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MASTER

FABRICATION, CHARACTERIZATION, AND
THERMAL-PROPERTY MEASUREMENTS OF
 $\text{ThO}_2\text{-UO}_2$ FUEL MATERIALS
(LWBR Development Program)

by

J. R. Springer, E. A. Eldridge, M. U. Goodyear,
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October 1, 1967

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FABRICATION, CHARACTERIZATION, AND THERMAL-PROPERTY
MEASUREMENTS OF ThO_2 - UO_2 FUEL MATERIALS

(LWBR Development Program)

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T. R. Wright, and J. F. Lagedrost

Thermophysical-property specimens of ThO_2 , ThO_2 -10 w/o UO_2 , and ThO_2 -20 w/o UO_2 were fabricated and characterized. Each material composition was represented by specimens with nominal densities of 95, 85, and 75 percent of theoretical. Thermal-diffusivity, linear-thermal-expansion, and specific-heat measurements were made over the temperature range from 300 to 1900 C and used to determine thermal conductivity.

Results of linear-thermal-expansion and specific-heat measurements were approximately the same for all materials. Values of linear thermal expansion ranged up to 2.2 percent in heating from room temperature to 2000 C. The specific heat ranged from 0.055 cal/(g)(C) at 0 C to 0.080 cal/(g)(C) at 2000 C. Thermal-diffusivity values ranged from $3.0 \times 10^{-2} \text{ cm}^2$ per sec at 300 C to $0.5 \times 10^{-2} \text{ cm}^2$ per sec at 1900 C. Thermal conductivities decreased in regular fashion with increased UO_2 content and porosity.

An equation is given which fits all of the data obtained; it is anticipated that it will fit the data for other compositions within the given limits.

INTRODUCTION

One of the most important limiting factors in reactor operation is the maximum temperature reached by its fuel. The maximum amount of heat that can be withdrawn from the fuel is determined in part by its thermal conductivity. The rate of heat transfer to the heat-exchange medium determines the temperature of the fuel materials. Great emphasis is placed, therefore, on the development of fuels with high thermal conductivities. Other requirements for solid materials to be useful as fuels include a high melting point, sufficient mechanical strength with resistance to thermal shock, good stability during irradiation at high temperatures, and others.

For a given solid fuel material, the thermal conductivity is highly dependent upon structure. Pore size, shape, distribution, and orientation play significant roles in materials which have densities less than 100 percent of theoretical. For high-depletion oxide-fueled reactors, the effects of porosity are particularly important since volume changes resulting from fission depletion may be accommodated by intentionally introduced porosity; thus, the fuel-element lifetime may be extended. Since increasing porosity leads to a decrease in thermal conductivity, the manner in which the porosity is introduced must be carefully controlled to ensure maximum fuel-element power capability. A reproducible fabrication technique and accurate methods of controlling thermal conductivity are essential. Addition of small amounts of extraneous materials to the base fuels, also significantly affect the conductivity.

For applications involving very high temperatures or corrosive atmospheres, ceramic fuel elements are of great interest. The $\text{ThO}_2\text{-UO}_2$ series is of special interest not only because of its high melting point (between 2870 and 3300 C), but also because of its possible use as a breeder. Since ThO_2 is a potential source of the secondary nuclear fuel U^{233} , the supply of fissionable material may be substantially increased. Although some testing of this material has been conducted, adequate information concerning its stability, thermal properties, fabricability, etc., is not available.

The objective of this program is twofold; first, to evaluate the performance of ThO_2 and binary alloys of ThO_2 - UO_2 (fabricated by a special technique) for fuel applications, and second, to determine the fundamental effect of porosity on thermal conductivity for these materials. The first part of this report is concerned with the fabrication and characterization of these materials; the later parts, with thermal-property measurements and analyses.

SPECIMEN FABRICATION AND CHARACTERIZATION

Objective

The objective of this task of the program was to fabricate and characterize suitable physical-property specimens from selected ThO_2 - UO_2 compositions. The selected binary compositions are defined in Table 1.

TABLE 1. ThO_2 -BASE BINARY FUEL COMPOSITIONS FOR
THERMAL-PROPERTY TEST SPECIMENS

Composition	Content				Desired Density, percent of theoretical	Theoretical Density of Composition, g per cm ³
	ThO ₂		UO ₂			
	W/O	M/O	W/O	M/O		
C-1	100		--	- -	≥ 95	10.00
C-2	100		--	- -	85	10.00
C-3	100		--	- -	75	10.00
D-1	90	90.20	10	9.80	≥ 95	10.09
D-2	90	90.20	10	9.80	85	10.09
D-3	90	90.20	10	9.80	75	10.09
E-1	80	80.36	20	19.64	≥ 95	10.19
E-2	80	80.36	20	19.64	85	10.19
E-3	80	80.36	20	19.64	75	10.19

Materials

Natural ceramic-grade UO_2 powder and ceramic-grade ThO_2 powder were obtained from a commercial vendor. The spectrographic analyses of the as-received UO_2 and ThO_2 are shown in Table 2.

TABLE 2. IMPURITY CONTENT OF AS-RECEIVED
 UO_2 AND ThO_2

Impurity	Impurity Content, ppm	
	UO_2	ThO_2
Aluminum	25	100
Chromium	50	75
Copper	--	10
Iron	100	100
Magnesium	50	5
Manganese	10	10
Molybdenum	25	10
Nickel	75	200
Silicon	75	50

Fabrication Procedures

All specimens were prepared according to a fabrication technique involving the formation of granules from blended powders which had been wet mixed with suitable amounts of binder and solvent.

The granules were dried and then calcined at 900 C in flowing CO_2 in order to remove the binder. Calcined granules were sintered for 12 hr at 1725 C in flowing dry hydrogen, after which they were comminuted to a mean particle diameter approximately 1 μ (determined by the Coulter Counter Technique) by wet-ball milling in a rubber-lined mill for 16 hr with stainless steel balls as a grinding medium.

After removal of essentially all the iron contamination (from the milling) by a leaching and washing technique, the comminuted powder was dried, wet mixed with the binder and solvent, regranulated, dried, and hydrostatically pressed at 60,000 psi into rods of the appropriate sizes required for the thermal-property measurements. The rods were calcined in flowing CO_2 at 900 C to remove the binder and then sintered to essentially full density at 1750 C for 14 hr in flowing dry hydrogen. The pure thorium specimens were fabricated from the as-received powder and were not subjected to the double sintering process.

The low-density specimens of 85 and 75 percent of theoretical were prepared by incorporating 2.0 w/o and 4.75 w/o, respectively, of minus 140 plus 200-mesh table sugar into the powder blends during the final wet-mixing treatment. Carbon from the sugar addition was completely removed during the final CO_2 calcining treatment.

Following densification, the rods were cut and ground to size under undiluted cutting oil. The thermal-diffusivity specimens were supplied for testing in the form of 3/8-inch diameter rods approximately 3/4- to 1-inch in length, from which wafers of suitable thickness could be cut. Thermal-expansion specimens were 3/8 inch in diameter by 1-3/4 to 1-1/2 inch long.

The machined specimens were ultrasonically cleaned for 10 min in trichloroethylene and ethyl alcohol before characterization. A typical set of specimens is shown in Figure 1.

Specimen Characterization

Specimen characterization consisted of density and porosity measurements, X-ray diffraction, chemical analysis for both compositional control and the U^{+6} concentration (O/U ratio), spectrographic analysis, and metallographic examination.

FIGURE 1. TYPICAL THERMAL-PROPERTY TEST SPECIMENS

Density and Porosity

Densities were calculated from direct measurements and weights of the machined and cleaned specimens. Porosity values were calculated from the bulk, apparent, and true volume relationships. The apparent volume was determined by CCl_4 immersion, while the true volume was calculated from the theoretical densities of the compositions. A description of the techniques and formulas utilized is given in Appendix A. The size, density, and porosity of the specimens are shown in Table 3.

The diameters listed in Table 3 are the average micrometer measurements of ten values taken along the length of each specimen. Length dimensions are averages of five measurements.

X-Ray Diffraction

Representative samples of the $\text{ThO}_2\text{-UO}_2$ primary compositions were submitted for examination by X-ray diffraction. A representative sample of Composition E-3 was also examined, as specimens of this composition were fabricated from a different powder batch than Composition E-1. The lattice parameters were determined from X-ray diffraction strip-chart recordings of intensity versus diffraction angle 2θ using nickel-filtered copper radiation, in which the interplanar spacing (d), determined from Bragg's Law, and the Miller indices of the [622] plane were used to calculate the lattice parameters. The results are shown in Table 4.

TABLE 4. X-RAY DIFFRACTION RESULTS ON AS-FABRICATED SPECIMENS OF ThO_2 -BASE COMPOSITIONS

Composition	Content, w/o		Crystal Structure	Lattice Parameter, $\text{\AA} \pm 0.001$
	ThO_2	UO_2		
C-1	100	--	FCC	5.594
D-1	90	10	FCC	5.586
E-1	80	20	FCC	5.580
E-3	80	20	FCC	5.567

TABLE 3. SIZE, DENSITY, AND POROSITY OF ThO₂-BASE THERMAL-PROPERTY TEST SPECIMENS

Composition	Specimen	Diameter, in.	Length, in.	Weight, gm.	Density, gm/cm ³	Density, (a) percent of theoretical	Porosity, percent		
							open	closed	total
C-1 (ThO ₂)	TE-1	0.3734	1.7450	29.3423	9.3700	93.37	0.45	6.18	6.63
	TE-2	0.3730	1.7451	29.3291	9.3856	93.86	- -	- -	- -
	SH-1	0.3728	1.2451	21.0720	9.4616	94.62	0.55	4.83	5.38
	SH-2	0.3735	1.2444	21.0761	9.4329	94.33	- -	- -	- -
	TD-1	0.3735	0.7460	15.5720	9.3862	93.86	1.20	4.94	6.14
	TD-2	0.3735	0.7471	12.6540	9.4341	94.34	- -	- -	- -
C-2 (ThO ₂)	TD-1	0.3757	1.0051	15.8252	8.6670	86.67	3.27	10.06	13.33
	TD-2	0.3755	1.0016	15.7091	8.6427	86.43	4.09	9.48	13.57
C-3 (ThO ₂)	TD-1	0.3748	1.0003	13.2736	7.3395	73.40	11.75	14.85	26.60
	TD-2	0.3746	1.0002	13.2604	7.3403	73.40	9.65	16.95	26.60
D-1 (ThO ₂ -10.3 w/o UO ₂)	TE-1	0.3754	1.7478	30.1540	9.5195	94.61	0.22	5.38	5.60
	TE-2	0.3755	1.7519	30.2331	9.5150	94.57	- -	- -	- -
	SH-1	0.3754	1.5030	25.9449	9.5263	94.68	0.05	5.32	5.37
	SH-2	0.3754	1.4992	25.8910	9.5296	94.71	- -	- -	- -
	TD-1	0.3755	1.0019	17.3453	9.5445	94.86	0.12	5.13	5.25
	TD-2	0.3754	0.9996	17.2967	9.5526	94.94	- -	- -	- -
D-2 (ThO ₂ -10.3 w/o UO ₂)	TD-1	0.3750	0.7500	11.4434	8.4341	83.83	0.75	15.56	16.29
	TD-2	0.3747	0.7474	11.5006	8.4862	84.34	0.65	15.15	15.80
D-3 (ThO ₂ -10.3 w/o UO ₂)	TD-1	0.3745	0.9993	13.4061	7.4321	73.86	11.75	14.38	26.13
	TD-2	0.3764	0.9968	13.4369	7.3922	73.47	10.41	16.11	26.52
E-1 (ThO ₂ -20.4 w/o UO ₂)	TE-1	0.3605	1.7440	28.1033	9.6343	95.08	0.20	4.71	4.91
	TE-2	0.3495	1.7420	26.3110	9.6074	94.81	- -	- -	- -
	SH-1	0.3601	1.2480	20.2776	9.7357	96.08	0.01	3.90	3.91
	SH-2	0.3596	1.2520	20.0466	9.6211	94.95	- -	- -	- -
	TD-1	0.3592	0.9717	15.4581	9.5804	94.55	0.35	5.10	5.45
	TD-2	0.3598	0.9692	15.5007	9.5991	94.73	- -	- -	- -
E-2 (ThO ₂ -20.4 w/o UO ₂)	TD-1	0.3093	0.7432	7.6150	8.3224	82.13	1.62	16.24	17.86
E-3 (ThO ₂ -20.1 w/o UO ₂)	TD-1	0.3753	0.9966	14.2100	7.8656	77.10	4.25	18.64	22.89
	TD-2	0.3747	0.9988	14.2818	7.9132	77.57	4.46	17.96	22.42

(a) Based on theoretical densities calculated from measured chemical analyses and lattice parameters of actual specimens.

