received" Tm_2O_3 and Yb_2O_3 (99.9% Michigan Chemical Co*) according to a caustic precipitation process reported in Phase I and Phase II of this study. Following calcining at 750°C for 1 hour in air, the 100% Tm_2O_3 and 80% Tm_2O_3 /20% Yb_2O_3 powders were cold pressed in stainless steel dies at 29 tsi subsequent to the addition of Carbowax 4000 as a binder (4% solution). The green wafers were sintered in air at 1450°C for 17 hours.

Density data were obtained by weighing on an analytical balance and computing the bulk volume from micrometer measurements of the thickness and diameter of the wafer. Chemical analysis for changes in impurity level were determined by atomic absorption spectrophotometric techniques; surface area measurements on pre and post calcined powder were run on an Aminco "SorBet*" using the BET technique with helium preconditioning at 150°C . For impact-fines analysis, wafers were impacted with a falling steel weight and resultant particles collected and fractionated through a series of sieves by a solution method⁽³⁾. Details of all procedures may be found elsewhere in this report⁽⁴⁾.

RESULTS

The experimental data is summarized in Table 4-1. Processing of "as received" Tm_2O_3 and Yb_2O_3 through the calcining stage produce a fine particulate white powder having several times the volume of the original "as received" oxide. Conversion efficiencies (oxide to oxide) were greater than 90%.

*All material used in this program was obtained from Michigan Chemical Co., Kalamazoo, Michigan.

*American Instrument Co., Silver Springs, Maryland.

SUMMARY OF BENCH MARK EXPERIMENTAL DATA

[illegible]

The "as sintered" 100% Tm_2O_3 and 80% Tm_2O_3 /20% Yb_2O_3 wafers were whole with no visible laminations. The 100% Tm_2O_3 wafers exhibited slight radial cracking and had a mottled appearance throughout the subsurface.

X-ray diffraction analyses identified only crystalline Tm_2O_3 or Yb_2O_3 . Lattice parameters were in good agreement with values calculated from the d spacing data report by Bommer⁽⁵⁾.

Metallographically, samples of both compositions exhibited slight laminar cracking but no other evidence of cracking was observed. The porosity patterns were different only in the greater population of smaller pores in the mixed oxide wafers (Figure 4-1). A rather large percentage of the wafer volume in both the 100% Tm_2O_3 and the mixed oxide was transparent. Grain size for 100% Tm_2O_3 wafers as determined from fractographs was <1-10 microns, while for the mixed oxide, the grain size could not be determined by optical microscopy and was therefore assumed to be less than one micron.

Wafers that received an aging treatment were pale green in color. The aging treatment consisted of exposing a stack of wafers encapsulated in tungsten to temperatures of 1600°C for periods of 500 hours. All wafers of both composition had bonded together but no metal to wafer bonding was observed. Vapor deposited crystals were found on the bottom side of the capsule and suggested that a temperature gradient was present within the capsule during test. Thicknesses of aged individual wafers measured macroscopically were unchanged from the "as sintered" thickness despite the bonding. Wafers of both compositions had a glazed appearance after 500 hours in tungsten.

Metallographically, some large voids had appeared as a result of aging. Numerous small pores were also observed that were conservatively estimated to be about 10 volume percent. A grain boundary network was present at the surfaces of the wafers and at the bonded interfaces that extended into the wafers. At least three phases were identifiable by both optical microscopy and

A. 100% Tm_2O_3

B. 80% Tm_2O_3 /20% Yb_2O_3

Figure 4-1 Bench Mark Wafers Sintered 1450°C in Air for 17 Hours
(as Polished - 200X).

Figure 4-2 100% Tm₂O₃ Wafer Sintered 1450°C in Air for 17 Hours
(as Polished - 100X).

A. 100% Tm_2O_3

B. 80% Tm_2O_3 / 20% Yb_2O_3

Figure 4-3 Bench Mark Wafers Sintered in Air $1450^{\circ}C$ for 17 Hours =
Fractured Surface (100X).

A. 100% Tm_2O_3

B. 80% Tm_2O_3 /20% Yb_2O_3

Figure 4-4 Bench Mark Wafers Aged 500 Hours at 1600°C, Then 20 Minute Rise to 2000°C and Shut Down (as Polished - 200X).

electron microprobe analysis. The microprobe showed calcium and silicon to be present in the phases in addition to rare earth; the amounts of calcium & silicon varied between phases. Figure 4-5 is an x-ray composition micrograph of the network. The darkest areas are the in calcium. In these areas, that element was 10 fold more abundant than silicon and about equal with respect to rare earth. The shape of the phase indicated melting had taken place. The eutectic point was somewhere below 2000°C, the maximum temperature of the final thermal spike.

The grain size of the aged bench mark wafers as determined by fractography ranged to 200μ, a marked contrast to the "as sintered" grain size. Figure 4-6 is a fractograph of the aged wafer. The grain size was typical of that observed throughout the aged bench mark wafers.

DISCUSSION

The surface area obtained for a randomly selected powder sample of 100% Tm_2O_3 was $\sim 12 \text{ m}^2/\text{gm}$ while that of 80% Tm_2O_3 /20% Yb_2O_3 was $\sim 5 \text{ m}^2/\text{gm}$. Since no difference in behavior during chemical processing was observed between the 100% Tm_2O_3 and mixed oxide powder, the difference is likely in manual grinding of calcined powders.

The bulk sintered density of 100% Tm_2O_3 wafers averaged $\sim 8.6 \text{ gm/cm}^3$ while that for the mixed oxide was 8.1 gm/cc. With all other conditions essentially equal, the smaller surface area of the mixed oxide powder did not provide quite the degree of sintering and therefore, slightly less bulk sintered density. Bulk density of the aged wafers was estimated from porosity to be somewhat less, conservatively about 90% of theoretical density. Many pores were trapped within the large grains indicative of rapid grain growth. The large grain size observed may have been influenced in part by calcium and silicon. The mechanism whereby these elements concentrate at grain boundaries is not understood. However, because it is surface initiated, it may well involve the encapsulant material. In those regions where the grain boundary network was observed, the

Figure 4-5 X-Ray Composition and Scan of 80% Tm_2O_3 /20% Yb_2O_3 Wafers
Aged at 1600°C for 500 Hours (600X).

Figure 4-6 100% Tm₂O₃ Wafer Aged 1600°C for 500 Hours
Fractured Surface (100X).

average volume of the phase was estimated to be approximately 5-6% of the bulk volume. In some cases, where surface grains had been completely enveloped, (Figure 4-7), the percentage was higher. The presence of calcium and silicon in the initial wafers was not surprising because it was present in the "as received" powder and reprecipitation by caustic addition was ideal for coprecipitation of these impurities. What the eventual disposition of this phase on further exposure would be, is not known. However, these observations strongly point to the need for close quality control of product prior to fuel form fabrication. There was no observable influence in the aged wafers of the presence of Yb_2O_3 .

The interwafer bonding precluded a determination of fines generation after aging. Therefore, comparisons with other aged products were limited mainly to microstructure.

4.2 PROCESS VARIABLE OPTIMIZATION

As stated earlier, the goal of this task was to assess the enhancement of mechanical, thermal, chemical stability of Tm_2O_3 through optimization of process variables. The variables included the following:

- Conditions for chemical reprocessing of "as received" Tm_2O_3 .
- Calcining conditions.
- Method of binder addition.
- Pressing pressure.
- Sintering time/temperature/atmosphere.
- Aging at 1600°C for 500 hours.

The investigation was divided into three (3) subtasks for logical sequence of study.

- Effects of varying chemical reprocessing of "as received" Tm_2O_3 .
- Effects of sintering - time/temperature/atmosphere.
- Effects of aging (T-111, TZM and tungsten capsules).

One set of process conditions that had emerged as the best,

Figure 4-7 100% Tm_2O_3 Bench Mark Aged 500 Hours at $1600^{\circ}C$
(as Polished - 500X).

based on inter-comparison of product properties was selected to produce 30 wafers for further testing by AEC.

4.2.1 EFFECTS OF VARYING CHEMICAL REPROCESSING OF "AS RECEIVED"

Experimentation utilized four different methods for reprocessing "as received" Tm_2O_3 . Two were homogeneous precipitations and two were heterogeneous precipitations. The homogeneous techniques utilized urea and methyl oxalate as primary reagent; the second technique used ammonium oxalate and oxalic acid. In three cases, thulium oxalate was the product obtained prior to calcining. The fourth (urea) formed thulium carbonate/oxycarbonate. Table 4-2 summarizes the conditions of reprocessing. Full details may be found in Part III of this report.

TABLE 4-2
SUMMARY OF CONDITIONS FOR REPROCESSING "AS RECEIVED" Tm_2O_3

Precipitating Agent	Thulium Concentration (Moles/liter)	Excess of Reagent to Thulium	pH	Temperature
Ammonium Oxalate	0.185	3.8:1	5.0	Ambient
Oxalic Acid	0.185	3.8:1	1	93°C
Urea	0.185	73:1	5.0	95°C
Methyl Oxalate	0.185	2.0:1	3.0	95°C

EXPERIMENTAL

"As received" Tm_2O_3 was converted to the nitrate and made 0.555N in strength. Following pH adjustment (where required), precipitation was initiated, the precipitate collected, filtered and washed to neutrality with distilled water and dried in a vacuum oven at 100°C overnight. Optimum calcining temperature was determined by heating samples of the dried powder for 1 hour at 1 atmosphere in a silicon globar furnace. Infrared spectra of calcined powders were obtained using the KBr disc technique in conjunction with a Beckman IR-12

Spectrophometer. The portion of the spectrum was 2.5 - 50 microns ($400 - 200 \text{ cm}^{-1}$). Surface area measurements on calcined powders, chemical purity and densities were obtained in the manner described previously. Thermal gravimetric analysis of Carbowax 4000 solution was obtained on a Perkin Elmer Thermal Gravimetric System in both air and nitrogen. Sample weight was 8 - 10 milligrams.

