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HIGH-TEMPERATURE THERMAL CONDUCTIVITY
OF "ROUND ROBIN" URANIUM DIOXIDE

J. Lambert Bates

July 1970

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OF "ROUND ROBIN" URANIUM DIOXIDE

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ABSTRACT

The thermal diffusivity of "round robin" uranium dioxide was measured from 16 to 2500 °C using a "flash" thermal diffusivity technique. The thermal diffusivity at lower temperatures was initially higher than expected during initial measurements. After heating to 1200 °C or above, the low temperature diffusivity decreased to a reproducible value representative of nearly stoichiometric UO_2 . This increased diffusivity is attributed to initially hypostoichiometric UO_2 which oxidized to a stoichiometric composition at 1200 °C or above. Calculated thermal conductivity values agree within $\pm 10\%$ below 600 °C and within $+5\%$ above 600 °C with other reported "round robin" UO_2 values. The thermal conductivity exhibits a minimum near 1600 °C.

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HIGH-TEMPERATURE THERMAL CONDUCTIVITY OF "ROUND ROBIN" URANIUM DIOXIDE

J. Lambert Bates

INTRODUCTION

In 1967, the United States Atomic Energy Commission established a "round robin" program to determine the thermal conductivity of stoichiometric uranium dioxide. The Nuclear Systems Program (NSP) of the General Electric Company, Cincinnati, Ohio, was asked to coordinate this program.^(1,2) The Pacific Northwest Laboratories of Battelle Memorial Institute was asked to participate in this program along with eight other laboratories.

The purpose of this "round robin" UO_2 thermal conductivity program was to determine from room temperature to 2500 °C the thermal conductivity - temperature relationship for stoichiometric UO_2 with the same composition and structure.^(1,2) It was important to determine if the thermal conductivity of UO_2 exhibits a minimum value near 1500 °C as predicted and as measured experimentally. In addition, the results would help to determine the agreement between the results of the nine laboratories using different experimental techniques. The purpose of this report is to describe in detail the results which were obtained at Pacific Northwest Laboratory using a pulse, thermal diffusivity technique.

SUMMARY

The thermal diffusivity of "round robin" uranium dioxide was measured from 16 to 2500 °C using a "flash" thermal diffusivity technique. The thermal diffusivity at lower temperatures was initially higher than expected during initial measurements. After heating to 1200 °C or above, the low temperature diffusivity decreased to a reproducible value representative of nearly stoichiometric UO_2 . This increased

diffusivity is attributed to initially hypostoichiometric UO_2 which oxidized to a stoichiometric composition at 1200 °C or above. Calculated thermal conductivity values agree within $\pm 10\%$ below 600 °C and within $+5\%$ above 600 °C with other reported "round robin" UO_2 values. The thermal conductivity exhibits a minimum near 1600 °C.

THERMAL DIFFUSIVITY TECHNIQUE

METHOD

The thermal diffusivity of the "round robin" uranium dioxide was measured using the "flash" or "pulse" technique. The flash method consists of heating one surface of a thin sample disc with a short heat pulse.⁽³⁻⁶⁾ The heat pulse passes through the sample, and the temperature transient on the back surface of the sample is measured. The temperature change is recorded, and the thermal diffusivity is determined from the shape of the temperature-versus-time curve.

For the technique to be valid,⁽³⁾ the following conditions must be met:

- The energy pulse is uniformly absorbed over the front surface of the sample and only at the surface.
- The pulse time of the heat source is small compared to the time for the heat pulse to pass through the sample.
- Heat flow is normal to the heated surface of the sample.
- No heat is lost from the sample during the measuring period.

If these conditions are met, the thermal diffusivity (a) can be determined from the shape of the time - temperature transient curve from the simple relationship

$$\alpha = \frac{1.37 d^2}{\pi^2 t_{1/2}} = \frac{0.137 d^2}{t_{1/2}} \quad (1)$$

where a is expressed in cm^2/sec , d is the sample thickness in cm, $t_{1/2}$ is the time in seconds for the temperature on the back surface to reach one half the maximum temperature rise. By measuring d and $t_{1/2}$, a can be easily calculated, Figure 1.

HEAT LOSS CORRECTION

Ideally, heat losses from the sample should be negligible, however, at higher temperatures radiation losses from the sample surfaces must be considered. Radial heat losses from edge of sample into the sample holder are small and in most measurements need not be considered. However, radiative heat losses from both the front and the back surfaces of the sample are significant and must be evaluated since the boundary conditions for Equation (1) are not valid.