Chemical and Spectrographic Analyses

The chemical analysis, calculated theoretical densities, O/U ratios, and U^{+6} concentrations are shown in Table 5. Since the chemical composition of Compositions D-2 and D-3 is the same as that of Composition D-1, and that of Composition E-2 is the same as that of Composition E-1, only Compositions D-1, E-1, and E-3 (prepared from a different powder batch than E-1) were analyzed by wet chemical techniques.

The O/U ratio of UO_2 was measured by polarographic techniques ⁽¹⁾ on all the mixed-oxide compositions and their corresponding U^{+6} concentration was calculated.

The impurity content was determined by spectrographic analyses of representative samples of the primary compositions and Compositions D-3 and E-3 (Table 6). The high iron content listed for Composition E-1 is believed to be in error since metallic inclusions were not observed metallographically, and all procedures for material preparation were identical with those reported previously. In addition, the chromium and nickel contents are within reason. Otherwise, the impurities present were within the allowable tolerances.

Metallographic Examination

All specimens were examined metallographically in both the as-polished and etched conditions. The resulting microstructures are shown in Figures 2 through 10. The etchant was a boiling solution of NH_4F and H_2O (1:1 ratio) and the metallographic procedures followed were the same as those described by Cohen and Schaner ⁽²⁾ for the UO_2 - ZrO_2 system. The inhomogeneities in the as-polished microstructure in Figure 9 are shallow pores filled with epoxy mounting material and are not inclusions in the material.

(1) References at end of text.

TABLE 5. CHEMICAL ANALYSIS, CALCULATED THEORETICAL DENSITIES, O/U RATIOS, AND U^{+6} CONCENTRATIONS FOR ThO_2 -BASE COMPOSITIONS

Composition	Content, w/o		Calculated Theoretical Density, ^(a) , g per cm ³	O/U Ratio	U^{+6} Concentration ^(b) , mg per g UO_2
	ThO_2	UO_2			
D-1	89.7	10.3	10.0613	2.005	3.8
D-2	(c)	(c)	(c)	2.005	3.8
D-3	(c)	(c)	(c)	2.003	2.5
E-1	79.6	20.4	10.1325	2.005	4.7
E-2	(d)	(d)	(d)	2.001	0.97
E-3	79.9	20.1	10.2005	2.009	8.6

(a) Calculation technique and sample calculation are shown in Appendix B.

(b) O/U Ratios and U^{+6} contents determined by polarographic techniques.

(c) Same as Primary Composition D-1.

(d) Same as Primary Composition E-1.

TABLE 6. SPECTROGRAPHIC ANALYSIS OF ThO_2 -BASE COMPOSITIONS^(a)

Impurity	Impurity Content for Indicated Composition, ppm				
	C-1 (ThO_2)	D-1 (ThO_2 -10 w/o UO_2)	D-3 (ThO_2 -10 w/o U_2)	E-1 (ThO_2 -20 w/o UO_2)	E-3 (ThO_2 -20 w/o UO_2)
Aluminum	15	50	10	20	20
Chromium	<2.5	N.D.	10	40	3
Copper	1	5	1	3	1
Iron	20	5	80	320	20
Magnesium	2.5	1	0.5	40	0.5
Manganese	T	N.D.	T	2	T
Molybdenum	<3	N.D.	<3	<2.5	<3
Nickel	10	5	2.5	10	<2.5
Silicon	40	50	40	40	10

(a) T = trace

N.D. = not detected.

100X

6B461

As Polished

250X

6B463

Etched

500X

6B464

Etched

750X

6B465

Etched

FIGURE 2. MICROSTRUCTURES OF COMPOSITION C-1 (ThO_2 ;
APPROXIMATELY 95 PERCENT DENSE)

100X

7B151

As Polished

250X

7B152

Etched

500X

7B153

Etched

750X

7B155

Etched

FIGURE 3. MICROSTRUCTURES OF COMPOSITION C-2 (ThO_2 ; APPROXIMATELY 85 PERCENT DENSE)

100X

6B462

As Polished

250X

6B466

Etched

500X

6B467

Etched

750X

6B468

Etched

FIGURE 4. MICROSTRUCTURES OF COMPOSITION C-3 (ThO_2 ; APPROXIMATELY 75 PERCENT DENSE)

100X

4A385

As Polished

250X

4A387

Etched

500X

4A388

Etched

750X

4A389

Etched

FIGURE 5. MICROSTRUCTURES OF COMPOSITION D-1 (ThO_2 -10 w/o UO_2 ; APPROXIMATELY 95 PERCENT DENSE)

50X

5A154

As Polished

100X

5A155

As Polished

250X

5A156

Etched

750X

5A157

Etched

FIGURE 6. MICROSTRUCTURES OF COMPOSITION D-2 (ThO_2 -10 w/o UO_2 ; APPROXIMATELY 85 PERCENT DENSE)

100X

6B237

As Polished

250X

6B238

Etched

500X

6B239

Etched

750X

6B240

Etched

FIGURE 7. MICROSTRUCTURES OF COMPOSITION D-3 (ThO_2 -10 w/o UO_2 ; APPROXIMATELY 75 PERCENT DENSE)

100X

9B119

As Polished

250X

9B121

Etched

500X

9B122

Etched

750X

9B123

Etched

FIGURE 8. MICROSTRUCTURES OF COMPOSITION E-1 (ThO_2 -20 w/o UO_2 ; APPROXIMATELY 95 PERCENT DENSE)

100X

9B147

As Polished

250X

9B148

Etched

500X

9B149

Etched

750X

9B150

Etched

FIGURE 9. MICROSTRUCTURES OF COMPOSITION E-2 (ThO_2 -20 w/o UO_2 ; APPROXIMATELY 85 PERCENT DENSE)

100X

3B962

As Polished

250X

3B964

Etched

500X

3B965

Etched

750X

3B966

Etched

FIGURE 10. MICROSTRUCTURES OF COMPOSITION E-3 (ThO_2 -20 w/o UO_2 ; APPROXIMATELY 75 PERCENT DENSE)

Posttest Examination

After testing, representative samples of the $\text{ThO}_2\text{-UO}_2$ primary compositions were submitted for the determination of the U^{+6} concentration, X-ray diffraction, and metallographic examination, while the ThO_2 primary composition was only examined metallographically. The results are summarized in Table 7 along with test parameters.

Specimens of the primary compositions were examined in both the as-polished and etched conditions at magnifications up to and including 750X. The resulting microstructures are shown in Figures 11 through 14, along with the pretest microstructures for purposes of comparison.

The specimens for the most part closely resembled the pretest microstructures. The photomicrographs of Composition C-1, shown in Figure 11, indicate that the posttest material has experienced slight grain growth or annealing. However, the porosity appeared unaffected with respect to amount, distribution, and shape after testing. The porosity of the posttest material for Composition D-1 (Figures 12 and 13) appears to have increased slightly, but this appearance is due to slight overetching of the microstructure. There is no apparent variation in the grain structure of the posttest material when compared to the pretest material, nor of the tested specimens with respect to the axial and radial directions of the fabricated rod. Cracking occurred in both the axial and radial thermal-diffusivity specimens tested for Composition D-1, with cracking being more severe in the radial specimen. No variation in the grain structure or porosity of the posttest material was observed for Composition E-1 when compared with the pretest material, as shown in Figure 14.

The oxygen content of Compositions D-1 and E-1 increased during testing as evidenced by the change in their O/U ratios (see Table 7). No change in the lattice parameter was observed for Composition D-1 whereas a slight decrease was observed for Composition E-1. A slight decrease in the lattice parameter because of the increased oxygen content would be expected.

TABLE 7. POSTTEST SPECIMEN DATA AND TEST PARAMETERS

Composition	Content, w/o		Lattice Parameter, A ± 0.001	O/U Ratio (a)	U^{+6} Content, mg per g UO_2	Test Parameters			
	ThO_2	UO_2				Specimen	Temperature, C	Time, min	Atmosphere
C-1	100	--	--	--	--	Thermal Expansion	2000	5	Argon
D-1	90	10	5.586	2.021	18.5	Thermal Diffusivity	1850	15	Vacuum
E-1	80	20	5.573	2.011	9.8	Thermal Expansion	2000	5	Argon

(a) O/U ratio and U^{+6} contents determined by polarographic techniques.

250X

6B463

Etched

750X

6B465

Etched

a. Before Testing

250X

OC138

Etched

750X

OC140

Etched

b. After Testing

FIGURE 11. MICROSTRUCTURES OF A THERMAL-EXPANSION TEST SPECIMEN OF COMPOSITION C-1 (ThO_2 ; APPROXIMATELY 95 PERCENT DENSE) BEFORE AND AFTER TESTING

250X

Etched

4A387

a. Before Testing

250X

Etched

3C576

b. After Testing

FIGURE 12. MICROSTRUCTURES OF A THERMAL-DIFFUSIVITY TEST SPECIMEN OF COMPOSITION D-1 (ThO_2 -10 w/o UO_2 ; APPROXIMATELY 95 PERCENT DENSE) BEFORE AND AFTER TESTING (AXIAL SECTION)

250X

Etched

3C582

FIGURE 13. MICROSTRUCTURE OF A THERMAL-DIFFUSIVITY
TEST SPECIMEN OF COMPOSITION D-1 (ThO_2 - 10 w/o UO_2 ;
APPROXIMATELY 95 PERCENT DENSE)
AFTER TESTING (RADIAL SECTION)

250X

9B121

Etched

750X

9B123

Etched

a. Before Testing

250X

OC145

Etched

750X

OC148

Etched

b. After Testing

FIGURE 14. MICROSTRUCTURES OF A THERMAL-EXPANSION TEST SPECIMEN OF COMPOSITION E-1 (ThO_2 -20 w/o UO_2 ; APPROXIMATELY 95 PERCENT DENSE) BEFORE AND AFTER TESTING

Tungsten Coating Examination

For the thermal-diffusivity measurements, it was necessary to apply a metallic coating to each face of the disk specimen to prevent direct transmission of radiated energy during measurements. This is necessary to satisfy a boundary condition of the measuring technique for non-opaque materials.

In this program, thin layers of tungsten were vapor deposited to each face of the diffusivity specimens. Prior to the deposition, the specimen was polished and cleaned. The thickness of the deposited coating, although uniform for a given specimen, varied somewhat among the specimens, but in most cases was probably in the range from 0.5 to 30 μ . This variation could not measurably affect the results of the measurements.

Figure 15 shows a typical tungsten coating.

THERMAL-PROPERTY MEASUREMENTS

Approach

To evaluate the performance of a fuel material, the thermal conductivity-temperature relation must be accurately known. Although many methods exist for determining this relation, a limitation is the large specimen size required for most steady-state techniques. For this program conductivity measurements were required on specimens as small as 0.20 in. in diameter by 0.040 in. long, although 0.375 in. was the customary diameter.

The method determined to be most suitable for the measurements is a transient technique in which thermal conductivity is calculated from measurements of thermal diffusivity, specific heat, and density. These three property measurements require relatively simple, small, rod or disk-shaped specimens. The thermal conductivity at a given temperature is equal to the product of thermal diffusivity, specific heat, and density at the same temperature. The three measured properties are also of value independently in reactor design and for evaluation of performance under transient conditions. The transient method also has the advantage that no measurement of heat flux is required and steady-state conditions are unnecessary. This eliminates problems often encountered in steady-state methods, particularly for poor thermal conductors.