Two methods of binder addition were compared. One, the method described in the modified Savannah River Laboratory process as employed in the preparation of the bench marks, and two, a spray drying technique whereby the binder was atomized and then dried on the particles with a stream of hot air.

All wafers prepared were cold pressed in steel dies at 29 tsi and sintered in air at 1450°C for 17 hours.

RESULTS

The procedures developed allowed the preparation of these thulium compounds with little difficulty. The precipitates in contrast to standardized SRL process material were easy to work with and processing through the calcining stage was straightforward. The thulium oxalate preparations were all white, crystalline solids that varied from fine powder (ammonium oxalate, methyl oxalate) to a granular texture (oxalic acid). Thulium carbonate was also a white crystalline solid of powdery texture. The yields obtained are listed in Table 4-3..

TABLE 4-3

CONVERSION EFFICIENCY OF CHEMICAL REPROCESSING - $\text{Tm}_2\text{O}_3 \rightarrow \text{Tm}_2\text{O}_3$ (%)

	<u>Percent</u>
Oxalic Acid	74.8 - 92.1
Ammonium Oxalate	59.7 - 75.0
Urea	37.8 - 99.5
Methyl Oxalate	33.8 - 70.8

The low yield listed for urea preparations was a first attempt and subsequent preparations were at least 88% efficient.

Several investigators⁶⁻¹⁰ have studied the conditions necessary for obtaining optimum yields of rare earth oxalates and their conclusions are somewhat contradictory. The work of Broadhead and Heady¹¹ however, was a more systematic analysis of the parameters involved and showed the important factors to be mineral acid concentration (pH should be greater than 2) and rare earth concentrations greater than 0.01M. All the precipitations performed in our laboratories were carried out at conditions that were in agreement with these criteria with the exception of the pH for the oxalic acid¹² (Table 4-2). In addition, the following experimental conditions were observed: a 2-5 fold excess of oxalate ion; a stirring time of several minutes and the absence of complexing agents.

The selection of a calcining temperature was based on laboratory experimentation and review of other work^(13, 14, 15, 16). The calcining temperature used in other laboratories varied from 750°C (generally for hydroxides and carbonates) to 900°C (oxalate). 950°C was selected as a standard calcining temperature to ensure complete compound conversion and to minimize levels of residual carbon and other elemental impurities. Once calcined at this temperature, the powders easily passed through a 100 mesh sieve with little grinding. Infrared spectra obtained on each product gave no evidence of residual reagent and were comparable with respect to pattern.

The results of the chemical impurity analyses are found in Table 4-4.

Processing reduced impurity levels by an order of magnitude. Powders calcined at 750°C had higher levels of impurity than precalcined powders. The source of these impurities is not known, however, calcining at 950°C had virtually returned these increases to precalcined levels.

TABLE 4-4

IMPURITY LEVELS (ppm) OF IRON, MAGNESIUM, ALUMINUM AND SILICON
IN "AS RECEIVED", PRECALCINED, CALCINED 750°C
AND CALCINED 950°C POWDERS

Impurity Levels (ppm) As Received Powders

	<u>Iron</u>	<u>Magnesium</u>	<u>Silicon</u>	<u>Aluminum</u>
S/N	120	13	246	34
UNH	100	10	200	30

Impurity Levels (ppm) Precalcined Powders

<u>Agent</u>	<u>Iron</u>	<u>Magnesium</u>	<u>Silicon</u>	<u>Aluminum</u>
Ammonium oxalate	25	2.5	< 40	< 25
Oxalic acid	17	1.0	< 40	< 19
Urea	18	0.5	< 40	< 17
Methyl oxalate	21	2.9	< 40	< 17

Impurity Levels (ppm) Powders Calcined at 750°C

<u>Agent</u>	<u>Iron</u>	<u>Magnesium</u>	<u>Silicon</u>	<u>Aluminum</u>
Ammonium Oxalate	20 - 40	0.9 - 12.1	< 40 - 125	< 17 - 30
Oxalic acid	11 - 40	0.7 - 6.4	< 40 - 70	< 17 - 40
Urea	21 - 50	0.9 - 4.4	< 40 - 270	< 17 - 50
Methyl oxalate	11 - 26	1.2 - 1.5	< 40	< 17

Impurity Levels (ppm) Powders Calcined at 950°C

<u>Agent</u>	<u>Iron</u>	<u>Magnesium</u>	<u>Silicon</u>	<u>Aluminum</u>
Ammonium oxalate	26	3.6	< 40	< 17
Oxalic acid	12	0.9	< 40	< 17
Urea	23	1.9	< 40	< 17
Methyl oxalate	10 - 21	1.1 - 1.3	< 40	< 17

Carbowax 4000 was also analysed for impurities by emission spectroscopy. The binder contained only copper as a cationic impurity. The level present was 0.001% or less, an amount considered to be ineffectual.

Surface area measurements were attempted on pre and post calcined powders. Precalcined powders gave highly erratic results due mainly to outgassing of the powder during the test even though preconditioned at 150°C. The results presented in Table 4-5 are for powders calcined at 950°C.

TABLE 4-5

SURFACE AREA OF Tm_2O_3 POWDERS CALCINED AT 950°C
DETERMINED BY BET NITROGEN ABSORPTION METHOD

<u>Process</u>	<u>Surface Area (m^2/gm)</u>
Ammonium oxalate	3.8
Oxalic acid	0.9
Urea	6.2
Methyl oxalate	2.1

The surface area data for ammonium oxalate and methyl oxalate appears to be higher than that expected from the pictorial representation of these powders (Figure 4-8). The remainder were in reasonable agreement; the nature of these discrepancies was not understood. Correlation of surface area to bulk sintered density (Table 4-6) was not observed. Generally, the bulk densities were within 15% of theoretical density (8.8 gm/cc); lack of correlation with density was attributed to the overriding effect of pressing pressure of 29 tsi.

TABLE 4-6

BULK - SINTERED DENSITIES (gm/cc)

	<u>Bulk Densities (gm/cc)</u>	<u>% Theo.</u>
Ammonium oxalate	7.6 - 8.4	86 - 95
Oxalic acid	6.7 - 7.5	76 - 84

A. UREA PROCESS (3000X)

B. AMMONIUM OXALATE
PROCESS (3000X)

C. METHYL OXALATE
PROCESS (1000X)

D. OXALIC ACID
PROCESS (1000X)

Figure 4-8 Tm_2O_3 Powders Calcined at 950°C .

TABLE 4-6
BULK - SINTERED DENSITIES (gm/cc) (Cont)

	Bulk Densities (gm/cc)	% Theo.
Urea	8.2 - 8.5	92 - 95
Methyl oxalate	7.5 - 7.9	84 - 89

Those wafers prepared by precipitation with ammonium oxalate had superior sintered bulk density than those prepared by oxalic acid. Wafers fabricated from thulia prepared by the urea route had a higher sintered bulk density than those prepared from powders obtained by methyl oxalate precipitation and had the highest sintered density of the four processes.

Substantial differences in appearance of wafer products were observed. The thulia wafers produced from urea and ammonium oxalate exhibited more shrinkage than those prepared from methyl oxalate and oxalic acid and were more translucent. All had some surface coloration and some wafers had a speckled appearance that extended into the subsurface. This phenomena did not appear with any consistency in a given type of preparation. Some of the wafers fabricated with thulia prepared from oxalic acid were severely laminated and disintegrated when handled in routine fashion. On the basis of sintered density and conversion efficiency, the urea and ammonium oxalate processes were selected.

4.2.2 EFFECTS OF SINTERING - TIME/TEMPERATURE/ATMOSPHERE ON Tm_2O_3

The objective of this task was to (1) determine the effects of varying pressing pressure and sintering time/temperature/atmosphere on Tm_2O_3 bodies made from powders reprocessed from "as received" Tm_2O_3 by two different chemical processes and (2) following this determination to select 5 processes that represented the optimum in process conditions with respect to mechanical, thermal and chemical stability. The pressing pressure investigated were 4, 15 and 29 tsi; air, vacuum and hydrogen atmospheres were employed for sintering wafers at temperatures to $1750^{\circ}C$ for times to 32 hours. Evaluation was performed according to the same format used in evaluating the bench marks.

EXPERIMENTAL

The two process selected for preparing Tm_2O_3 for this evaluation were the urea and ammonium oxalate precipitation processes⁽¹³⁾. Both of these were scaled up 10 fold for these experiments (20 gm to ~ 200 gm) with improved efficiency realized for the ammonium oxalate method (~ 90%). No change in surface area of the powder nor impurity level of the four elements occurred as a consequence of scale up.

The wafers were cold pressed in steel dies as described previously at 4, 15 and 29 tsi subsequent to binder addition and sintered on tungsten or aluminum oxide setters covered with Tm_2O_3 powder. Sintering was carried out according to the matrix outlined in Table 4-7. Density, chemical analysis and "mechanical strength" test were performed as previously described. The mechanical strength test was identical to the fines analysis test except one screening at 149 μ was used instead of three different sizings. A summary of experimental data is given in Table 4-8.

RESULTS AND DISCUSSION

The wafers analysed in this group of work were representative of 54 different sets of processing conditions. The broad matrix had no effect however, on the Tm_2O_3 structure as determined from x-ray diffraction nor was any change in lattice parameter observed.

EFFECTS OF SINTERING IN AIR AT 1450°C

Tm_2O_3 wafers were sintered in air for times to 32 hours, were off white in color and were in one piece at the end of the maximum time period. Sintered densities of wafers from both processes increased with increasing pressure to a maximum of 8.1 gm/cc for the urea process and 7.4 gm/cc for the oxalate method. Elemental levels of iron were slightly higher in urea process wafers. The remaining three elements were either constant or changed erratically. The particle population in the sub 149 micron range for all wafers was essentially the same considering the statistical error band.