750X

As-polished

3C277

FIGURE 15. MICROSTRUCTURE OF TYPICAL THERMAL DIFFUSIVITY SPECIMEN SHOWING VAPOR-DEPOSITED TUNGSTEN COATING (COATING THICKNESS $\sim 2.5 \mu$)

Measuring Techniques

Enthalpy and Specific Heat

Measurements of enthalpy from which specific heat is calculated were made in a Bunsen ice calorimeter. Figure 16 is a photograph of the apparatus and Figure 17 is a sketch of the calorimeter well.

In the Bunsen ice calorimeter heat is released by the specimen to its capsule, thus melting ice which is in equilibrium with water in the closed calorimeter well. As the ice melts to water there is a reduction in volume. Mercury entering the system from an external accounting system to equalize the volume is accurately weighed. Both Battelle-Columbus and the National Bureau of Standards have measured the ice calorimeter heat quantity versus mercury weight constant as 270.48 joules per g. This is the constant of the measuring method and should not vary among Bunsen ice calorimeters. It is a function of the volume change of ice melting to water and the heat of fusion involved in the change of state. Since specimen heat content is measured at the ice point, as ice melts to water, there is no need to measure temperature in the calorimeter well, as is necessary in copper-block or bath calorimeters.

For the present measurements, the specimens were wrapped in molybdenum foil and sealed in a tantalum capsule under 0.5 atm of helium. The capsules were sealed by electric welding. An empty capsule was fabricated, assembled, and welded in the same manner as the previous capsule including the same weight of molybdenum foil used to wrap around the specimen.

As the previously heated, encapsulated specimen is dropped into the central chamber of a double-walled vessel, it gives up heat to the ice-covered finned section which is enclosed in water in equilibrium. The portion of heat released by the specimen only is determined by subtracting from the total that contribution made by the capsule. This latter amount is evaluated by a separate drop of an empty capsule.

FIGURE 16

BUNSEN ICE CALORIMETER

FIGURE 17

The furnace for heating of the specimen uses a double-walled tantalum element capable of operation to over 2000 C. It is operated under vacuum. Specimen temperatures are measured either by suitably positioned thermocouples or by an optical pyrometer which can view the capsule. Calibration of the apparatus is checked frequently, using both thermocouples and optical pyrometers, with National Bureau of Standards Al_2O_3 as the specimen standard. Measured enthalpies agree routinely with NBS values for this standard to within 1 percent.

The error of enthalpy measurements made as described is estimated to not exceed ± 1 percent. The error of specific-heat values calculated from equations fitted to curves through the plotted enthalpy data is estimated to not exceed ± 3 percent.

Linear Thermal Expansion and Density

Linear-thermal-expansion measurements were made in a recording dilatometer. Figure 18 is a photograph of the high-temperature recording dilatometer. Figures 19 and 20 are a photograph and sketch, respectively, showing design details.

The specimen is a right cylinder positioned vertically between two small platforms in an electric tube furnace. Each platform is supported by three rods which extend downward to a cooled zone outside the furnace. A fine-grained high-purity graphite is used for these components.

A change of length of the specimen, resulting from thermal expansion or contraction, causes a relative displacement of the two platforms which is transferred through the structures to a linear-variable-differential transformer (LVDT). In this specialized transformer, a displacement of the movable core causes a proportional emf change in the secondary coil, which when amplified drives one axis of a flat-bed x-y plotter.

The emf from a thermocouple attached to the specimen drives the other axis of the plotter, thus continuously plotting linear expansion as a function of temperature. The signal from a second thermocouple is used for automatic temperature control. Above about 1100 K the thermocouple temperature measurements are compared with optical pyrometer readings of the specimen surface.

HIGH-TEMPERATURE RECORDING DILATOMETER

FIGURE 18

FIGURE 19

HIGH-TEMPERATURE DILATOMETER ASSEMBLY

Provision was made to protect the specimen and tube furnace element by an inert atmosphere. Covers were used on top of the tabular furnace and the surrounding thermal-radiation shielding to minimize thermal convection. The specimen temperature was controlled by a cam-programmed, fully-proportional temperature controller. The cam on the programmer was cut to provide heating and cooling rates of approximately 7 C per min.

The recording dilatometer is calibrated using a material of known expansion. Any deviation from this known expansion is applied to the unknown sample as a correction. The main source of error is expected to be temperature measurement and the accuracy of the standard materials. The error in the linear-thermal-expansion measurements is estimated to not exceed ± 2 percent.

Data of linear thermal expansion versus temperature for solids are readily converted to density-at-temperature values. Volume-at-temperature values for isotropic materials are calculated from expansion data along one axis.

The expression used to calculate density at temperature for an isotropic solid is as follows:

$$\rho_T = \frac{\rho_o V_o}{V_T} \quad , \quad (1)$$

where

ρ_T = density at temperature

ρ_o = density at room temperature

V_o = relative volume at room temperature

V_T = relative volume at temperature.

The relative volumes of the specimens measured are calculated from thermal-expansion measurement using the following expression:

$$V_T = V_o [1 + (\Delta l)]^3 \quad , \quad (2)$$

where

(Δl) = linear thermal expansion of
an isotropic material.

The error of density-at-temperature data is estimated to not exceed ± 1 percent with the use of expansion data from the recording dilatometer.

Thermal Diffusivity

The method used for determining the thermal diffusivity of the given materials is commonly known as the flash-diffusivity method. It is based on the transient behavior of a specimen subjected to a short-time thermal pulse incident on one side of the specimen.

Description of Method. The technique employed by Battelle for diffusivity measurements is to position a thin, disk-shaped specimen in an isothermal zone of a furnace and to irradiate the front face by a short-duration (about 1 millisecon) laser pulse. As the heat pulse travels through the specimen, the temperature rise of the back face is recorded as a function of time, using an IR detector-oscilloscope-camera system. This temperature-time history of the back face is directly related to the thermal diffusivity of the specimen. Figure 21 shows a typical photograph of the oscilloscope trace of the temperature-time function.

Parker, et al.⁽³⁾ are usually credited as being the originators of the method and deriving the simple relationship

$$\alpha = \frac{0.139 L^2}{t_{1/2}}, \quad (3)$$

where

α = thermal diffusivity

L = specimen thickness

$t_{1/2}$ = time required for back face of specimen to reach one-half its maximum temperature rise.

This relationship involves several simplifying assumptions:

- (1) The heat flow is one-dimensional from the front face directly to the back face.

- (2) The incident heat pulse is of negligible duration compared to the time required for significant heat propagation through the specimen.
- (3) The incident heat pulse is uniformly absorbed on the front face of an opaque specimen.
- (4) Heat losses off the faces are negligible.
- (5) The temperature rise within the specimen is small enough to consider the thermal properties as constant.

The extent to which any or all of these assumptions is justified must be assessed for each individual case but, clearly, at high temperatures where radiation losses are significant further refinement is indicated. Other researchers⁽⁴⁻⁷⁾ as well as unpublished work at Battelle have made it possible to develop and improve the technique to the point where appropriate adjustments to experimental values determined by Equation (3) can be applied on a routine basis. One method consists of directly examining the shape of the heat-pulse curve and applying a correction factor developed by Cowen⁽⁶⁾. This method is used periodically for comparison with a simpler method used at Battelle based on the theory of Cape and Lehman⁽⁵⁾ and also Cowen⁽⁶⁾. With this method a correction factor is obtained from analytical solutions presented in the above references and verified by numerical thermal analysis performed at Battelle. For specimens with small lengths in comparison with diameters, a heat-loss parameter is calculated:

$$Y = 4 \sigma \epsilon T_o^3 \left(\frac{L}{K} \right) , \quad (4)$$

where

- σ = Stephen-Boltzman constant
- ϵ = emittance of specimen or coating
- T_o = ambient temperature, Kelvin
- L = specimen thickness
- K = thermal conductivity of specimen.

The thermal conductivity K is obtained from measurements of thermal diffusivity, density, and specific heat plus an estimate of the heat-loss correction. The correction factor is then obtained with this parameter (Y) from a theoretical heat-transfer solution discussed in the above references. Figure 22 presents the correction factor as a function of the heat-loss parameter Y . Multiplication of the appropriate correction factor by the measured diffusivity yields the corrected value.

Additional precautions must be taken when the sample material cannot be considered opaque to the initial laser radiation. In this case, the specimens must be coated with an opaque material. Energy may also be re-radiated inside the surface of non-opaque specimens. This radiant energy contribution to the heat flow has not at present been qualitatively isolated for transient situations. An opaque coating on the back side of the specimens, however, effectively prevents this radiation from reaching the detector directly. It is possible to assess qualitatively the radiant energy contribution in partially transparent materials by varying the thickness of the specimens. If the radiant energy contribution is significant, measurements of thermal diffusivity (and thus conductivity) should be dependent upon length, primarily because of reflection to the surfaces. Also, measurements are expected to be dependent upon the emissive properties of the coating. Thus, careful analysis of the results of measurement for non-opaque materials must be made in order to apply them to the situation at hand, i.e., the size and shape of materials being considered. Materials in the immediate vicinity also must be taken into consideration in order to determine the conductivity which actually applies to the given situation.

In general, however, for partially transparent materials, measurements of diffusivity at sufficiently high temperatures (depending on the material) should yield values higher than those expected from phonon conduction alone since the radiation component of conductivity, K_{rad} , is proportional to $\frac{T^3}{\alpha}$ (21), where α is the absorption coefficient (the dependence of α on wavelength further complicates the problem). Thus, for a given material, if the temperature dependence of conductivity, as determined from diffusivity measurements, is satisfied over a wide temperature range by a relation of the form:

FIGURE 21. PHOTOGRAPH OF TYPICAL OSCILLOSCOPE TRACE OF TEMPERATURE-TIME HISTORY OF THERMAL DIFFUSIVITY SPECIMEN

FIGURE 22. DIFFUSIVITY-MEASUREMENT CORRECTION FOR RADIATION LOSS

$$K = \frac{1}{A + BT} \quad , \quad (5)$$

where A and B are constants, it may be tacitly assumed that the radiant energy contribution to conductivity is negligible.

Description of Apparatus. Figure 23 is a photograph representing Battelle's thermal-diffusivity apparatus. The tube furnace and thermal shielding are inside a vacuum/atmosphere, water-cooled vessel. This chamber, with other parts of the apparatus, is mounted on a metal stand which also holds the vacuum system and vacuum gages. The vacuum system, consisting of a mechanical pump and diffusion pump, gives specimen vacuum protection to about 2×10^{-6} torr.

The liquid-nitrogen-cooled laser head uses a ruby crystal $3/8$ in. in diameter and $6-1/2$ in. long. The rated output of this laser is in the range of 20 to 30 joules. The laser power supply can be adjusted to fire the laser at any desired voltage above threshold, to about 2800, and is fired by a trigger pulse delay unit.

The radiation detector is shown in position to view the back face of the specimen. A lead sulfide cell is used as the radiation receiver and is cooled by liquid nitrogen to increase its sensitivity. An optical system focuses a small diameter of the back face of the specimen on the radiation receiver. The detector is used in one arm of a bridge circuit, the unbalance of which is shown on an oscilloscope and photographed by a camera.

Specimen temperatures are measured by a thermocouple with the head placed near the specimen.

Figure 24 is a sectional sketch of a thermal-diffusivity apparatus. The specimen is a small disk nominally $3/8$ in. in diameter with a thickness depending upon the material. It is held in a compatible holder inside a double-walled tantalum tube heater. Thermal radiation shielding surrounds the heater.

The vacuum/atmosphere chamber has windows in its walls so placed that the pulsed beam of the laser is directed on one side of the specimen and the radiation detector views the other side through an optical system.

FIGURE 23

THERMAL DIFFUSIVITY APPARATUS

FIGURE 24

Preparation of Specimens For Diffusivity Measurements. The sample materials as fabricated were in the form of right cylinders, 0.375 in. in diameter by 0.75 to 1.00 in. long. Thin wafers 0.030 to 0.060 in. thick were cut from these cylinders using a high-speed silicon carbide wheel. The wafers were cleaned ultrasonically in ethyl alcohol and polished with diamond dust. Densities for these specimens were determined by weight and dimensional measurements. If examination under the microscope showed that any chipping had occurred, both weight and dimensional and wet densities were measured. Postmeasurement densities were also determined and averaged with the premeasurement values to arrive at the densities used for calculating the thermal conductivity. These values differed by as much as 2 percent, with premeasurement values always higher. After polishing, a thin tungsten coating was applied to the ends of the specimen by an electron-beam evaporation technique. The coating was thick enough to absorb or reflect all of the energy of the laser pulse, yet thin enough to have negligible effect on the diffusivity of the specimens. The thickness of the coating was of the order of 0.5 to 30 μ as measured on photomicrographs.

Error Analysis for Diffusivity Measurements. The accuracy of measurements by the above technique is quite reasonable. It is based on diffusivity measurements made on standard materials. In the temperature range from 300 to 1000 C these materials include Armco iron (Round Robin iron) and Type 347 stainless steel. From 300 to 2000 C, arc-cast molybdenum is used. The diffusivity values for these materials were obtained through both transient and steady-state techniques.

In general, values for thermal diffusivity measured by this apparatus differ by less than 5 percent from the standard values. Periodic checks are made to maintain this accuracy and to determine the stability of the apparatus.

The precision or repeatability of measurements determined from the standard deviation of data points obtained on both heating and cooling from a given, drawn in, smooth curve is usually less than 2 percent. At the lowest temperatures, around 300 C, the precision is poorest. This results from the low intensity of radiation from the specimen giving rise to a small signal-to-noise ratio for the detector.

A breakdown of potential errors is given in Appendix C.

Results of Thermal-Property Measurements

Specific Heat

Table 8 gives the experimental enthalpy values for ThO_2 , ThO_2 -10 w/o UO_2 , and ThO_2 -20 w/o UO_2 . Figures 25, 26, and 27 show graphically the enthalpy-temperature relation for the three curves.

The constants of a power series equation relating enthalpy and temperature from 0 to 2000 C were determined by the method of least squares and are as follows:

for ThO_2

$$H = -18.44 + 6.027 \times 10^{-2} T + 4.562 \times 10^{-6} T^2 + 416.9 T^{-1}, \quad (5)$$

for ThO_2 -10 w/o UO_2

$$H = -19.95 + 6.319 \times 10^{-2} T + 3.245 \times 10^{-6} T^2 + 628.4 T^{-1}, \quad (6)$$

for ThO_2 -20 w/o UO_2

$$H = -20.83 + 6.465 \times 10^{-2} T + 3.133 \times 10^{-6} T^2 + 767.7 T^{-1}, \quad (7)$$

where

H = enthalpy, cal/per g

T = temperature, K.

The first derivatives of Equations 5, 6, and 7 give the specific heat equations as follows:

for ThO_2

$$C_P = 6.027 \times 10^{-2} + 9.124 \times 10^{-6} T - 416.94 T^{-2}, \quad (8)$$

for ThO_2 -10 w/o UO_2

$$C_P = 6.319 \times 10^{-2} + 6.490 \times 10^{-6} T - 628.4 T^{-2}, \quad (9)$$

for ThO_2 -20 w/o UO_2

$$C_P = 6.465 \times 10^{-2} + 6.266 \times 10^{-6} T - 767.7 T^{-2}, \quad (10)$$

TABLE 8. OBSERVED ENTHALPY VALUES FOR ThO_2 ,
 ThO_2 -10 w/o UO_2 and ThO_2 -20 w/o UO_2

ThO_2		ThO_2 -10 w/o UO_2		ThO_2 -20 w/o UO_2	
Temperature, C	Enthalpy, cal per g	Temperature, C	Enthalpy, cal per g	Temperature, C	Enthalpy, cal per g
0	0	0	0	0	0
101	5.77	67	3.80	51	2.83
101	5.80	68	3.85	52	2.92
255	15.40	156	9.12	142	8.24
259	15.58	156	9.15	143	8.36
404	25.11	262	15.75	239	14.47
607	25.23	263	15.84	245	14.85
846	38.90	304	18.56	351	22.01
939	54.86	403	25.15	354	22.15
999	61.38	4.07	25.43	499	32.13
1105	65.88	533	33.99	506	32.64
1243	74.47	536	34.30	654	43.07
1504	83.18	697	45.43	880	58.57
1673	103.87	835	55.06	893	58.67
1865	109.83	884	58.34	1060	71.82
1985	115.18	950	62.82	1151	78.30
	131.33	996	65.95	1301	89.16
	141.54	1001	66.26	1503	104.36
		1103	73.17	1746	122.44
		1314	88.63	1997	142.68
		1497	102.17		
		1599	110.00		
		1799	125.25		
		1998	140.80

FIGURE 25. ENTHALPY OF ThO₂

FIGURE 26. ENTHALPY OF ThO₂ - 10 w/o UO₂

FIGURE 27. ENTHALPY OF ThO₂-20 w/o UO₂

where

C_p = specific heat, cal per (g)(C)

T = temperature, K.

Table 9 gives the specific heat values calculated from Equations (9), (10), and (11). Figures 28, 29, and 30 show the specific heat-temperature relation for the three materials. The values obtained for ThO_2 agree to within the reported accuracy (± 3 percent) with the best literature data^(*) in the temperature range of interest (300 to 1900 C). Figure 31 shows a composite of specific heat curves for the given materials. As anticipated, the specific heat varies little with the addition of UO_2 (up to 20 w/o).

No phase changes were noted for the materials over the measured temperature ranges. Enthalpy values were remeasured at low temperatures to determine whether the material changed after exposure to high temperature. No change was observed in the materials; they appear to be very stable between 0 and 2000 C.

Linear Thermal Expansion and Density

Tables 10 through 12 give the linear thermal expansion, relative volume, and density values for the ThO_2 - UO_2 materials. Figures 32 through 34 are plots of linear thermal expansion for the given materials. Comparison shows the results are about the same for the three materials. No phase changes or permanent length changes were noted for these materials. One curve was adequate to fit the data on both heating and cooling parts of the thermal cycle. The overall error for density values is estimated to not exceed ± 1 percent. Comparison with best literature values^(*) for ThO_2 shows agreement to this accuracy.

(*) See Appendix D.

TABLE 9. SPECIFIC HEAT VALUES FOR ThO_2 , ThO_2 -10 w/o UO_2 , and ThO_2 -20 w/o UO_2

Temperature, C	Specific Heat of Indicated Material, cal/(g)(C)		
	ThO_2	ThO_2 -10 w/o UO_2	ThO_2 -20 w/o UO_2
0	0.057 ₂	0.056 ₅	0.056 ₁
100	0.060 ₇	0.061 ₁	0.061 ₅
200	0.062 ₇	0.063 ₅	0.064 ₂
400	0.065 ₅	0.066 ₈	0.067 ₂
600	0.067 ₇	0.068 ₀	0.069 ₁
800	0.069 ₇	0.069 ₆	0.070 ₇
1000	0.071 ₆	0.071 ₁	0.072 ₂
1200	0.073 ₅	0.072 ₅	0.073 ₅
1400	0.075 ₄	0.073 ₈	0.074 ₉
1600	0.077 ₂	0.075 ₂	0.076 ₂
1800	0.079 ₁	0.076 ₅	0.077 ₅
2000	0.080 ₉	0.077 ₈	0.078 ₇

FIGURE 28. SPECIFIC HEAT OF ThO₂

FIGURE 29. SPECIFIC HEAT OF ThO₂-10w% UO₂

FIGURE 30. SPECIFIC HEAT OF $\text{ThO}_2\text{-20w\% UO}_2$

FIGURE 31. COMPOSITE OF SPECIFIC HEAT CURVES FOR ThO₂-UO₂ MATERIALS

TABLE 10. THERMAL EXPANSION AND DENSITY VALUES
FOR ThO_2

Temperature, C	Linear Expansion, Percent	Relative Volume	Density of Indicated Specimen, g per cm ³		
			Composition C-1 ^(a)	Composition C-2 ^(b)	Composition C
20		1.0000	9.49	8.65	7.34
200	0.13	1.0039	9.46	8.62	7.30
400	0.30	1.0090	9.41	8.58	7.26
600	0.49	1.0148	9.36	8.53	7.22
800	0.70	1.0211	9.30	8.47	7.17
1000	0.92	1.0279	9.24	8.42	7.13
1200	1.14	1.0346	9.18	8.35	7.09
1400	1.37	1.0417	9.11	8.29	7.04
1600	1.60	1.0488	9.05	8.24	6.99
1800	1.84	1.0562	8.99	8.19	6.94
2000	2.08	1.0637	8.93	8.13	6.89

(a) Value measured by weight and dimensions of linear expansion samples.

(b) Value measured by weight and dimensions of thermal diffusivity samples (bulk cylinders).

TABLE 11. THERMAL EXPANSION AND DENSITY VALUES FOR
 ThO_2 -10 w/o UO_2

Temperature, C	Linear Expansion, Percent	Relative Volume	Density of Indicated Specimens g per cm ³		
			Composition D-1(a)	Composition D-2(a)	Composition D-3(b)
20	0	1.0000	9.52	8.46	7.29
200	0.17	1.0051	9.47	8.42	7.25
400	0.36	1.0108	9.42	8.37	7.21
600	0.57	1.0172	9.36	8.33	7.16
800	0.77	1.0233	9.30	8.27	7.12
1000	0.99	1.0300	9.24	8.22	7.08
1200	1.21	1.0367	9.18	8.16	7.03
1400	1.44	1.0438	9.12	8.10	6.98
1600	1.67	1.0509	9.06	8.04	6.93
1800	1.90	1.0581	9.00	8.00	6.89
2000	2.14	1.0656	8.93	7.95	6.84

Value measured by weight and dimensions of linear expansion samples.

Value measured by weight and dimensions of thermal diffusivity samples (bulk cylinders).

TABLE 12. THERMAL EXPANSION AND DENSITY VALUES
FOR ThO_2 -20 w/o UO_2

Temperature,	Linear Expansion, Percent	Relative Volume	Density, of Indicated Specimen, g per cm ³		
			Composition E-1(a)	Composition E-2(b)	Composition E-3(b)
20	0	1.0000	9.61	8.32	7.90
200	0.16	1.0048	9.56	8.28	7.86
400	0.35	1.0105	9.51	8.23	7.82
600	0.55	1.0166	9.45	8.18	7.77
800	0.76	1.0230	9.39	8.13	7.72
1000	0.99	1.0300	9.33	8.08	7.67
1200	1.22	1.0370	9.27	8.02	7.62
1400	1.47	1.0448	9.20	7.96	7.56
1600	1.72	1.0525	9.13	7.90	7.51
1800	1.98	1.0606	9.06	7.84	7.45
2000	2.24	1.0687	8.99	7.79	7.39

(a) Value measured by weight and dimensions of linear expansion samples.

(b) Value measured by weight and dimensions of thermal diffusivity samples (bulk cylinders).