TABLE 4-7 TEST MATRIX TO OPTIMIZE PRODUCTION PROCESS VARIABLES
AS MEANS TO Tm_2O_3 FUEL FORM STABILITY ENHANCEMENT

Process	Pressing Pressure (tsi)	Sintering Temperature	Time	Sintered ⁽¹⁾ Product Tests
A - Urea precipitation method	4.5	1450°C (air)	8 hrs	1) Visual
			16 hrs	2) Density
			32 hrs	3) Metallographic
		1750°C (H_2)	4 hrs	Grain Size
			8 hrs	Lattice parameters
			16 hrs	Microprobe
		1750°C (Vac)	2 hrs	4) Atomic Absorption
			4 hrs	Spectroscopy
			8 hrs	5) Mechanical Strength 3 wafers
A	15	Same as above	Same as above	Same as above
A	29	Same as above	Same as above	Same as above
B - Ammonium Oxalate precipitation method	SAME AS ABOVE FOR PROCESS A			

(1) 54 production processes are evaluated using 270 wafers; five processes are selected for evaluation in Phase III on the bases of sintered product tests.

TABLE 4-8

EXPERIMENTAL DATA SUMMARY - EFFECTS OF SINTERING - TIME/TEMPERATURE/ATMOSPHERE ON Tm ₂ O ₃																				
Tm ₂ O ₃ Prepared Via Urea Process											Tm ₂ O ₃ Prepared Via Ammonium Oxalate Process									
Sintering Conditions	Pressure (psi)	Density (gm/cc)	Grain Size (μ)	Lattice Param. (Å)	Elemental		Levels	(ppm)	Mech. Strength (% fines)		Density (gm/cc)	Grain Size (μ)	Lattice Param. (Å)	Elemental		Levels	(ppm)	Mech. Strength (% fines)		
					Fe	Al		Si						Mg	Fe		Al		Si	Mg
1450°C (Air) 8 hrs	20000	5.5	<1		23	<17	<40	15.5	3.1		5.3	<1	10.47	10	28	80	1.9	2.4		
	90000	7.0	<1		22	<17	80	6.2	1.9		6.4	<1	10.47	15	<17	40	2.0	2.4		
	180000	7.8	<1		30	17	80	6.3	1.6		7.3	<1	10.47	18	<17	60	1.9	1.8		
	20000	5.4	<1		24	<17	50	6.7	3.3		5.3	<1	10.47	12	33	80	2.0	2.1		
	90000	6.9	<1		27	<17	60	18.6	1.7		6.6	<1	10.47	14	<17	60	2.3	2.2		
	180000	7.7	<1		22	17	80	6.9	2.4		7.4	<1	10.47	15	<17	80	1.8	0.7		
	20000	5.8	<1	10.47	25	<17	60	2.3	3.4		5.5	<1	10.47	23	26	70	4.6	2.3		
	90000	7.4	<1	10.47	29	<17	90	2.2	1.2		6.6	<1	10.48	18	<17	40	8.1	1.9		
	180000	8.1	<1	10.47	26	23	130	2.3	1.8		7.4	<1	10.47	16	<17	50	1.9	0.7		
1750°C (H ₂) 4 hrs	20000	8.3	≤10	10.47	26	43	430	<0.15	1.1		8.5	<1-10	10.47	20	28	220	1.7	1.1		
	90000	8.7	≤30	10.48	20	39	270	1.3	2.0		8.6	<1-10	10.47	12	<17	250	<0.15	0.5		
	180000	8.6	≤20	10.47	24	50	110	1.4	2.7		8.7	<1-10	10.48	15	43	270	1.7	1.0		
	20000	8.4	≤30	10.48	16	<17	310	<0.15	1.8		8.4	<1-20	10.46	17	<17	240	<0.15	0.9		
	90000	8.5	20-60	10.47	19	<17	300	1.2	1.1		8.6	<1-20	10.47	28	<17	170	<0.15	0.3		
	180000	8.5	20-60	10.47	29	33	110	1.4	2.1		8.7	<1-20	10.48	14	33	280	1.3	0.6		
	20000	8.4	20-70	10.47	19	20	140	1.0	1.3		8.5	<1-20	10.47	11	33	250	<0.15	0.8		
	90000	8.4	40-100	10.47	19	<17	<340	1.3	1.2		8.6	<1-20	10.47	9	<17	160	<0.15	0.2		
	180000	8.5	40-100	10.47	20	50	380	1.8	1.5		8.7	<1-20	10.47	12	<17	300	<0.15	0.2		
1750°C (Vac.) 2 hrs	20000	8.2	<1-10	10.47	12	33	500	0.33	0.5		8.4	<1-10	10.47	16	25	110	0.8	0.6		
	90000	7.7	<1-10	10.47	17	40	180	1.5	1.0		8.6	<1-10	10.47	18	33	170	1.1	0.6		
	180000	6.9	<1-10	10.47	14	<17	100	1.5	2.0		8.6	<1-10	10.48	16	43	250	0.88	0.6		
	20000	8.5	<1-10	10.47	11	25	<40	1.4	1.7		8.6	<1-10	10.47	8	15	290	1.1	0.3		
	90000	7.9	<1-10	10.47	25	25	210	<0.15	1.1		8.7	<1-10	10.47	9	30	150	1.2	1.8		
	180000	7.0	<1-10	10.48	18	<17	80	1.1	1.9		8.7	<1-10	10.48	23	30	210	1.3	0.5		
	20000	8.6	<1-10	10.47	20	40	<40	<0.15	0.9		8.6	<1-10	10.48	14	28	170	1.2	0.4		
	90000	7.6	<1-10	10.47	20	33	220	1.5	0.8		8.7	<1-10	10.47	15	25	160	<0.15	1.2		
	180000	7.04	<1-10	10.47	14	33	320	1.7	1.4		8.7	<1-10	10.47	15	43	270	<0.15	0.4		

In cross section, the wafers were observed to have different colorations. Laminations were present in some instances, particularly at low pressing pressure that nearly split the wafer in two. These laminations were due to non-uniform die pressure, the magnitude thereof suggested that more binder might have been used particularly for the low pressing pressure. Microprobe analysis of these areas confirmed that both contained only thulium.

The wafers from both processes were very soft and difficult to polish. Fractographs of these wafers indicated a grain size below the resolving power of a light microscope, i.e., less than 1 micron. Metallographically, the porosity appeared to be very fine and uniformly distributed. No other phases were observed.

No differences in microstructure were observed that might explain the two textures present in both of the types of processes. The degree to which fines production was attributable to pressure or some other set of factors was difficult to determine because of poor statistics. No major differences attributable to processing were observed.

EFFECTS OF SINTERING IN VACUUM AT 1750°C

Wafers were sintered in vacuum of $\sim 10^{-6}$ torr for times to 8 hours, were pale green in color and were visually free of cracks. The surfaces were smooth and glossy with well defined edges. Sintered densities of urea process wafers increased with increasing pressure for a 4.5 tsi pressure to a maximum of 8.6 gm/cc. Increasing pressures produced little or no improvement in density for this material. Wafers of the oxalate material attained densities to 8.7 gm/cc. Densities in this group were comparably higher for all conditions. Also, densities were generally higher under these conditions than for air sintering, at 1450°C, the major reason being the increased temperature.

Levels of the 4 elements checked were essentially the same process for process, but slightly lower in magnesium when compared to air sintering. This effect was also primarily attributed to increased temperature.

Fractographs showed an increase in grain growth to a maximum of 10 microns in both cases and a slight reduction in particles of less than 149 microns. Comparing process for process, the fines fractions again fell within the statistical error band.

Attempts to chemically etch samples to enhance grain structure were ineffective throughout this entire investigation. Sintered wafers could be dissolved only after lengthy grinding and strong nitric acid treatment at elevated temperatures. No better testimony of the chemical resistance of Tm_2O_3 was required to rate the chemical stability of this ceramic extremely high. Because of this resistance to etching, fractured surfaces were used to assess grain size.

No other phases were observed metallographically. The void pattern observed supported the higher sintered density measured. In both cases, there was evidence of lamination to a much lesser extent than the prior observations. Crack healing was observed and adjacent to crack areas, the oxide had developed transparency. The wafers were also less opaque than air sintered wafers. Small, transparent grains were observed randomly in the wafers produced from urea process materials.

A small difference in sintered density was observed to be the distinguishing feature between processes under these conditions. There were, however, many improvements in specific properties over air sintered wafers, particularly in sintered density.

EFFECTS OF SINTERING IN HYDROGEN AT 1750°C

Tm_2O_3 wafers were sintered in hydrogen at 1750°C for times to 16 hours. The wafers were black, were visually free from cracks, and smooth like the wafers sintered in vacuum. Sintered densities of wafers made from urea process material increased with time when originally pressed at 4.5 tsi. Although increased pressure produced a slight increase in density for the same sintering time, a longer sintering time induced a decrease in density. This effect may have been true for oxalate method wafers also, but the

data were too close to define a pattern. Sintered densities ranged from 8.3 - 8.7 gm/cc, the highest spread of densities achieved in this phase of study.

Elemental levels of iron were slightly higher in this series for urea process wafers, but about the same as those found in air sintered product. Levels of the remaining elements were essentially unchanged. The particle population in the sub 149 micron range for oxalate method wafers was the lowest observed throughout. This reduction was accompanied by corresponding increase in grain size to 20 microns, about twice that for wafers sintered in vacuum. Urea process product however, maintained the same particle population in the sub 149 micron range even though grain size increased up to 100 microns. Grain growth was both pressing pressure and time dependent for this product. The increased grain size observed in urea method wafers and the behavior observed in the oxalate product would lead to a first prediction that sub 149 particles in urea process product would be lower than what was actually found. Since this was not observed, it suggests that fracturing was dependent on parameters not identified. Figures 4-9 to 4-31 contrast these two product types.

Metallographically, wafers from both processes were highly translucent to transparent and colored throughout suggesting that in situ reduction of some impurity had occurred or deposition of impurity on the surface during processing or sintering and then subsequent diffusion. Some lamination was observed in both types of wafers. The urea process wafers were studded with transparent grains that were particularly dense along crack surfaces exposed to environment (Figure 4-14). This grain phenomenon was observed in oxalate method wafers, but to a much lesser degree. Microprobe analysis of these grains showed equal concentration of thulium with respect to surrounding areas. It was concluded that the population of these grains was a function of the hydrogen atmosphere and that some subtle process dependent factor was either responsible

for the grain growth observed in the urea process product or was acting as a controlling agent in the oxalate method wafers.