FIGURE 32. LINEAR THERMAL EXPANSION OF ThO₂

FIGURE 33. LINEAR THERMAL EXPANSION OF
ThO₂-10 w% UO₂

FIGURE 34. LINEAR THERMAL EXPANSION OF
ThO₂ - 20w% UO₂

Thermal Diffusivity

Figures 35 through 45 give the results of thermal diffusivity measurements on all fabricated materials. Tabular results are given in Appendix E. In most cases measurements were made on two thicknesses of the sample material with good agreement of data. Corrections for heat losses by radiation at high temperatures were made following the procedure as outlined previously. The maximum corrections, which occurred at 1900 C, were less than 25 percent, while corrections at 1000 C were usually of the order of 6 percent. Occasionally, cracking of the specimens occurred during heating or cooling (heating and cooling rates were approximately 10 C per min). If postmeasurement examination of the specimens revealed any cracking, the data were discarded. Also, if data obtained on the heating and cooling sections of the thermal cycle differed by more than ± 2 percent, either microcracking or evaporation of tungsten coating was assumed and the data were discarded. This occurred for only two specimens. In general, good agreement was obtained for heating and cooling data points. Comparison of these data with the best literature values available for ThO_2 ⁽⁹⁾ (diffusivity calculated from conductivity) shows fair agreement. The literature values show considerable scattering which is not unexpected since the values are apparently highly dependent on the fabrication technique. Data not included in this report are those obtained with specimens not coated with tungsten. It was not known initially whether or not the subject material was opaque to light from the laser (6943 A). Therefore, measurements were made on both coated and uncoated specimens. Diffusivity values obtained ranged from 10 to 50 percent higher for the uncoated specimens; this indicated partial transparency of the materials, and the data for these specimens were discarded. Other data not reported are those for the high-density ThO_2 -10 w/o UO_2 1 material (for measurement of heat flow in the radial direction). Measurements on this material were made early in the program and microcracks were later observed in the specimen. These were believed to be caused during machining of the specimen for diffusivity measurement.

FIGURE 35. THERMAL DIFFUSIVITY OF ThO_2 SAMPLE C-1, 93.0% TD

FIGURE 36. THERMAL DIFFUSIVITY OF ThO_2 SAMPLE C-2, 86.6 % TD

FIGURE 37. THERMAL DIFFUSIVITY OF ThO₂ SAMPLE C-3, 73.6 % TD

FIGURE 38. THERMAL DIFFUSIVITY OF ThO_2 -10 UO_2 SAMPLE D-1, 92.8% TD

FIGURE 39. THERMAL DIFFUSIVITY OF $\text{ThO}_2-10 \text{ UO}_2$ SAMPLE D-2, 82.1% TD

FIGURE 40. THERMAL DIFFUSIVITY OF ThO_2 -10 UO_2 SAMPLE D-3, 71.8% TD

FIGURE 41. THERMAL DIFFUSIVITY OF $\text{ThO}_2-20 \text{ UO}_2$ SAMPLE E-1, 92.5 % TD

FIGURE 42. THERMAL DIFFUSIVITY OF $\text{ThO}_2\text{-20 UO}_2$ SAMPLE E-2, 82.0 % TD

FIGURE 43. THERMAL DIFFUSIVITY OF ThO_2 -20 UO_2 SAMPLE E-3, 76.5 % TD

FIGURE 44. THERMAL DIFFUSIVITY OF ThO_2 SAMPLE C-2 $\perp$, 85.9% TD

FIGURE 45. THERMAL DIFFUSIVITY OF ThO_2 -20 UO_2 SAMPLE E-3 $\perp$ 76.5 % TD

Generally, the measurements were made on specimens cut normal to the axis of the prepared rods. In this way, heat flow is parallel to the axis. Figures 44 and 45 show data for specimens cut so that heat flux was normal to the axis, or in the radial direction.

Calculated Thermal Conductivity

Data. Tables 13, 14, and 15 give values at specific intervals of thermal conductivity calculated as the product of diffusivity, density, and specific heat. The values are displayed graphically in Figures 46 through 56. The data points displayed in these figures were obtained using actual diffusivity data points. The corresponding conductivity data are given in tabular form in Appendix E. Specific heat values were taken at corresponding temperatures from the smooth curves in the respective figures from 300 to 1900 C. Density values at the given temperatures were calculated from the proper data for linear thermal expansion. Density values reported in the section on linear thermal expansion are those for the as-fabricated bulk cylinders, while those used in calculating conductivity were for the individual specimens used for diffusivity measurements. Comparison of the present data with literature values is given in Appendix D.

Error Analysis. An estimate of errors for conductivity values is as follows:

<u>Measurement</u>	<u>Estimated Maximum Error</u>
Diffusivity	± 5 %
Specific Heat	± 3 %
Density	± 1 %

The maximum error involved in computed thermal conductivity is thus about ± 9 percent. However, a comparison of thermal conductivity values computed at Battelle for standard or reference materials over a long period of time indicates a more probable error of ± 6 percent.

TABLE 13. COMPUTED THERMAL CONDUCTIVITIES OF
ThO₂ MATERIALS

Temperature, C	Milliwatts/cm C		
	Composition	Composition	Composition
	C-1 93.9 Percent Dense	C-2 86.6 Percent Dense	C-3 73.6 Percent Dense
300	75.3	64.5	46.9
400	65.3	55.7	41.0
600	50.2	43.5	31.1
800	40.0	35.0	25.2
1000	34.3	29.7	20.9
1200	30.3	25.2	17.9
1400	26.4	21.2	15.6
1600	23.4	18.9	14.0
1800	20.9	17.6	12.6
1900	20.5	17.3	12.1

TABLE 14. COMPUTED THERMAL CONDUCTIVITIES OF
 ThO_2 -10 UO_2 MATERIALS

Temperature, C	Milliwatts/cm C		
	Composition	Composition	Composition
	D-1 92.8 Percent Dense	D-2 82.1 Percent Dense	D-3 71.8 Percent Dense
300	55.3	46.5	39.4
400	49.0	41.6	33.9
600	39.2	33.5	26.7
800	32.2	28.2	22.6
1000	27.8	24.1	19.4
1200	24.6	21.1	16.9
1400	21.9	18.3	14.9
1600	19.9	16.3	13.4
1800		14.3	12.0
1900		13.4	11.4

TABLE 15. COMPUTED THERMAL CONDUCTIVITIES OF
 ThO_2 -20 UO_2 MATERIALS

Temperature, C	Milliwatts/cm C		
	Composition	Composition	Composition
	E-1 92.5 Percent Dense	E-2 82.0 Percent Dense	E-3 76.5 Percent Dense
300	52.7	43.1	40.9
400	46.9	38.4	36.7
600	37.4	31.3	29.8
800	31.5	25.7	24.3
1000	27.0	22.1	20.5
1200	23.7	19.1	17.7
1400	21.1	17.4	15.8
1600	18.5	15.8	14.4
1800	16.6	14.1	13.3
1900	15.9	13.4	13.1

FIGURE 46. THERMAL CONDUCTIVITY OF C-1, ThO₂, 93.0% TD

FIGURE 47. THERMAL CONDUCTIVITY OF C-2, ThO₂, 86.6% TD

FIGURE 48. THERMAL CONDUCTIVITY OF C-3, ThO₂, 73.6% TD

FIGURE 49. THERMAL CONDUCTIVITY OF D-1 ThO_2 -10 UO_2 , 92.8% TD

FIGURE 50. THERMAL CONDUCTIVITY OF D-2 ThO₂-10 UO₂, 82.1% TD

FIGURE 51. THERMAL CONDUCTIVITY OF D-3 ThO_2 -10 UO_2 , 71.8% TD

FIGURE 52. THERMAL CONDUCTIVITY OF E-1 ThO₂-20 UO₂, 92.5% TD

FIGURE 53. THERMAL CONDUCTIVITY OF E-2 ThO₂-20 UO₂, 82.0% TD

FIGURE 54. THERMAL CONDUCTIVITY OF E-3 ThO₂-20 UO₂, 76.5% TD

FIGURE 55. THERMAL CONDUCTIVITY OF C-2 ThO_2 , 86.6% TD

FIGURE 56. THERMAL CONDUCTIVITY OF E-3 ThO_2 -20 UO_2 , 76.2% TD

ANALYSIS OF RESULTS

Analyses directed toward the objective of the subject program include the following:

- (1) Analysis of mechanisms contributing to the thermal conductivity of $\text{ThO}_2\text{-UO}_2$ materials
- (2) Relation between conductivity and porosity
- (3) Relation between conductivity and UO_2 content
- (4) Effect of variation of direction of heat flow on conductivity
- (5) Evaluation of fabrication technique.

Analysis of Mechanisms Contributing to Thermal Conductivity

Figures 57, 58, and 59 show composites of thermal conductivities for all axial-heat-flow samples measured. The shape of each curve at all temperatures is in excellent agreement with the $1/T$ law of Peierls⁽¹⁰⁾. At the higher temperatures, agreement is generally within the precision of measurement. This would be anticipated for a crystalline insulator where conduction is due primarily to phonon transport. The $1/T$ law follows from the theory of phonon interaction (Umklapp process in which two phonons interact to form a third).

Thermal conduction by the radiation mechanism should also be considered. For sintered oxides in general, however, the photon energy transfer process through the solid material becomes important only at temperatures greater than about 1500 C. If this component of conduction is appreciable, an upswing at high temperatures should occur since this contribution is proportional to T^3 .^(11, 12) Radiant heat transfer can occur also across the surface of a pore as well as through the dense material. This component⁽¹³⁾ also is proportional to T^3 and increases with pore size (assuming the material is fairly opaque). Thus an upswing in thermal conductivity should occur at high temperatures and the effect should be most pronounced for

FIGURE 57. THERMAL CONDUCTIVITY OF ThO₂ MATERIALS

FIGURE 58. THERMAL CONDUCTIVITY OF ThO₂-UO₂ MATERIALS

FIGURE 59. THERMAL CONDUCTIVITY OF ThO_2 -20 UO_2 MATERIALS

the material of lowest density. Since neither of these effects is evident, it is tacitly assumed that photon contribution to heat transport for these materials in the given temperature range is small compared with the phonon contribution.

An electronic contribution to thermal conductivity⁽¹¹⁾ would be expected to follow, to some degree, the Wiedemann-Franz relation:

$$K_e = L \tau T \quad , \quad (12)$$

where

K_e = Electronic component of thermal conductivity

L = Lorenz number

τ = Electronic conductivity

T = Absolute temperature.

Since little data are available on the mobilities of electrons and holes for the given materials it is difficult to evaluate the electrical conductivity. However, an upswing might be anticipated for the thermal conductivity at high temperatures. Again, this is not evidenced. It is assumed, therefore, that the main contribution to thermal conductivity is through the phonon mechanism.

Relation Between Conductivity and Porosity

Figures 57 through 59 show the relationship between conductivity and porosity p as defined by

$$\rho = \rho_0 (1-p) \quad , \quad (13)$$

where ρ is the density of the porous material and ρ_0 is 100 percent theoretical density. To evaluate the effect of porosity on conductivity, two distinct equations often used are the Loeb equation⁽¹²⁾,

$$K_p = K_{100} (1-p) \quad , \quad (14)$$

and the Maxwell-Eucken⁽¹¹⁾ relation in the form

$$K_p = K_{100} \left(\frac{1-p}{1+\beta} \right) , \quad (15)$$

where

K_p = thermal conductivity of sample with
percent of porosity p

K_{100} = conductivity of fully dense sample

β = parameter dependent on the size, shape,
degree of uniformity, and spatial
distribution of the porosity.

A true evaluation of these equations is seen more vividly in terms of thermal diffusivity rather than conductivity. Composites of the diffusivity curves are given in Figures 60 through 62. For conductivity defined in terms of diffusivity α , density ρ , and specific heat C as

$$K = \alpha \rho C, \quad (16)$$

the Loeb equation assumes the diffusivity to be constant for a given material, and independent of porosity. For the D and E materials, (Figures 61 and 62) this appears to be a reasonable approximation. For the E-2 and E-3 materials (porosities 18.0 and 23.5 percent respectively), the measured diffusivities are the same, at least to within the limits of the precision of measurements (± 2 percent). The largest deviation from this diffusivity-porosity relation occurs for the C material (Figure 60) where diffusivity decreases considerably with increasing porosity.

A better fit to the data is obtained with the Maxwell-Eucken relation. In Appendix F, it is shown that the ratio of diffusivities for samples of the same material with different porosities is given by

$$\frac{\alpha_{P_1}}{\alpha_{P_2}} = \frac{1 + P_2^\beta}{1 + P_1^\beta} , \quad (17)$$

FIGURE 60. COMPOSITE OF THERMAL DIFFUSIVITY CURVES FOR ThO_2

FIGURE 6I. COMPOSITE OF THERMAL DIFFUSIVITY CURVES FOR ThO₂-10 UO₂

FIGURE 62. COMPOSITE OF THERMAL DIFFUSIVITY CURVES FOR $\text{ThO}_2\text{-20 UO}_2$

Using this relation and averaging values of the ratio α_{p1}/α_{p2} obtained at 400, 1000, and 1600 C, the values listed in Table 16 are obtained for β . The values of $\alpha 0.000$ for 100 percent dense material used in the diffusivity ratios for radial ($\perp$) heat flow were calculated using the Eucken relation with the average value of β obtained from axial ($\parallel$) heat flow. The indicated error is the maximum, assuming a precision of ± 2 percent (i.e., + 2 percent for high density material and -2 percent for low density, or vice-versa). Deviations from β average at the three temperatures where computations were made were small (see Appendix F). For the D material, only the high-density D-1 and low-density D-3 diffusivity values were used to determine β since the curves for these materials had good correlation in shape. The curve for the intermediate density material, D-2, deviated slightly from the others. This was apparently due to precision errors.

The value used for porosity in determining β for the low density E material was the average of the porosities of E-2 and E-3, for which the measured diffusivities were the same.

Although an accurate determination of β is difficult, the results obtained for the D and E materials are what would be expected for pores of fairly spherical shape⁽¹¹⁾.

The higher values of β obtained for the C materials cannot be explained completely. An error in measurement is unlikely since nearly the same value was obtained independently for two sets of curves. Since the same fabrication process was used for all materials, with the exception that the ThO_2 material was not subjected to the double sintering process, one would expect better agreement between the C and other materials. Assuming the Maxwell-Eucken relation is a valid one, it might be anticipated that more is involved in β than pore shape, etc.

For purposes of computing thermal conductivity for various porosities of the given materials, as fabricated, we may conclude that the Eucken Relation is a good one subject to proper choices of β . For the C, D, and E materials, these are 1.5, 0.5, and 0.5, respectively. This may be approximated fairly well in the equation:

TABLE 16. PORE SHAPE FACTOR β FOR $\text{ThO}_2\text{-UO}_2$ MATERIALS

Material	Direction of Heat Flow Relative to Cylinder Axis	Diffusivity Ratio Used	β ave.
C: ThO_2	11	$\frac{\alpha_{.070}}{\alpha_{.134}}$	1.46 ± 0.26
	11	$\frac{\alpha_{.070}}{\alpha_{.264}}$	1.58 ± 0.28
	$\perp$	$\frac{\alpha_{.141}}{\alpha_{.000}}$	2.90 ± 0.30
D: $\text{ThO}_2\text{-10 UO}_2$	11	$\frac{\alpha_{.072}}{\alpha_{.282}}$	0.46 ± 0.23
E: $\text{ThO}_2\text{-20 UO}_2$	11	$\frac{\alpha_{.075}}{\alpha_{.207}}$	0.55 ± 0.31
	$\perp$	$\frac{\alpha_{.223}}{\alpha_{.000}}$	0.95 ± 0.18

$$\beta = \frac{1 + 0.092 U}{0.282 U + 0.67} , \quad (18)$$

where U is the percentage UO_2 content.

Relation Between Conductivity and UO_2 Content

Figures 63 through 66 show the relationship between conductivity and UO_2 content. For a given porosity, the results are about the same. A large drop in conductivity occurs from the pure ThO_2 material to the 10 w/o UO_2 material. A much smaller drop occurs from the 10 w/o UO_2 to the 20 w/o UO_2 material. For the low-density material, the inverted order of Compositions E-3 and D-3 apparently is due to the higher density of Composition E-3.

A general direct relationship between conductivity and UO_2 content in ThO_2 - UO_2 alloys cannot be well established without further measurements with increased UO_2 content. It may be concluded from the given data, however, that conductivity decreases with increasing UO_2 up to a content of 20 w/o UO_2 . This might be anticipated on the assumption that the addition of UO_2 results in additional phonon scattering centers. Figure 66 displays the conductivity-versus- UO_2 content in a more readable fashion. From these curves it appears that the conductivity relation involving the UO_2 content depends on the temperature as well as the UO_2 content. (The dependence is small, however.) The difference in shape for various densities results from the fact that the parameter β takes on different values for the given materials. A fair approximation for relating the change in conductivity to change in UO_2 content is obtained with inclusion of the term:

$$K(U) = K(o) \left(\frac{1 + 0.291 U}{1 + 0.400 U} \right) , \quad (19)$$

where U is the percentage UO_2 and T is the absolute temperature, Kelvin.

FIGURE 63. THERMAL CONDUCTIVITY OF HIGH DENSITY ThO₂-UO₂ MATERIALS

FIGURE 64. THERMAL CONDUCTIVITY OF INTERMEDIATE DENSITY ThO₂-UO₂ MATERIALS

FIGURE 65. THERMAL CONDUCTIVITY OF LOW DENSITY ThO₂-UO₂ MATERIALS

FIGURE 66.THERMAL CONDUCTIVITY Vs UO₂ CONTENT

Effect of Variation of Direction on Heat Flow
on Conductivity

Since conductivity for heat flow in the radial direction is of primary interest in fuel rod operation, it is essential to determine whether or not the conductivity is isotropic with respect to direction of measurement. Figures 67 and 68 show the relationships between the thermal diffusivities (and thus conductivities) of specimens cut parallel and perpendicular to the axes of the cylindrical materials. In both cases the diffusivities of the radial specimens are lower than those of the axial specimens, with the difference varying from about 5 to 20 percent. Similar results were obtained for the D materials (ThO_2 -10 UO_2) before tungsten coatings were applied to the Specimens for diffusivity measurements. Possible explanations for this effect include the following.

- (1) Anisotropy due to pore shape.
- (2) Non-uniformity of porosity in the radial direction of the bulk cylinders.
- (3) Anisotropy due to structural defects introduced during the fabrication process.
- (4) Microcracks occurring during machining of diffusivity specimens.

Each of these items is discussed below.

(1) Anisotropy Due to Pore Shape. According to Belle, et al⁽¹¹⁾ a preferred orientation of non-spherical pores introduced during the fabrication process will result in a distinct difference in conductivity for various directions of heat flow, the degree depending upon the general shape of the pores. For instance, for two-dimensional heat flow and 2:1 ellipses, a β factor (from the Eucken relation) of about 0.5 should result for heat flow parallel to the long axis, and about 2.0 for heat flow perpendicular to the long axis. For measurements on the E materials in this program, a value for β of about 0.5 resulted for heat flow in the longitudinal direction (parallel to axis of fabricated cylinder) while a value of about 1.0 resulted for heat flow in the

FIGURE 67. COMPARISON OF THERMAL DIFFUSIVITY OF ThO_2 , SAMPLE C-2 FOR RADIAL (TRANSVERSE) AND AXIAL (LONGITUDINAL) HEAT FLOW

FIGURE 68. COMPARISON OF THERMAL DIFFUSIVITY OF $\text{ThO}_2\text{-}20\text{UO}_2$, SAMPLE E-3 FOR
 RADIAL (TRANSVERSE) AND AXIAL (LONGITUDINAL) HEAT FLOW

transverse direction (perpendicular to cylinder axis). This ratio for β of 0.5/1.0 or 1/2 obtained for the E material is about the same as that obtained for the C material (1.5/2.9). Metallographic examination of the pore structure shows the pores (in two dimensions) to be of various odd shapes, some approximately ellipses, other circles, etc. Assuming all of the pores to be ellipses, and considering the analysis of Belle, a slightly preferred orientation of 2:1 ellipses, or ellipses of axis ratio somewhat less than 2:1, could result in the measured differences if the long axis were in the direction of the cylinder axis. However, with the use of a qualitative television microscope (Quantimet Image Analyzing Computer), it was clearly demonstrated that preferential pore orientation did not exist.

(2) Non-Uniformity of Porosity In the Radial Direction of the Bulk Cylinders. To effect a change in β of the magnitude suggested here for radial and axial specimens, a density gradient of very large proportion in the radial direction of the fabricated cylinders would be required. If the density at the center of the cylinder were less than that at the outer edges, this would result in a lower density for radial cut diffusivity specimens. However, since the densities of diffusivity specimens as measured were essentially the same, this is ruled out. In addition, measurements with the Quantimet Image Analyzing Computer confirmed uniform porosity.

(3) Anisotropy Due to Structural Defects Introduced During the Fabrication Process. Structural defects are found in any given material. The most important of these are dislocations, grain boundaries, and vacancies, all of which are expected to have some effect on the thermal conductivity. With the exception of grain boundaries, however, these defects are temperature dependent, and any effect of anisotropy introduced during fabrication should be annealed out at high temperatures. The apparent anisotropy as seen in the conductivity data, however, is fairly independent of temperature and data obtained on heating and cooling are consistent. For grain boundaries, since the ratio of the average grain size of sintered oxides (~ 10 microns) to the wave length of phonons at elevated temperatures ($\sim 50 \text{ \AA}$)⁽¹¹⁾ is large, these

defects should have negligible effect on the thermal conductivity or resistivity. Thus, any anisotropy due to structural defects should be very small, certainly not of the proportion encountered in the present measurements.

(4) Microcracks Occurring During Machining of Diffusivity Specimens.

The cutting and preparation of disk specimens from cylinders in such a manner that heat flow will be measured perpendicular to the cylinder axis is more difficult than preparation of specimens simply sliced off the ends of the cylinder. Radial specimens are subjected to additional vibrations and mechanical shock during fabrication.

As discussed earlier, postmeasurement metallographic examination of the D-1 diffusivity specimens revealed considerable microcracking (see Figures 12 and 13). This was more extensive in the radial specimen than in the axial one, and was assumed to have occurred during machining of the specimens. The data for the axial specimen were those anticipated on the basis of composition, density, etc., and were retained. The data for the radial specimen, however, deviated considerably from those expected and were discarded. Microcracking was not evident in other specimens initially examined metallographically (not all specimens run were examined) before or after diffusivity measurements. This did not include the C-2 radial specimen, however, and metallographic examination revealed fairly extensive microcracking. Although no microcracking was evident for the E-3 radial specimen, the difference in data for this material could be explained on the basis of curve fitting and precision errors. Thus, it is assumed that the apparent anisotropy as indicated from measurements of thermal diffusivity is due not to an inherent property of the fabricated material, but to microcracks introduced during machining of specimens.

Evaluation of Fabrication Technique

Essential elements desired from the given method of fabrication include the following:

- (1) Reproducibility (controlled porosity)
- (2) Stability under thermal shock
- (3) Maximum conductivity for given porosity

- (4) Uniform porosity
- (5) Isotropy with respect to pore orientation.

(1) Although the actual porosity obtained for various materials sometimes differed from that intended, it is estimated that porosity for the given materials is controllable to better than ± 1 percent, based on experience gained in this program.

(2) During heating and cooling of the materials for various measurements, very fine, long cracks (not microcracks as discussed previously) were sometimes observed, particularly in diffusivity specimens. (This may have been caused by holding the specimen too tightly in its holder.) This occurred in about one out of ten specimens, with the result usually being a decrease in the thermal diffusivity (and thus conductivity). This depended upon the extent of cracking and the orientation of the cracks. Heating rates were of the order of 10 C per min. No cracking was observed in the larger, cylindrical, linear-expansion specimens for which the heating rate was about the same. The stability of these materials under thermal shock is thus considered fair.

(3) For isotropic material with a given porosity, maximum conductivity should occur when the pore shape factor β is 0.5⁽¹¹⁾. For the ThO₂-UO₂ materials, this value was obtained (approximately), and maximum conductivity was thus assumed to be achieved. For the pure ThO₂ materials, the value of β obtained was higher (about 1.5), which indicates less than the maximum conductivity achievable. Belle, et al.⁽¹¹⁾, attributed high values of β for ThO₂ as measured by other researchers to imperfect sintering.