CONCLUSIONS

54 sets of processing conditions were used to prepare Tm_2O_3 wafers. Processing conditions included chemical processing, pressing pressure, atmosphere, temperature and time. The product properties used as indicators of process condition influence were crystalline structure, wafer integrity, chemical purity sintered density, grain size and fines generation.

The cubic crystalline structure of Tm_2O_3 was insensitive to any of the test matrix conditions. All wafers were whole following sintering, but some degree of lamination could be observed in most samples. The laminating was attributed to the cold pressing techniques used for product preparation.

Although chemical processing, pressing pressure, atmosphere and time were observed to influence levels of impurity, sintered density, grain size and fines generation, temperature was the major influence on these properties. Sintering at $1750^{\circ}C$, clearly improved density and lowered fines generation when compared with products sintered at $1450^{\circ}C$. At $1750^{\circ}C$, relatively low percentages of particles of less than 149 microns were observed and bulk sintered densities approaching theoretical density (8.9 gm/cc) were prevalent.

It was concluded from these results that pressing pressure, time, atmosphere and chemical processing were secondary to temperature in influencing process conditions and that $1750^{\circ}C$ was the optimum temperature for sintering Tm_2O_3 wafers. The insensitivity of Tm_2O_3 properties to such a wide range of process variables at $1750^{\circ}C$ provided great flexibility in the selection of conditions for the 5 process required for further study.

The resultant five sets of process conditions selected are given in Table 4-9.

TABLE 4-9
PROCESS CONDITIONS SELECTED FOR PREPARING WAFERS FOR
STUDYING "EFFECTS OF AGING ON Tm_2O_3 "

METHOD	SINTERING CONDITIONS (TEMPERATURE, PRESSING PRESSURE, TIME, ATMOSPHERE)
Ammonium oxalate	*1750°C, 29 tsi, 6 hours, hydrogen
Ammonium oxalate	1750°C, 29 tsi, 8 hours, vacuum
Ammonium oxalate	1750°C, 15 tsi, 6 hours, hydrogen
Ammonium oxalate	1750°C, 4.5 tsi, 4 hours, vacuum
Urea	*1750°C, 4.5 tsi, 8 hours, vacuum

*Selected for preparing 80% Tm_2O_3 /20% Yb_2O_3 wafers.

4.2.3 EFFECTS OF AGING ON MECHANICAL, CHEMICAL AND THERMAL STABILITY

The object of this task was to expose test samples to an environment that represented nominal operation mission conditions and to determine the degree of mechanical, chemical and thermal stability enhancement realized from this environment. Susceptibility or resistance of encapsulated 100% Tm_2O_3 or 80% Tm_2O_3 /20% Yb_2O_3 to these artificially imposed conditions was assessed from metallographic, x-ray diffraction and impact-fines generation analyses. The three encapsulants selected, tungsten, TZM and T-111 were from a group of seven candidate encapsulant materials that had been tested for compatibility with Tm_2O_3 in a previous study⁽¹⁾. Aging consisted of heat treating encapsulated wafers for 500 hours at 1600°C followed by a thermal spike at 2000°C. Enhancement of mechanical, thermal and chemical stability was determined by comparison with bench marks that had been similarly treated.

EXPERIMENTAL

5 sets of 100% Tm_2O_3 wafers were prepared according to the five processes identified previously. 2 sets of 80% Tm_2O_3 /20% Yb_2O_3 were also fabricated. Seven wafers with the same process history

A. 2 HOURS

B. 4 HOURS

C. 8 HOURS

Figure 4-9 Urea Process Tm_2O_3 Wafers, Pressed at 4.5 tsi, Sintered 1750°C , Vacuum (as Polished - 70X).

A. 2 HOURS

B. 4 HOURS

C. 8 HOURS

Figure 4-10 Urea Process Tm_2O_3 Wafers, Pressed at 15 tsi, Sintered $1750^{\circ}C$, Vacuum (as Polished - 70X).

A. 2 HOURS

B. 4 HOURS

C. 8 HOURS

Figure 4-11 Urea Process Tm_2O_3 Wafers, Pressed at 29 tsi, Sintered $1750^{\circ}C$, Vacuum (as Polished - 70X).

A. 4 HOURS

B. 8 HOURS

C. 16 HOURS

Figure 4-12 Urea Process Tm_2O_3 Wafers, Pressed at 4.5 tsi, Sintered $1750^{\circ}C$, Hydrogen (as Polished - 70X).

A. 4 HOURS

B. 8 HOURS

C. 16 HOURS

Figure 4-13 Urea Process Tm_2O_3 Wafers, Pressed at 15 tsi, Sintered $1750^{\circ}C$, Hydrogen (as Polished - 70X)

A. 4 HOURS

B. 8 HOURS

C. 16 HOURS

Figure 4-14 Urea Process Tm_2O_3 Wafers, Pressed at 29 tsi, Sintered $1750^{\circ}C$, Hydrogen (as Polished - 70X).

A. 2 HOURS

B. 4 HOURS

C. 8 HOURS

Figure 4-15 Urea Process Tm_2O_3 Wafers, Pressed at 4.5 tsi, Sintered 1750°C , Vacuum (Fractograph 100X).

A. 2 HOURS

B. 4 HOURS

C. 8 HOURS

Figure 4-16 Urea Process Tm_2O_3 Wafers, Pressed at 15 tsi, Sintered $1750^{\circ}C$, Vacuum (Fractograph 100X).

A. 2 HOURS

B. 4 HOURS

C. 8 HOURS

Figure 4-17 Urea Process Tm₂O₃ Wafers, Pressed at 29 tsi, Sintered 1750°C, Vacuum (Fractograph 100X).

A. 4 HOURS

B. 8 HOURS

C. 16 HOURS

Figure 4-18 Urea Process Tm_2O_3 Wafers, Pressed at 4.5 tsi, Sintered 1750°C , Hydrogen (Fractograph 100X).

A. 4 HOURS

B. 8 HOURS

C. 16 HOURS

Figure 4-19 Urea Process Tm_2O_3 Wafers, Pressed at 15 tsi, Sintered $1750^{\circ}C$, Hydrogen (Fractograph 100X).

A. 4 HOURS

B. 8 HOURS

C. 16 HOURS

Figure 4-20 Urea Process Tm_2O_3 Wafers, Pressed at 29 tsi, Sintered 1750°C , Hydrogen (Fractograph 100X).

A. 4 HOURS

B. 8 HOURS

C. 16 HOURS

Figure 4-21 Ammonium Oxalate Process Tm_2O_3 Wafer, Pressed at 4.5 tsi, Sintered $1750^{\circ}C$, Hydrogen (as Polished - 70X).

A. 4 HOURS

B. 8 HOURS

C. 16 HOURS

Figure 4-22 Ammonium Oxalate Process Tm_2O_3 Wafers, Pressed at 15 tsi, Sintered $1750^{\circ}C$, Hydrogen (as Polished - 70X).

A. 4 HOURS

B. 8 HOURS

C. 16 HOURS

Figure 4-23 Ammonium Oxalate Process Tm_2O_3 Wafers, Pressed at 29 tsi, Sintered $1750^{\circ}C$, Hydrogen (as Polished - 70X).

A. 2 HOURS

B. 4 HOURS

C. 8 HOURS

Figure 4-24 Ammonium Oxalate Process Tm_2O_3 Wafers, Pressed at 15 tsi,
Sintered 1750°C , Vacuum (as Polished - 70X).

A. 2 HOURS

B. 4 HOURS

C. 8 HOURS

Figure 4-25 Ammonium Oxalate Process Tm_2O_3 Wafers, Pressed at 29 tsi, Sintered $1750^{\circ}C$, Vacuum (as Polished - 70X).

A. 2 HOURS

B. 4 HOURS

C. 8 HOURS

Figure 4-26 Ammonium Oxalate Process Tm_2O_3 Wafers, Pressed at 4.5 tsi, Sintered 1750°C , Vacuum (Fractograph - 100X).

A. 2 HOURS

B. 4 HOURS

C. 8 HOURS

Figure 4-27 Ammonium Oxalate Process Tm_2O_3 Wafers, Pressed at 15 tsi, Sintered 1750°C , Vacuum (Fractograph - 100X).

A. 2 HOURS

B. 4 HOURS

C. 8 HOURS

Figure 4-28 Ammonium Oxalate Process Tm_2O_3 Wafers, Pressed at 29 tsi, Sintered 1750°C , Vacuum (Fractograph - 100X).

A. 4 HOURS

B. 8 HOURS

C. 16 HOURS

Figure 4-29 Ammonium Oxalate Process Tm_2O_3 Wafers, Pressed at 4.5 tsi, Sintered 1750°C , Hydrogen (Fractograph - 100X).

A. 4 HOURS

B. 8 HOURS

C. 16 HOURS

Figure 4-30 Ammonium Oxalate Process Tm_2O_3 Wafers, Pressed at 15 tsi, Sintered 1750°C , Hydrogen (Fractograph - 100X).

A. 4 HOURS

B. 8 HOURS

C. 16 HOURS

Figure 4-31 Ammonium Oxalate Process Tm_2O_3 Wafers, Pressed at 29 tsi, Sintered $1750^{\circ}C$, Hydrogen (Fractograph - 100X).

were placed in each capsule and aged for 500 hours at 1600°C in a static vacuum. Because interceramic bonding had been observed in the bench mark wafers, a 2-3 mil metal foil was placed between each wafer in the capsule to prevent interceramic bonding. Tantalum foil was used in T-111, molybdenum foil in TZM and tungsten foil in tungsten. Following 500 hours at 1600°C, all but two of the capsules were given a 2000°C thermal spike (a 20 minute rise to 2000°C and then shut down).

The T-111 capsule removed prior to thermal spike contained wafers made from 100% Tm_2O_3 in one and 80% Tm_2O_3 /20% Yb_2O_3 in the other. These controls were to give indication of annealing effects due to the thermal spike. All capsules were leak tested before and after aging to ensure capsule integrity.