(4) Because of the apparent anisotropy in the materials, measurements of porosity versus radial distance from the axis of the fabricated cylinders were made using a qualitative television microscope (Quantimet Image Analyzing Computer). With this instrument the area porosity at any location on a given specimen can be obtained instantaneously and read directly from a calibrated dial indicator. The results indicated porosity to be very uniform throughout the material with no measurable net increase or decrease along the radial direction.

(5) As indicated earlier, measurements made with the qualitative television microscope revealed that there was no preferred orientation of non-spherical pores. In a given mode of operation, the mean pore chord length was determined for various specimens and various orientations of specimens. The results indicated no difference in mean pore chord length in any direction.

Thermal Conductivity For ThO_2 - UO_2 Materials in General

The conductivity data for the 100 percent dense ThO_2 material, obtained from the Eucken relation using Equation (18), can be fitted with the equation:

$$K = \frac{1}{0.79 (1 + 0.09U) + 0.0185T} \quad \text{w/(cm)(K)}, \quad (20)$$

where T is the absolute temperature, Kelvin, U = 0 for this case.

Neglecting the lower values of conductivity data for heat flow in the radial direction, the data for all materials measured can be fitted with the equation:

$$K(P, T, U) = \left[\frac{1 - P}{1 + P \left(\frac{1 + 0.092 U}{0.67 + 0.282 U} \right)} \right] \left[\frac{1}{0.79 (1 + 0.09 U) + 0.0185 T} \right] \left[\frac{1 + 0.291 U}{1 + 0.400 U} \right] \text{w/(cm)(K)} . \quad (21)$$

The variables are porosity P (pore fraction), temperature T, and weight percentage UO_2 content, U. The first factor on the right in this equation is from the Eucken relation, Equation (15), with proper substitution for β , Equation (18). The second factor gives the general shape of the curve for 100 percent dense ThO_2 , Equation (20). This also includes a term which takes into account the change in shape resulting from the addition of UO_2 . The third factor, from Equation (19), accounts for the general decrease in conductivity with increasing UO_2 content.

Figures 69 through 71 show the conductivity data with the curve from Equation (21) drawn in. The maximum error involved using this equation is generally less than ± 2 percent, which is the precision of measurement. It is anticipated that this equation will give good results for $\text{ThO}_2\text{-UO}_2$ materials fabricated by the given process for any porosity up to 30 percent and any UO_2 content up to 20 w/o.

FIGURE 69. THERMAL CONDUCTIVITY OF ThO₂ MATERIALS WITH SMOOTH CURVE FROM EQUATION DRAWN IN

FIGURE 70. THERMAL CONDUCTIVITY OF ThO_2 -10 UO_2 MATERIALS WITH SMOOTH CURVE FROM EQUATION DRAWN IN

FIGURE 71. THERMAL CONDUCTIVITY OF ThO_2 -20 UO_2 MATERIALS WITH SMOOTH CURVE FROM EQUATION DRAWN IN

CONCLUSIONS

The objective of this program was the evaluation of the performance of ThO_2 - UO_2 binary alloys for reactor fuel rod applications. With this goal in mind the following conclusions may be drawn:

- (1) The fabrication process is reproducible with intentionally introduced porosity controllable to an estimated ± 1 percent. The material seems fairly stable under thermal shock as evidenced by little cracking during heating and cooling for various measurements. With respect to orientation of pores, the material is quite isotropic, and the pores are uniformly distributed.
- (2) Thermal conductivity as a function of composition and porosity may be accurately determined for materials fabricated by the given process within the limits specified. Equation (20) may be used to determine the optimum values of composition and porosity in conjunction with other fuel element requirements. Compared with that of UO_2 , the thermal conductivity of ThO_2 is slightly higher but decreases with the addition of UO_2 to the point where the two are comparable.

Further studies might include the following:

- (1) Effect of stoichiometry on conductivity - During irradiation, the O/U ratio increases due to fission of the uranium atoms. Also, at high operating temperatures and for extended periods of time, loss of oxygen is likely, and it is doubtful that stoichiometry will be maintained. Thus for design purposes, a study could be made of the effect of

stoichiometry on thermal conductivity for the $\text{ThO}_2\text{-UO}_2$ series. Since the above-mentioned effects can result in either an increase or decrease in the O/U ratio, this study should include measurements on both hypo- and hyperstoichiometric compositions.

(2) Effect of grain size on conductivity - Grain boundaries are discontinuities in the general lattice structure, and as such contribute to scattering of phonons and photons. Although scattering for phonons is expected to have little effect on the lattice thermal resistance (and this is in question), the effect on photons and radiant heat transfer could be appreciable. An investigation of this effect would involve further study of the fabrication technique along with appropriate thermal property measurements.

(3) High-temperature effects - Since operating temperatures for reactor fuels often approach the melting point, thermal property measurements could be conducted at temperatures above those attained in the subject program (1900 C). To this end, Battelle is presently designing thermal diffusivity apparatus using induction heating, which should allow measurements at 2500 C or higher. For the $\text{ThO}_2\text{-UO}_2$ series (m.p. > 2800 C), thermal properties at these temperatures should be of extreme value (the debate over whether or not thermal conductivity of UO_2 increases at high temperatures has not yet been resolved).

(4) Low temperature measurements - Recent modifications in the thermal diffusivity apparatus have extended the lower temperature limit for measurements to room temperature. For completeness, diffusivity measurements could be extended to include this lower temperature.

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APPENDIX A

CALCULATION OF OPEN, CLOSED, AND
TOTAL POROSITIES

APPENDIX A

CALCULATION OF OPEN, CLOSED, AND
TOTAL POROSITIES

Technique

The technique utilized to determine the porosity relationships consisted of first determining the bulk, apparent, and true volumes of selected samples.

The bulk volume (V_b) is a geometric relationship consisting of the sum of the volumes occupied by the material, the open, and the closed pores. The bulk volume was determined using the average diameter and length of a cylindrical specimen.

The apparent volume (V_a), or that volume occupied by the material and the closed pores, was determined by measuring the weight of a specimen saturated and suspended in CCl_4 . The open pores were completely filled with CCl_4 by inserting the specimen into a vacuum chamber, introducing CCl_4 to the chamber under vacuum, and continuing the vacuum until all air had been removed from the specimen. The specimen was then weighed suspended in CCl_4 by means of a thin copper wire attached to the balance. Weight corrections were made for the copper wire immersed in CCl_4 and the apparent volume was calculated from the following relationship:

$$V_a = \frac{(\text{dry weight}) - (\text{saturated and suspended weight})}{\text{density of } \text{CCl}_4 \text{ at room temperature}} .$$

The true volume (V_t), or the volume of the material alone, is calculated from the dry weight of the material divided by the theoretical density that particular composition.

Porosity Calculations

After the preceding volume relationships are determined, the open, closed, and total porosities can be calculated from the following relationships:

$$\text{Percent open porosity} = \frac{V_b - V_a}{V_b} \times 100$$

$$\text{Percent closed porosity} = \frac{V_a - V_t}{V_a} \times 100$$

$$\text{Percent total porosity} = \frac{V_b - V_t}{V_b} \times 100 \quad .$$

APPENDIX B

CALCULATION OF THEORETICAL DENSITIES
FROM MEASURED CHEMICAL ANALYSES
AND LATTICE MEASUREMENTS

APPENDIX B

CALCULATION OF THEORETICAL DENSITIES
FROM MEASURED CHEMICAL ANALYSES
AND LATTICE MEASUREMENTS

The theoretical densities of the actual compositions were calculated from the measured chemical analysis and X-ray lattice measurements by the following relationship:

$$\text{Density} = \frac{n(M_1 F_1 + M_2 F_2 + \dots)}{VA}$$

n = number of atoms per unit cell

M = atomic weight of constituent

F = atomic fraction of constituent

V = lattice volume in cm.³ [(a)³ for cubic system
and (a)²c for tetragonal system]

A = Avogadro's number (6.03 x 10²³)

For Composition E-1, the measured chemical composition was 20.4 w/o UO₂ and 79.6 w/o ThO₂ or 20.04 a/o UO_{2.005} and 79.96 a/o ThO₂. This in turn converts to the following atomic fractions of constituent atoms: uranium = 0.0668, thorium = 0.2665, and oxygen = 0.6667.

The volume of a unit cell from X-ray lattice measurements is

$$V = (\alpha_o)^3 = (5.5801 \times 10^{-8} \text{ cm})^3 = 173.7503 \times 10^{-24} \text{ cm}^3$$

Incorporation of these terms into the formula

$$\text{Density} = \frac{12 [0.0668)(238) + (0.2665)(232) + (0.6667)(16)]}{(6.03 \times 10^{23}) (173.7503 \times 10^{-24})}$$

yields the theoretical density of Composition E-1 as 10.1325.

APPENDIX C

SUMMARY OF POTENTIAL ERRORS IN THERMAL-DIFFUSIVITY
MEASUREMENTS

APPENDIX C

SUMMARY OF POTENTIAL ERRORS IN THERMAL-DIFFUSIVITY
MEASUREMENTS

Possible errors in accuracy due to:	<u>Percent</u>
1. Temperature reading	<u>±0.5</u>
2. Finite laser pulse time	<u>±0.5</u>
3. Effect of specimen coating	<u>±0.5</u>
4. Electronics	<u>±0.5</u>
5. Detector time constant	<u>±1.0</u>
6. Conduction heat losses	<u>±0.5</u>
7. Heat loss correction	<u>±2.0</u>
Total (maximum)	<u>±5.5</u>
RMS	<u>±2.5</u>
Reported accuracy based on measurements on standard materials	<u>±5.0</u>
Possible precision errors due to:	
1. Reading photograph of specimen time-temperature history	<u>±1.0</u>
2. Electronics	<u>±1.0</u>
Total (maximum)	<u>±2.0</u>
RMS	<u>±1.4</u>
Reported precision based on standard deviation of data points from drawn in, smooth curve	<u>±2.0</u>

APPENDIX D

LITERATURE VALUE COMPARISON

FIGURE D-1. SPECIFIC HEAT OF ThO_2

FIGURE D-2. LINEAR THERMAL EXPANSION OF ThO_2

FIGURE D-3. THERMAL CONDUCTIVITY OF ThO_2 MATERIALS

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APPENDIX E

THERMAL-CONDUCTIVITY AND DIFFUSIVITY DATA

TABLE E-1. THERMAL-CONDUCTIVITY DATA FOR ThO₂ MATERIALS

Composition C-1		Composition C-2		Composition C-2(L)	
Temperature, Conductivity,		Temperature, Conductivity,		Temperature, Conductivity,	
C	10 ⁻² w/(cm) (C)	C	10 ⁻² w/(cm) (C)	C	10 ⁻² w/(cm) (C)
258	7.55	294	6.55	280	5.88
264	6.64	296	6.42	407	4.64
268	8.36	493	4.69	495	4.45
309	5.65	549	4.62	604	3.54
491	6.01	516	5.01	692	3.33
510	5.62	576	4.33	798	2.90
574	3.92	695	4.05	902	2.62
633	5.01	723	3.86	1022	2.34
816	4.05	894	3.25	1098	2.37
827	3.14	897	3.21	1200	2.12
955	3.54	1013	2.72	1301	1.96
998	5.65	1018	2.82	1375	1.91
1000	3.42	1020	3.16	1480	1.87
1107	3.14	1021	2.34	1606	1.73
1275	2.95	1090	2.76	1805	1.59
1350	2.82	1091	2.61	1887	1.60
1398	2.54	1216	2.08	Composition E-3	
1548	2.49	1225	2.45		
1552	2.30	1265	2.19	251	5.07
1640	2.39	1299	2.39	308	4.55
1653	2.19	1305	2.16	494	3.69
1755	2.19	1385	1.90	628	3.00
1900	1.94	1398	2.49	741	2.76
1905	2.04	1495	2.06	875	2.32
		1497	1.61	997	2.12
		1508	1.93	1120	1.88
		1583	1.86	1193	1.81
		1592	2.04	1363	1.61
		1686	1.84	1515	1.50
		1698	1.70	1623	1.40
		1768	1.87	1791	1.35
		1775	1.79	1882	1.21
		1866	1.80		
		1867	1.71		