A summary of experimental data is presented in Table 4-10.

RESULTS AND DISCUSSION

All wafers removed from encapsulants were in one piece. Wafers that were black in color from sintering in hydrogen were unchanged after aging. Other wafer colorations were also unchanged as a result of aging. Vapor deposited crystals were observed in the bottom of all capsules for both 100% Tm_2O_3 and 80% Tm_2O_3 /20% Yb_2O_3 wafers.

X-ray diffraction patterns obtained on wafers representative of each process were typical of crystalline Tm_2O_3 or Yb_2O_3 . Lattice parameters calculated from these x-ray patterns were in good agreement with bench mark lattice parameters.

In most cases, iron, magnesium, and aluminum levels decreased as a result of aging. Level of iron, however, increased markedly in two wafers aged in TZM (see data - Table 4-11). Changes in levels with respect to process conditions and encapsulant were random. Correlation of impurity level with grain size was difficult because of the irregular behavior of both these properties.

Grain size was obtained by fractography (see Figures 4-32

Table 4-10
EXPERIMENTAL DATA SUMMARY - EFFECTS OF AGING ON MECHANICAL, THERMAL
AND CHEMICAL STABILITY

Sintering Conditions	Composition	Pressure (tons)	Aged T-111							Aged TZM							Aged W			
			Grain Size (μ)	Lattice Param. ($\text{\AA}$)	Elemental Level (ppm)				Grain Size (μ)	Lattice Param. ($\text{\AA}$)	Elemental Level (ppm)				Grain Size (μ)	Lattice Param. ($\text{\AA}$)	Elemental Level (ppm)			
					Fe	Al	Si	Mg			Fe	Al	Si	Mg			Fe	Al	Si	Mg
1750°C (Vac) 8 hrs	UR8A	4.5	40	10.47	50	17	230	1.2	20-100	10.47	121	17	230	1.1	30-80	10.47	19	20	310	1.4
1750°C (Vac) 4 hrs	CD6A	4.5	20	10.47	39	20	220	1.0	10	10.47	18	20	190	1.1q	20	10.47	23	20	230	1.0
1750°C (Vac) 8 hrs	CD6A	29	20-60	10.47	54	17	320	1.8	30	10.47	26	17	330	6.9	20	10.47	18	18	190	0.9
1750°C (H ₂) 6 hrs	CD6A	15	10-40	10.47	41	17	330	2.5	10-50	10.47	84	17	180	1.3	30	10.47	55	17	330	5.3
1750°C (H ₂) 6 hrs	CD6A	29	20	10.47	272	17	150	1.7	30	10.47	38	17	230	1.9	5-30	10.47	52	17	260	1.9
				10.46	43	48	430	13.6												
1750°C (vac) 8 hrs	UR8A/UR2K	4.5	20	10.46	43	20	320	1.1	40-100	10.45	35	55	380	3/0	5-60	10.46	71	17	170	9.3
1750°C (H ₂) 6 hrs	CD6A/CD1K	29	5-20	10.45	54	17	260	56	5-40	10.46	36	17	180	2.9	20-100	10.46	27	17	220	1.9
				10.45	48	17	250	8.4												

MECHANICAL STRENGTH (% fines)

Sintering Conditions	Composition	Pressure (tons)	<10 μ				10 - 44 μ			
			Pre-aged	Aged-T111	Aged-TZM	Aged-W	Pre-aged	Aged-T111	Aged-TZM	Aged-W
1750°C (Vac) 8 hrs	UR8A	4.5	0.30 $\pm$ 0.09	0.175 $\pm$ 0.066	0.219 $\pm$ 0.078	0.376 $\pm$ 0.113	0.21 $\pm$ 0.02	0.284 $\pm$ 0.064	0.458 $\pm$ 0.126	0.810 $\pm$ 0.136
1750°C (Vac) 4 hrs	CD6A	4.5	0.28 $\pm$ 0.08	0.235 $\pm$ 0.063	0.209 $\pm$ 0.025	0.198 $\pm$ 0.047	0.17 $\pm$ 0.03	0.215 $\pm$ 0.026	0.272 $\pm$ 0.051	0.301 $\pm$ 0.046
1750°C (Vac) 8 hrs	CD6A	29	0.26 $\pm$ 0.09	0.044 $\pm$ 0.039	0.072 $\pm$ 0.020	0.085 $\pm$ 0.064	0.22 $\pm$ 0.08	0.040 $\pm$ 0.025	0.058 $\pm$ 0.030	0.038 $\pm$ 0.011
1750°C (H ₂) 6 hrs	CD6A	15	0.33 $\pm$ 0.13	0.151 $\pm$ 0.041	0.134 $\pm$ 0.085	0.094 $\pm$ 0.042	0.22 $\pm$ 0.03	0.373 $\pm$ 0.054	0.274 $\pm$ 0.162	0.065 $\pm$ 0.039
1750°C (H ₂) 6 hrs	CD6A	29	0.37 $\pm$ 0.20	0.075 $\pm$ 0.051	0.071 $\pm$ 0.051	0.070 $\pm$ 0.036	0.16 $\pm$ 0.03	0.125 $\pm$ 0.034	0.095 $\pm$ 0.027	0.094 $\pm$ 0.036
1750°C (Vac) 8 hrs	UR8A/UR2K	4.5	0.35 $\pm$ 0.14	0.279 $\pm$ 0.035	0.345 $\pm$ 0.131	0.332 $\pm$ 0.078	0.30 $\pm$ 0.09	0.354 $\pm$ 0.062	0.553 $\pm$ 0.106	0.642 $\pm$ 0.049
1750°C (H ₂) 6 hrs	CD6A/CD1K	29	0.31 $\pm$ 0.17	0.067 $\pm$ 0.027	0.094 $\pm$ 0.048	0.135 $\pm$ 0.139	0.22 $\pm$ 0.08	0.101 $\pm$ 0.033	0.131 $\pm$ 0.027	0.105 $\pm$ 0.043

Sintering Conditions	Composition	Pressure (tons)	44 - 149 μ				>149 μ			
			Pre-aged	Aged-T111	Aged-TZM	Aged-W	Pre-aged	Aged-T111	Aged-TZM	Aged-W
1750°C (Vac) 8 hrs	UR8A	4.5	1.182	1.131	1.426	2.292	98.268	98.514	97.940	96.316
1750°C (Vac) 4 hrs	CD6A	4.5	1.077	1.012	1.057	1.024	98.444	98.449	98.532	98.553
1750°C (Vac) 8 hrs	CD6A	29	1.163	0.135	0.250	0.231	98.333	99.871	98.715	99.755
1750°C (H ₂) 6 hrs	CD6A	15	1.019	0.975	0.730	0.218	98.526	98.524	98.876	99.759
1750°C (H ₂) 6 hrs	CD6A	29	0.903	0.460	0.326	0.348	98.522	99.480	99.640	99.568
1750°C (Vac) 8 hrs	UR8A/UR2K	4.5	1.467	0.997	2.078	1.936	97.788	98.388	96.785	96.984
1750°C (H ₂) 6 hrs	CD6A/CD1K	29	1.098	0.142	0.372	0.322	98.299	99.800	99.484	99.459

A. T-111

B. TZM

C. TUNGSTEN

Figure 4-32 100% Tm_2O_3 , Pressed at 4.5 tsi, Sintered $1750^{\circ}C$, 8 Hours Vacuum, Aged 500 Hours, $1600^{\circ}C$ (100X).

A. CONTROL—NO AGE

B. T-111

C. TZM

D. TUNGSTEN

Figure 4-33 80% Tm_2O_3 /20% Yb_2O_3 , Pressed at 4.5 tsi, Sintered 1750°C ,
8 Hours Vacuum, Aged 500 Hours, 1600°C (100X).

A. T-111

B. TZM

C. TUNGSTEN

Figure 4-34 100% Tm_2O_3 , Pressed at 4.5 tsi, Sintered $1750^{\circ}C$, 4 Hours Vacuum, Aged 500 Hours, $1600^{\circ}C$ (100X).

A. T-111

B. TZM

C. TUNGSTEN

Figure 4-35 100% Tm_2O_3 , Pressed at 29 tsi, Sintered $1750^{\circ}C$, 8 Hours Vacuum,
Aged 500 Hours $1600^{\circ}C$ (100X).

A. T-111

B. TZM

C. TUNGSTEN

Figure 4-36 100% Tm_2O_3 , Pressed at 15 tsi, Sintered $1750^{\circ}C$, 6 Hours
Hydrogen, Aged 500 Hours, $1600^{\circ}C$ (100X).

A. T-111

B. TZM

C. TUNGSTEN

Figure 4-37 100% Tm_2O_3 , Pressed at 29 tsi, Sintered 1750°C, 6 Hours
Hydrogen, Aged 500 Hours, 1600°C (100X).

A. T-111

B. TZM

C. TUNGSTEN

Figure 4-38 80% Tm_2O_3 /20% Yb_2O_3 , Pressed at 29 tsi, Sintered $1750^{\circ}C$,
6 Hours Hydrogen, Aged 500 Hours, $1600^{\circ}C$ (100X).

to 4-38). Grain sizes measured in these wafers were related to chemical process and capsule material. The data are presented in Table 4-11.

Grain size of wafers made by urea process 100% Tm_2O_3 and 80% Tm_2O_3 /20% Yb_2O_3 were enhanced when encapsulated but particularly when encapsulated in TZM and tungsten. Grain size of wafers made by ammonium oxalate process were also enhanced by encapsulation, but particularly the 80% Tm_2O_3 /20% Yb_2O_3 wafer encapsulated in tungsten. The 10 micron enhancement observed in grain size of all wafers beyond that of preaged wafers was attributed primarily to the extended time at temperature. Increases in grain size beyond the 10 micron base level were interpreted as being a function of the encapsulant.

Metallographic analysis was performed on cross sectioned wafers in the as polished condition. Wafers sintered in hydrogen prior to aging were black throughout and highly translucent to transparent. Vacuum sintered samples were green to grey following aging and also highly translucent. Laminar cracking was observed in wafers pressed at 4.5, 15 and 29 tsi. Crack healing was observed in all these wafers.

Figures 4-39 to 4-45 are micrographs of the as-polished surfaces. The microstructure of the 80% Tm_2O_3 /20% Yb_2O_3 wafers prepared from urea processed materials contained areas of clustered porosity whereas the porosity in 100% Tm_2O_3 wafers was uniformly distributed. A Yb_2O_3 effect was also observed in wafers prepared from ammonium oxalate process (see Figures 4-39, 4-40 and 4-45). A brittle phase had formed in the mixed oxide samples that was most prevalent in wafers encapsulated in T-111. Large voids were also observed in the mixed oxide wafers. 100% Tm_2O_3 wafers were free of both these effects.

All wafers regardless of pre-aging history contained areas that were elliptically shaped and were integral part of the matrix. In 100% Tm_2O_3 , these wafers were quite clear and relatively void

TABLE 4-11

GRAIN SIZE OF 100% Tm_2O_3 - 80% Tm_2O_3 /20% Yb_2O_3 WAFERS AGED
IN T-111, TZM AND TUNGSTEN FOR 500 HOURS AT 1600°C FOLLOWED BY
MINUTE RISE TO 2000°C AND SHUT DOWN

<u>PROCESS</u>	<u>PREAGED</u>	<u>AGED T-111</u>	<u>AGED TZM</u>	<u>AGED W</u>
1750°C (Vac) 8 hrs	< 1-10	< 40	20-100	30-80
1750°C (Vac) 4 hrs	< 1-10	< 20	< 10	< 20
1750°C (Vac) 8 hrs	< 1-10	20-60	30	20
1750°C (H_2) 6 hrs	< 1-20	10-40	10-50	30
1750°C (H_2) 6 hrs	< 1-20	< 20	< 30	5-20
1750°C (Vac) 8 hrs	< 1-10	< 20	40-100	5-60
1750°C (H_2) 6 hrs	< 1-10	5-20	5-40	20-100

A. T-111

B. TZM

C. TUNGSTEN

Figure 4-39 100% Tm_2O_3 , Pressed at 4.5 tsi, Sintered $1750^{\circ}C$ Vacuum 8 Hours,
Aged 500 Hours, $1600^{\circ}C$ (70X).

A. T-111

B. TZM

C. TUNGSTEN

Figure 4-40 80% Tm_2O_3 /20% Yb_2O_3 Wafers, Pressed at 4.5 tsi, Sintered $1750^{\circ}C$, 8 Hours Vacuum, Aged 500 Hours, $1600^{\circ}C$ (70X).

A. T-111

B. TZM

C. TUNGSTEN

Figure 4-41 100% Tm_2O_3 , Pressed at 4.5 tsi, Sintered at $1750^{\circ}C$, 4 Hours Vacuum, Aged 500 Hours, $1600^{\circ}C$ (70X).

A. T-111

B. TZM

C. TUNGSTEN

Figure 4-42 100% Tm_2O_3 , Pressed at 29 tsi, Sintered 1750°C , 8 Hours Vacuum, Aged 500 Hours, 1600°C (70X).

A. T-111

B. TZM

C. TUNGSTEN

Figure 4-43 100% Tm_2O_3 , Pressed at 15 tsi, Sintered at $1750^{\circ}C$, 6 Hours
Hydrogen, Aged 500 Hours, $1600^{\circ}C$, (20 Min) Rise to $2000^{\circ}C$ (70X).

A. T-111

B. TZM

C. TUNGSTEN

Figure 4-44 100% Tm_2O_3 , Pressed at 29 tsi, Sintered 1750°C , 6 Hours Hydrogen, Aged 500 Hours, 1600°C (70X).

A. CONTROL

B. T-111

C. TZM

D. TUNGSTEN

Figure 4-45 80% Tm_2O_3 /20% Yb_2O_3 Wafers, Pressed at 29 tsi, Sintered 1750°C , 6 Hours Hydrogen, Aged 500 Hours, 1600°C (70X).

free under electron microprobe, these areas were free of structure. In the mixed oxide samples, microprobe showed considerable structure not only in the elliptical areas but throughout the wafers (Figure 4-46). Microprobe analyses for elements related to the metal matrix proved the wafers to be free of any of these elements. However, evidence of ytterbium segregation in the elliptical areas was found. Figure 4-46b was a sweep scan for ytterbium and clearly showed the segregation pattern. This pattern was typical of that found in all wafers and therefore, seemed to be insensitive to the encapsulant materials. The long axis of the elliptical areas was generally perpendicular to the pressing direction. This pattern suggested the source of this phenomena to lie with the calcined powder and may be due to agglomerates or groups of agglomerates that formed during calcining and when cold pressed assumed these shapes.

The major data points in determining stability enhancement in this task were the fines generated from impacting wafers. Although the calculated final velocity at impact was only 10 ft/sec, far lower than the operational 325 ft/sec, the test did serve to distinguish among process conditions. Of particular interest was the fraction of particles in the sub 10 micron range as these particles may become airborne on impact and present a potential source of radiological contamination. Fines (10 micron particles) ranges from 0.04% to 0.38% of total mass for the products analyzed. Fines data were random with respect to all process and/or aging parameters except for pressing pressure. Figure 4-47 depicts the relationship between particles of less than 10 microns and pressing pressure for all conditions. Bulk sintered density was also included for reference. The data showed that increasing pressing pressure proportionally produced fewer fines. A preview of this behavior would have been expected from preaged wafers, however, as shown in the graph, fines generated from these wafers were essentially constant for all pressing pressures. How aging developed this relationship was unknown but the potential of predicting and possible influencing % fines generated on impact

A. TOPOGRAPHICAL REPRESENTATION

B. YTTERBIUM X-RAY SWEEP

C. COMPOSITION IMAGE

Figure 4-46 80% Tm_2O_3 /20% Yb_2O_3 Wafers Aged for 500 Hours at 1600°C
Followed by 20 Minute Rise to 2000°C .

Figure 4-47 Pressing Pressure vs % Fines-Sub 10 Micon. Wafers Aged in T-111, TZM and Tungsten for 500 hrs at 1600°C

with initial pressing pressure was considered tantalizing.

COMPARISON OF WAFERS PROPERTIES - BENCH MARKS VS. PROCESS
VARIABLE OPTIMIZATION WAFERS

Comparison of properties of wafers produced from the process variable optimization study with bench marks showed the bulk sintered densities of bench marks to be the same as bulk sintered densities of wafers representative of several sets of processing conditions. Fines generation data of bench mark wafers aged for 500 hours at 1600°C were not available because of inter wafer bonding and hence comparison with wafers representative of optimal processing conditions, was impossible. A qualified comparison suggest that of the several optimal processes selected for study any single process was capable of producing an equally acceptable Tm_2O_3 wafer. A more refined test matrix would be required to further grade the stability enhancement of these wafers.

CONCLUSIONS

The absence in Tm_2O_3 of infused elements related to the metal matrix and of any reaction products with the encapsulant were strong evidence of the chemical inertness of Tm_2O_3 . The high degree of resistance of aged Tm_2O_3/Yb_2O_3 to a wide range of chemical etchants further support the conclusion that Tm_2O_3/Yb_2O_3 produced under a variety of process conditions and subsequently aged at 1600°C for 500 hours will maintain a high degree of chemical stability.

Mechanical stability enhancement, as defined previously, was observed as a result of aging in the reduction of post impact fines (particles < 10 microns in diameter) particularly in those wafers pressed initially at pressures of 29 tsi. The relationship of fines and pressing pressure observed in aged samples suggests that further stability enhancement can be achieved once an understanding of this relationship is developed.

Excellent thermal stability of Tm_2O_3/Yb_2O_3 was maintained throughout the aging period. It was concluded that Tm_2O_3 was

insensitive to thermal effects except for the possible inter-relationship of temperatures with the fines generation pattern previously described.

4.3 METAL OXIDE ADDITIVES - A MEANS TO PRODUCT STABILITY ENHANCEMENT

The introduction described the object of this task and the rationale for investigation. Criteria for selection were based on material properties most likely to influence solubility.

Atomic size and valence state of the cation were prime factors, however, melting point, subsequent thermal neutron activation and its resultant radiation contribution (if cold encapsulated) and additive concentration were considered.

In general, a limited solubility would result if the atomic radius of the additive cation is $\pm 8\%$ relative to thulium and very limited solubility (usually less than 1%) if greater than $\pm 15\%$. Limited solubility was also indicated if the valence state of the cation was different from that of the host cation.

Based on valence state and atomic size, aluminum oxide (Al_2O_3), calcium oxide (CaO) and titanium dioxide (TiO_2) were chosen. The melting points of these ceramics are given in Table 4-12 along with atomic size relative to thulium and valence state of the metal ion.

TABLE 4-12

MELTING POINTS, VALENCE STATE OF CATIONS AND ATOMIC
SIZE RELATIVE TO THULIUM OF 3 METAL OXIDE ADDITIVES

<u>Oxide</u>	<u>M.P. ($^{\circ}\text{C}$)</u>	<u>Cation Valence (as oxide)</u>	<u>Atomic Size (%)</u>
Al_2O_3	2045	+ 3	- 18
CaO	2614	+ 2	+ 13
TiO_2	1838	+ 4	- 16

The concentration of additive to be used was 1%, thus providing sufficient material for an insoluble grain boundary phase, but not sufficient to cause a significant melting point depression. Thermal neutron activation of Tm_2O_3 - additive in the severest case (production of Ca-45) provides a separation of thulium 170 to impurity of $\sim 10^5$. Even at this level no significant

contribution to Bremsstrahlung would result.

4.3.1 EXPERIMENTAL

Thulium oxide and ytterbium oxide (Yb_2O_3) used in the preparation of samples was processed from "as received" Tm_2O_3 by the urea homogenous precipitation process⁽⁴⁾. Weighed quantities of $\text{Tm}_2\text{O}_3/\text{Yb}_2\text{O}_3$ and reagent grade metal oxide additive were allowed to mix overnight in individual containers. Appropriate amounts of material were removed for screening tests prior to addition of 4% Carbowax 4000 binder.