TABLE E-2. THERMAL-CONDUCTIVITY DATA FOR ThO_2 -10 w/o UO_2 MATERIALS

Composition D-1		Composition D-2		Composition D-3	
Temperature, Conductivity,		Temperature, Conductivity,		Temperature, Conductivity,	
C	10^2 w/(cm) (C)	C	10^2 w/(cm) (C)	C	10^2 w/(cm) (C)
316	5.35	193	5.05	250	4.39
524	4.26	273	4.88	363	3.26
698	3.56	276	4.50	473	3.29
884	3.12	334	4.10	567	3.12
1021	2.80	395	4.17	584	2.63
1060	2.75	460	4.01	660	2.64
1179	2.47	466	4.03	828	2.22
1367	2.27	611	3.08	865	1.90
1501	2.15	650	3.26	930	1.85
		828	2.78	952	2.14
		959	2.52	1045	1.87
		1222	2.07	1109	1.65
		1357	1.75	1212	1.64
		1420	1.83	1269	1.72
		1640	1.66	1285	1.45
		1778	1.37	1390	1.39
		1882	1.34	1394	1.49
				1585	1.35
				1700	1.27
				1750	1.12
				1804	1.22
				1990	1.10

TABLE E-3. THERMAL-CONDUCTIVITY DATA FOR ThO_2 -20 w/o UO_2 MATERIALS

Composition E-1		Composition E-2		Composition E-3	
Temperature, Conductivity,		Temperature, Conductivity,		Temperature, Conductivity,	
C	$10^{-2} w / (\text{cm})(\text{C})$	C	$10^{-2} w / (\text{cm})(\text{C})$	C	$10^{-2} w / (\text{cm})(\text{C})$
232	5.68	248	4.75	224	4.71
276	5.58	275	4.28	230	4.41
427	4.34	420	3.80	288	4.27
457	4.56	448	3.49	397	3.74
497	4.26	511	3.36	401	3.77
555	4.07	605	3.08	401	3.77
593	3.66	721	2.63	531	2.95
711	3.40	731	2.69	574	3.12
758	3.28	882	2.35	602	2.97
800	3.05	932	2.26	677	2.72
888	2.91	996	2.23	780	2.50
951	2.85	1093	2.04	784	2.52
984	2.88	1146	2.01	891	2.22
993	2.61	1176	2.01	972	2.16
1041	2.61	1187	1.91	983	2.10
1089	2.54	1296	1.88	1004	2.05
1180	2.66	1360	1.75	1072	1.92
1201	2.38	1410	1.77	1105	1.83
1293	2.37	1495	1.77	1160	1.85
1332	2.15	1548	1.66	1167	1.84
1352	2.13	1560	1.62	1345	1.61
1472	2.12	1628	1.50	1395	1.61
1473	2.21	1735	1.56	1424	1.57
1599	1.79	1794	1.39	1561	1.45
1605	1.87	1805	1.39	1674	1.43
1730	1.68	1848	1.38	1755	1.35
1697	1.74			1896	1.23
1798	1.58				
1858	1.53				

Table E-3 continued

<u>Composition E-3 (L)</u>	
<u>Temperature,</u>	<u>Conductivity,</u>
<u>C</u>	<u>$10^{-2} w / (cm) (C)$</u>
224	4.28
400	3.24
474	3.26
592	2.70
682	2.60
800	2.20
894	2.11
998	1.88
1085	1.82
1142	1.72
1290	1.61
1391	1.51
1490	1.47
1690	1.29
1776	1.23

TABLE E-4. THERMAL-DIFFUSIVITY DATA FOR ThO_2 MATERIALS

Composition C-1		Composition C-2		Composition C-2(L)	
Temperature, Diffusivity,		Temperature, Diffusivity,		Temperature, Diffusivity,	
C	$10^{-2} \text{ cm}^2 \text{ per sec}$	C	$10^{-2} \text{ cm}^2 \text{ per sec}$	C	$10^{-2} \text{ cm}^2 \text{ per sec}$
258	3.10	294	2.84	280	2.55
264	2.70	296	2.79	407	1.97
268	3.39	493	1.97	495	1.87
309	2.28	549	1.93	604	1.47
491	2.35	516	2.10	692	1.37
510	2.19	576	1.80	798	1.18
574	1.97	695	1.66	902	1.05
633	1.93	723	1.58	1022	.930
816	1.53	894	1.31	1098	.934
827	1.48	897	1.29	1200	.831
955	1.31	1013	1.08	1301	.761
998	1.18	1018	1.12	1375	.737
1000	1.27	1020	1.25	1480	.714
1107	1.15	1021	0.93	1606	.650
1275	1.06	1090	1.09	1805	.588
1350	1.01	1901	1.03	1887	.590
1398	.91	1216	0.812	Composition C-3	
1548	.879	1225	0.958	251	2.62
1552	.818	1265	0.851	308	2.32
1640	.835	1299	0.925	494	1.82
1653	.765	1305	0.838	628	1.46
1755	.760	1385	0.732	741	1.33
1900	.666	1398	0.959	875	1.10
1905	.700	1495	0.785	997	.997
		1497	0.613	1120	.872
		1508	0.735	1193	.838
		1583	0.704		
		1592	0.769	1363	.729
		1686	0.689	1515	.674
		1698	0.635	1623	.622
		1768	0.697	1791	.591
		1775	0.665	1882	.526
		1866	0.664		
		1867	0.631		

TABLE E-5. THERMAL-DIFFUSIVITY DATA FOR ThO_2 -10 w/o UO_2 MATERIALS

Composition D-1		Composition D-2		Composition D-3	
Temperature, Diffusivity,		Temperature, Diffusivity,		Temperature, Diffusivity,	
C	$10^{-2} \text{ cm}^2 \text{ per sec}$	C	$10^{-2} \text{ cm}^2 \text{ per sec}$	C	$10^{-2} \text{ cm}^2 \text{ per sec}$
316	2.11	276	2.02	250	2.26
524	1.64	466	1.76	473	1.64
698	1.35	193	2.31	660	1.31
884	1.17	395	1.84	828	1.08
1021	1.04	273	2.19	1045	0.895
1060	1.02	460	1.75	1212	0.777
1179	0.911	650	1.40	1394	0.700
1367	0.824	828	1.18	1585	0.630
1501	0.778	959	1.06	1804	0.560
		1222	0.860	1990	0.500
		1420	0.749	1700	0.585
		1640	0.673	1483	0.700
		1882	0.538	1269	0.815
		1778	0.552	952	1.03
		1357	0.720	567	1.54
		611	1.33	363	1.65
		334	1.82	584	1.30
				865	0.925
				1109	0.790
				1390	0.655
				1750	0.515
				1285	0.685
				930	0.895

E-6 (a)

TABLE E-6. THERMAL-DIFFUSIVITY DATA FOR ThO_2 -20 w/o UO_2 MATERIALS

Composition E-1		Composition E-2		Composition E-3	
Temperature, Diffusivity,		Temperature, Diffusivity,		Temperature, Diffusivity,	
C	$10^{-2} \text{ cm}^2 \text{ per sec}$	C	$10^{-2} \text{ cm}^2 \text{ per sec}$	C	$10^{-2} \text{ cm}^2 \text{ per sec}$
232	2.25	275	1.90	224	2.27
497	1.61	511	1.44	401	1.74
711	1.26	731	1.13	602	1.35
888	1.06	932	0.939	780	1.12
1089	0.917	1146	0.825	983	0.926
1293	0.845	1296	0.763	1167	0.803
555	1.56	1495	0.710	1395	0.695
984	1.05	1735	0.621	531	1.34
1422	0.751	1848	0.551	1004	0.905
1697	0.610	1805	0.554	1674	0.607
1858	0.534	1560	0.649	1896	0.518
1798	0.555	1410	0.715	1755	0.571
1599	0.629	1176	0.821	1105	0.804
1352	0.758	996	0.924	230	2.11
1201	0.855	795	1.12	397	1.73
993	0.948	605	1.31	574	1.42
800	1.12	420	1.65	784	1.12
593	1.37	248	2.12	972	0.955
427	1.65	616	1.28	1160	0.805
276	2.28	882	.978	1424	0.675
593	1.52	1187	.777	1561	0.620
951	1.04	1548	.664	1345	0.695
1180	0.957	1794	.555	1072	0.845
1473	0.782	1628	.600	891	0.985
1730	0.590	1360	.709	677	1.23
1605	0.658	1093	.837	288	2.02
1332	0.766	721	1.11		
1041	0.948	448	1.51		
758	1.21				
457	1.73				

Table E-6 continued

E-6(b)

<u>Composition E-3 (1)</u>	
<u>Temperature,</u>	<u>Diffusivity,</u>
<u>C</u>	<u>$10^{-2} \text{ cm}^2 \text{ per sec}$</u>
224	2.04
474	1.48
682	1.16
894	0.925
1085	0.789
1290	0.692
1490	0.626
1690	0.541
1776	0.515
1391	0.625
1142	0.745
998	0.823
800	0.974
592	1.21
400	1.48

APPENDIX F

DETERMINATION OF PORE SHAPE FACTOR β IN THE
MODIFIED EUCKEN RELATION

APPENDIX F

DETERMINATION OF PORE SHAPE FACTOR β IN THE MODIFIED
EUCKEN RELATION

Assumptions for a given material: (1) $\rho = (1 - P) \rho_o$
 (2) $K = \alpha \rho C$
 (3) $\beta = \text{constant for given material,}$

where

ρ = density
 ρ_o = 100 percent theoretical density
 K = thermal conductivity
 α = thermal diffusivity
 C = specific heat
 β = factor dependent upon size, shape, degree of
 uniformity, and special distribution of pores.

Using the modified Eucken relation:

$$\frac{K_p}{K_o} = \frac{1 - P}{1 + \beta P} \quad , \quad (F-1)$$

we have by Assumption (2):

$$\frac{\alpha_p \rho_p C_p}{\alpha_o \rho_o C_o} = \frac{1 - P}{1 + \beta P} \quad . \quad (F-2)$$

Since the specific heat is independent of P and using Assumption (1), this evaluation reduces to

$$\frac{\alpha_p}{\alpha_o} = \frac{1}{1 + \beta P_1} \quad (F-3)$$

Examples:

$$\frac{\alpha_{P_1}}{\alpha_o} = \frac{1}{1 + \beta P_1} \quad . \quad (F-4)$$

$$\frac{\alpha_{P_2}}{\alpha_o} = \frac{1}{1 + \beta P_2} \quad . \quad (F-5)$$

Dividing Equation (F-4) by Equation (F-5):

$$\frac{\alpha_{P_1}}{\alpha_{P_2}} = \frac{1 + \beta P_2}{1 + \beta P_1} \quad . \quad (F-6)$$

Thus β is a direct function of diffusivity and may be calculated from the given diffusivity data.

A summary of β values calculated at various temperatures is tabulated below.

<u>Composition</u>	<u>Material</u>	<u>Value of β at Indicated Temperature</u>				
		<u>Heat Flow</u>	<u>400 C</u>	<u>1000 C</u>	<u>1600 C</u>	<u>β Average</u>
C	ThO ₂	Axial	1.43	1.31	1.63	1.46
		Axial	1.48	1.53	1.73	1.58
		Radial(<u>L</u>)	3.07	3.01	2.63	2.90
D	ThO ₂ -10 w/o UO ₂	Axial	0.36	0.47	0.54	0.46
E	ThO ₂ -20 w/o UO ₂	Axial	0.55	0.72	0.40	0.55
		Radial(<u>L</u>)	0.89	1.04	0.91	0.95