Melt samples were produced by placing a mixed oxide sample in a calcia stabilized zirconia crucible and thermally cycling the samples with an induction heater. An argon atmosphere prevailed throughout the controlled thermal cycling.

Wafers were pressed at 29 tsi and sintered in air at 1450°C for 17 hours. Impact tests and fines analyses were performed according to the methods described previously. A summary of experimental data is given in Table 4-13

4.3.2 RESULTS AND DISCUSSION

The melt samples were obtained as a preliminary screening test to observe the effects of additives on the stability of Tm_2O_3 . Initial thermal arrests were observed to occur at points coincidental with those of pure Tm_2O_3 observed during phase diagram studies of the $\text{Tm}_2\text{O}_3\text{-Yb}_2\text{O}_3$ system. The presence of 1% of Al_2O_3 , CaO or TiO_2 , respectively, did not depress the melting point of Tm_2O_3 or $\text{Tm}_2\text{O}_3/\text{Yb}_2\text{O}_3$ mixtures within experimental error nor was any phase change of $\text{Tm}_2\text{O}_3\text{-Yb}_2\text{O}_3$ cubic structure observed.

The melt samples were cross sectioned for evaluation. The Tm_2O_3 had wetted the ZrO_2 crucible indicating melting had taken place. A grain boundary phase or phases was observed similar to that reported by Anderson in earlier work⁽¹⁷⁾. These phases were lower melting than the $\text{Tm}_2\text{O}_3/\text{Yb}_2\text{O}_3$ as indicated by their shape. A scanning composition image of the cross section showed

A. $\text{Tm}_2\text{O}_3/\text{Yb}_2\text{O}_3 + 1\% \text{TiO}_2$

B. $\text{Tm}_2\text{O}_3/\text{Yb}_2\text{O}_3 + 1\% \text{Al}_2\text{O}_3$

C. $\text{Tm}_2\text{O}_3/\text{Yb}_2\text{O}_3 + 1\% \text{CaO}_2$

Figure 4-48 $\text{Tm}_2\text{O}_3/\text{Yb}_2\text{O}_3 + 1\%$ Additive, Melt Samples (300X).

A. $\text{Tm}_2\text{O}_3 + 1\% \text{CaO}$

B. $80\% \text{Tm}_2\text{O}_3 / 20\% \text{Yb}_2\text{O}_3 + 1\% \text{CaO}$

C. $\text{Tm}_2\text{O}_3 + 1\% \text{Al}_2\text{O}_3$

D. $80\% \text{Tm}_2\text{O}_3 + 1\% \text{Al}_2\text{O}_3$

Figure 4-49 Tm_2O_3 and $80\% \text{Tm}_2\text{O}_3 / 20\% \text{Yb}_2\text{O}_3 + 1\%$ Additive. Wafers Aged 500 Hours in Tungsten Capsules at 1600°C .

A. 100% Tm_2O_3 + 1% Al_2O_3

B. 100% Tm_2O_3 + 1% CaO

C. 100% Tm_2O_3 + 1% TiO_2

Figure 4-50 100% Tm_2O_3 + 1% Additive Sintered at 1450°C in Air for 17 Hours (100X).

the segregate phases (Figure 4-48). A sufficient difference in atomic number existed between the matrix and the boundary phases to clearly depict the composition difference. In addition to thulium, each phase contained silicon, calcium and trace zirconium. The darker areas contained 15 - 20 times the levels of calcium found in the lighter areas. In those samples containing alumina and titania, the aluminum and titanium also appeared in the segregate phases. Microprobe evaluation of a pure Tm_2O_3 sample showed the same pattern found with the samples containing additives. An electron microprobe sweep showed the distribution of silicon and calcium throughout the sample (Figure 4-51). Trace amounts of Ca, Si, and Zr were detected in the thulium matrix in all melt samples. Aluminum and titanium were also detectable in trace amounts in the matrix of their respective melts. From these observations, it was concluded that the presence of 1% of CaO , Al_2O_3 and TiO_2 had no significant effect on the behavior of $\text{Tm}_2\text{O}_3/\text{Yb}_2\text{O}_3$ in a dynamic thermal system. However, the presence of calcium in a grain boundary phase gave speculation as to how it might behave in a sintered wafer.

Wafers representative of each of the additives were cross sectioned following sintering in air at 1450°C for 17 hours. Microprobe analysis showed each of the respective metal ions to be dispersed within the wafers, however, the dispersion patterns were different. The aluminum containing areas (grey) were dispersed through the wafer as shown in Figure 4-52. Calcium was well dispersed in very small areas throughout the sample whereas titanium was found localized in only a few areas (Figures 4-52 f, i). X-ray diffraction patterns obtained from each representative wafer were characteristic of crystalline Tm_2O_3 or Yb_2O_3 . The lattice parameter values were in good agreement with those values calculated from the data of Bommer⁽⁵⁾ for 100% Tm_2O_3 .

The final test performed on the preaged wafers, the impact test, indicated a particle population pattern for the Al_2O_3 & TiO_2 additives to be about the same as that for wafers containing no

A. COMPOSITION (300X)

B. SILICON X-RAY (300X)

C. CALCIUM X-RAY (300X)

Figure 4-51 Tm_2O_3 Melt Sample Electron Microprobe
Composition and Sweep (300X).

A. $\text{Tm}_2\text{O}_3 + 1\% \text{Al}_2\text{O}_3$ (100X)

B. 80% $\text{Tm}_2\text{O}_3/20\% \text{Yb}_2\text{O}_3 + 1\% \text{Al}_2\text{O}_3$ (100X)

C. ELECTRON MICROPROBE SWEEP OF B.
ALUMINUM X-RAY (600X).

Figure 4-52 Tm_2O_3 and 80% $\text{Tm}_2\text{O}_3/20\% \text{Yb}_2\text{O}_3 + 1\%$ Additive. Wafers
Sintered in Air at 1450°C , 17 Hours (3 of 3 Pages).

D. $\text{Tm}_2\text{O}_3 + 1\% \text{CaO}$ (100X)

E. $80\% \text{Tm}_2\text{O}_3 / 20\% \text{Yb}_2\text{O}_3 + 1\% \text{CaO}$ (100X)

F. ELECTRON MICROPROBE SWEEP OF E,
CALCIUM X-RAY (100X)

Figure 4-52 Tm_2O_3 and $80\% \text{Tm}_2\text{O}_3 / 20\% \text{Yb}_2\text{O}_3 + 1\%$ Additive. Wafers
Sintered in Air at 1450°C , 17 Hours (1 of 3 Pages).

G. $\text{Tm}_2\text{O}_3 + 1\% \text{TiO}_2$ (100X)

H. 80% $\text{Tm}_2\text{O}_3/20\% \text{Yb}_2\text{O}_3 + 1\% \text{TiO}_2$ (100X)

I. ELECTRON MICROPROBE SWEEP OF B.
TITANIUM X-RAY (300X)

Figure 4-52 Tm_2O_3 and 80% $\text{Tm}_2\text{O}_3/20\% \text{Yb}_2\text{O}_3 + 1\%$ Additive. Wafers Sintered in Air at 1450°C , 17 Hours (2 of 3 Pages).

additive. However, the bulk sintered densities of the additive wafers were between 8.4 and 8.5 gm/cc, about 10% higher than those containing no additive. The CaO additive showed a factor of 2 reduction in the particle population in the 44 - 149 micron range and a slight reduction in population in the 10 - 44 micron group. The less than 10 micron particle group was unchanged. Figure 4-52 are photomicrographs of fractured surfaces representative of each of the additive wafers and one control. The difference in grain size between the CaO - Tm_2O_3 wafers and the others was striking and explained the increase in bulk density observed. An increase in grain size with a corresponding reduction in particle population in the 10 - 149 micron range suggested a relationship between these properties.

Several wafers were aged in tungsten capsules at 1600°C for 500 hours. Wafers containing only the same additive were placed in each capsule. Post aging observation showed interwafer bonding had taken place, but no ceramic to metal bonding. The x-ray diffraction patterns contained no new lines and the lattice parameters remained the same within experimental error.

Microscopic examination of cross sectioned wafers confirmed the presence of additive phases. The aging process had caused the titanium to segregate into a very few areas one of which was located at a wafer - wafer interface. Many voids had formed and the wafer thickness had increased 10 - 13% for 100% Tm_2O_3 and 6.5 - 10% for 80% Tm_2O_3 /20% Yb_2O_3 . Segregation and swelling were also noted in those wafers containing 1% Al_2O_3 . Thicknesses of wafers, although bonded, had increased 13% for the mixed oxide and 23% for 100% Tm_2O_3 . Many voids had formed, some quite large. Microprobe showed aluminum to have a greater distribution density than that of titanium and to be associated with voids. In rare instances, a third phase was observed, again associated with a void. This phase was not identified. Neither calcium nor silicon could be found in either additive with microprobe analysis.

The $\text{Tm}_2\text{O}_3/\text{Yb}_2\text{O}_3$ - CaO additive wafers also contained voids, some very large. A grain boundary phase was observed that extended from the wafer surface into the matrix. Microprobe confirmed the presence of calcium in this phase. The swelling phenomena could be observed in both compositions. 100% Tm_2O_3 had swelled in thickness from 0 - 10% and the mixed oxide from 0 - 36%.

The swelling observed in these wafers was greatest in 100% Tm_2O_3 when Al_2O_3 was the additive and greatest in the 80% $\text{Tm}_2\text{O}_3/20\%$ Yb_2O_3 when CaO was the additive. The bench marks did not exhibit any swelling of this magnitude, although void formation was observed; the wafers did have calcium and silicon present. Since inter wafer bonding was observed in both sets of samples, it was concluded that the presence of these specific additives in conjunction with an unknown process related factor were responsible for this behavior.

The elemental levels of iron were reduced for each additive in the aged wafers. The data are presented in Table 4-14 for each of the elements exclusive of silicon. The net increases in aluminum content observed were likely due to random sampling. The presence of Yb_2O_3 was not influential in determining the level of these elements.

TABLE 4-14

NET CHANGES IN LEVELS (ppm) OF ALUMINUM, IRON AND MAGNESIUM IN 100% Tm_2O_3 AND 80% $\text{Tm}_2\text{O}_3/20\%$ Yb_2O_3 WAFERS AS A CONSEQUENCE OF AGING FOR 500 HOURS AT 1600°C IN A TUNGSTEN CAPSULE

	<u>Iron</u>	<u>Aluminum</u>	<u>Magnesium</u>
100% Tm_2O_3 + 1% CaO	- 11	+ 5	- 0.5
1% Al_2O_3	- 23	+ 907	+ 0.9
1% TiO_2	- 13	- 19	+ 0.3
80% $\text{Tm}_2\text{O}_3/20\%$ Yb_2O_3 + 1% CaO	- 28	+ 15	- 0.2
1% Al_2O_3	- 15	+ 307	- 0.1
1% TiO_2	- 17	- 5	----

A comparison of some additive and bench mark data is presented in Table 4-15 for 100% Tm_2O_3 . The only detectable grain growth in preaged samples was in those wafers containing CaO. However, both CaO - Tm_2O_3 and bench mark grains had grown markedly as a result of aging at 1600°C for 500 hours. As was indicated before, both the presence of calcium and another process factor might be involved. Alternatively, Al_2O_3 and TiO_2 could be acting as controlling agents repressing grain growth. Thirdly, the role of the encapsulant material, in this case tungsten, is unknown and may be yet another factor.

These observed differences in grain growth were felt to be responsible for the reduction in population of grains in the 10 - 149 fraction in the preaged wafers. One can only speculate what the population pattern might be for the aged wafers, however, the inter wafer bonding precluded testing these wafers under identical conditions. It would seem, however, that a further gain in reductions could be anticipated by virtue of the grain size observed particularly for fines in the sub 10 micron fraction.

SUMMARY

The behavior of three additive metal oxides support the correctness of the original selection criteria as each proved to be insoluble in the $\text{Tm}_2\text{O}_3/\text{Yb}_2\text{O}_3$ matrix and did not effect any of the major physical properties of the matrix. The original rationale, the presence of a grain boundary phase that would provide an alternate means of dissipating the kinetic energy of impact so as to reduce transgranular cracking, was also successfully achieved by means of CaO addition. This additive produced a grain boundary phase that reduced the particle population in the 10 - 149 μ range and proved to be a sintering aid as well.

Comparison of additives with bench marks suggested that mechanical stability was improved to some degree and offered potentially greater enhancement in the case of calcium oxide. The presence of Yb_2O_3 did not appear to influence behavior in any measurable way.

TABLE 4-15

COMPARISON OF BENCH MARK AND ADDITIVE DATA FOR PRE AND POST AGED 100% TiO_2

	P. (gm/cc)	G.S. (μ)	Lattice Param. ($\text{\AA}$)	Elemental (ppm)			Fines Analysis (% $\pm$ 1 σ)			
				Fe	Al	Mg	< 10 μ	10-44 μ	44-142 μ	> 142 μ
100% TiO_2 bench mark	8.6	< 1	10.49	79	52	16	0.40 $\pm$.14	0.19 $\pm$.11	0.73	98.92
CaO	8.5	< 1-5	10.47	28	18	4.5	0.43 $\pm$.30	0.12 $\pm$.05	0.49	99.23
Al_2O_3	8.5	< 1	10.47	48	467	1.7	0.34 $\pm$.11	0.17 $\pm$.09	0.94	98.67
TiO_2	8.4	< 1	10.47	43	42	1.9	0.39 $\pm$.21	0.15 $\pm$.03	0.99	98.49
Aged 100% TiO_2 bench mark	-	< 200	10.48	27	57	16				
CaO	-	< 500	10.45	17	23	4.0				
Al_2O_3	-	< 10-30	10.49	25	1374	2.6				
TiO_2	-	< 10-20	10.44	30	23	2.2				

4.4 AN ASSESSMENT OF MECHANICAL, THERMAL AND CHEMICAL STABILITY ENHANCEMENT

The thermal and chemical stability of the $\text{Tm}_2\text{O}_3/\text{Yb}_2\text{O}_3$ structure was consistently of high degree throughout the entire study. The products resulting from ranging process parameters and from adding metal oxide additives exhibited the same high degree of stability observed in the bench mark wafers. The interceramic bonding of Tm_2O_3 wafers that occurred during aging suggests the need for individually encapsulated wafers particularly in light of the very high centerline temperatures predicted for bulk encapsulated Tm_2O_3 ⁽¹⁸⁾. Individual encapsulation would be expected to preserve the benefits of fines generation observed in aged wafers.

Both process variable optimization and metal oxide additive wafers influenced particle populations within certain size ranges; full assessment of the past aged metal oxide additive and bench mark wafers was precluded by interceramic bonding. The preaged fines behavior of the additive samples particularly in those wafers containing 1% CaO however, suggest that aging may improve the post impact fines generation more favorably than the levels observed in the products of process variable optimization.

In the latter study, fines ranged from 0.04% to 0.38% of the total wafer weight and were related to initial pressing pressure after aging. Development of an understanding of this relationship would provide a valuable tool in selecting an ultimate set of process conditions for fabricating an actual fuel form, particularly when optimum wafer properties can be achieved from a wide range of process conditions.

SECTION 5
ASSESSMENT OF Tm_2O_3 AS A POTENTIAL HEAT SOURCE EMBODIMENT

The objective of this study was to show the feasibility of Tm_2O_3 as an isotopic heat source embodiment. The basic behavioral patterns of Tm_2O_3 were established from containment compatibility studies, phase diagram and melting point determinations, theoretical dose rate calculation and experimental measurements, thermal profiles and environmental exposure. Falling in these basic behavioral patterns was the effect of processing parameters on Tm_2O_3 properties.

DESIGN AND PROPERTIES

The experimentation was designed to encompass with margin the anticipated operating temperatures and conditions of a Tm_2O_3 fueled capsule. Several encapsulant materials of current favor, Hastelloy X, Hastelloy C-276, Haynes 25, T-111, TZM and tungsten were used in compatibility experiments and to generate the thermal profiles and centerline melt temperatures obtained in the fuel capsule parametric design study.

The melting points determined for Tm_2O_3 and Yb_2O_3 were 2301 and $2327 \pm 33.5^\circ\text{C}$. The cubic crystalline structure of both Tm_2O_3 and Yb_2O_3 was maintained up to the melting point and the system was typical of a solid solution system. Containment of $\text{Tm}_2\text{O}_3/\text{Yb}_2\text{O}_3$ over a wide range of temperatures to 2000°C for times to 10,000 hours was successfully achieved with the candidate encapsulant materials. Further, Tm_2O_3 was chemically inert with respect to the encapsulants, except for some x-ray evidence that tungsten interacts with Tm_2O_3 . The thermal stability exhibited herein supported the fuel capsule design study.

Thermal profiles generated from the fuel capsule parametric design study used the encapsulant materials previously mentioned, helium and argon as fill gases, three different power densities, and two basic types of encapsulation, (1) individually encapsulated wafers and (2) a bulk encapsulant stack of wafers. The results showed that bulk encapsulation leads to centerline temperatures that exceeded the melting point of the encapsulant or fuel in many instances. Individual encapsulation provided a much lower and acceptable centerline temperature in nine of the sets of conditions studied, particularly where power densities were similar to the 17 watts/cc achieved at Savannah River Laboratory. These activated fuel sources were also in the form of wafers.

The environmental behavior of $\text{Tm}_2\text{O}_3/\text{Yb}_2\text{O}_3$ was assessed by analysing wafers exposed to air, dynamic vacuum and static vacuum (tungsten encapsulated) at temperatures to 2000°C for times to 100 hours. Under these conditions, the $\text{Tm}_2\text{O}_3/\text{Yb}_2\text{O}_3$ cubic structure was maintained. Vapor phase mass transport was observed in the encapsulated samples, the amount being related to the Yb_2O_3 content. Containment in these instances was unaffected.

From these data it was concluded that the $\text{Tm}_2\text{O}_3/\text{Yb}_2\text{O}_3$ cubic structure was stable up to the melting point of $2301 \pm 33.5^\circ\text{C}$ and that $\text{Tm}_2\text{O}_3/\text{Yb}_2\text{O}_3$ can be successfully contained for times to 10,000 hours at temperatures to 1600°C . Containment materials having demonstrated compatibility with $\text{Tm}_2\text{O}_3/\text{Yb}_2\text{O}_3$ include Haynes 25, Hastelloy X, Hastelloy C-276, TZM and tungsten.

FABRICABILITY

Several sets of processing conditions were studied. These conditions included chemical processing of "as received" Tm_2O_3 , pressing pressure, sintering time/temperature/atmosphere (air, vacuum and hydrogen) and aging (500 hours at 1600°C followed by a thermal spike to 2000°C). The results of these experiments showed that high quality, high sintered density (95% of theoretical or better) wafers could be reproducibly fabricated by several different sets of conditions. From chemical processing to sintering the processes

were easily carried out and did not require the use of exotic equipment on materials.

As raw material is readily available and fabrication of wafers easily achieved, subsequent thermal neutron activation of these wafers could provide a relatively low cost fuel with relatively short lead times.

SAFETY

Excellent containment of $\text{Tm}_2\text{O}_3/\text{Yb}_2\text{O}_3$ has been demonstrated. Additionally a high degree of chemical resistance was experienced throughout these studies. The $\text{Tm}_2\text{O}_3/\text{Yb}_2\text{O}_3$ cubic structure was stable up to the melting point thereby eliminating the need to accommodate the expansion that results from phase changes. Excellent thermal, chemical and mechanical stability results after aging of samples. Initial studies show that fines generated upon impact may be controlled with process parameters including the use of additives. Improvement of mechanical strength in this sense coupled with the superior thermal, chemical stability already demonstrated would place Tm_2O_3 high on the list of viable fuel forms.

SECTION 6
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