The effect of radiation heat losses from the sample surfaces has been considered by Parker and Jenkins,⁽⁵⁾ Cowan,⁽⁶⁾ and Cape and Lehman.⁽⁷⁾ The method proposed by Cowan⁽⁶⁾ considers losses at the elevated temperatures from both front and back surfaces and was used in calculating the thermal diffusivity of the "round robin" UO_2 . If heat losses occur, the shape of the temperature response curves changes as the sample surfaces are cooled (Figure 1). The correction can be made by comparing the back surface temperature at some multiple of the half time with the maximum temperature rise.

$$\Delta T(n \cdot t_{1/2}) / \Delta T(t_{1/2}). \quad (2)$$

ΔT is the incremental temperature rise above ambient temperature measured at n multiple time interval of $t_{1/2}$ (Figure 1). By using the above ratio, a characteristic time (t_c) or the approximate time for a heat pulse to pass through the sample can be determined graphically from theoretical curves. t_c is defined by the relationship

FIGURE 1. Schematic Tracing of Temperature Transients at Rear Surface of Thermal Diffusivity Sample Describing Analysis Measurements Necessary for Calculating Thermal Diffusivity and Correcting for Radiation Heat Losses

$$t_c = \frac{d^2}{\alpha \pi^2} \quad (3)$$

When there are no heat losses, the ratio of Equation (2) is 2.00 and t_c is equal to $\frac{1.39}{t_{1/2}}$. As the heat losses increase, this ratio decreases with a corresponding increase in t_c . t_c is determined graphically using theoretical expressions for the heat losses derived from an analysis of the time-temperature-rise curve recorded by the oscilloscope (Figure 1).

Although some question has arisen as to which value of n provides the most accurate determination of the radiation correction, values of 5, 10, and 20 are the values most generally used. Values used in this study were 5 and 10, depending upon the time scale and $t_{1/2}$ value and were chosen to provide the smallest error in reading the photographs of t versus AT .

FINITE PULSE TIME CORRECTION

When the heating pulse time (τ) of the laser is comparable to the time for the heat pulse to pass through the sample, the rate of the temperature rise is delayed.^(7,8) This results in an apparent decrease in the thermal diffusivity. While radiation losses are reduced by decreasing the sample thickness, finite pulse time effects are increased. Thus, there is an optimum sample thickness which will minimize the error in calculating the thermal diffusivity. For a square heating pulse,⁽⁸⁾ such as that from a pulse laser used in these experiments (Figure 2), t_c can be expressed as

$$t_c = \frac{t_{1/2} - 0.55 \tau}{1.37} \quad (4)$$

When t_c is $>50\tau$, Equation (1) can be used to calculate within $\pm 1\%$. No corrections for finite pulse time effects were required for the measurements of "round robin" UO_2 .

Neg 6943A

FIGURE 2. Oscilloscope Trace of Ruby Laser Pulse
(Sweep time - 0.2 msec/cm; laser pulse
width 0.54 msec)

EXPERIMENTAL EQUIPMENT AND PROCEDURES

FURNACE

The thermal diffusivity of the "round robin" uranium dioxide was measured from 16 to 2500 °C in a tungsten resistance furnace (Figures 3 and 4). The furnace consisted of a tungsten mesh heating element with an internal diameter of 3.2 cm and hot zone of 8.9 cm. The heating element was surrounded with tungsten and molybdenum heat shields, all of which were contained in a water-cooled, copper jacket. The tungsten element was heated by direct resistance from a low voltage (<20 V), high amperage (up to 1800 A), direct current from motor-driven welding generators connected in parallel. The furnace was controlled manually with a saturable reactor. A 1.9 cm diameter tungsten tube was inserted inside the heating element to minimize temperature fluctuations and temperature gradients. The

Neg 701212-1CN

FIGURE 3. Thermal Diffusivity Apparatus

FIGURE 4. Schematic Representation of Thermal Diffusivity Apparatus

specimens was supported in a sintered UO_2 holder with small pointed tungsten pins. The sample and holder were positioned inside the furnace cavity on a 1.4 cm tungsten tube. A thermocouple was inserted into a hole in the sample holder, as close to the sample as possible.

TEMPERATURE MEASUREMENTS

Temperatures were measured with a W-5%Re versus W-26%Re thermocouple (Figure 4). Temperatures of the back surface of the specimen were also measured above 900 °C with an optical brightness pyrometer. However, because of the long sight tube used to shield the infrared detector from extraneous radiation, the optical cone of the pyrometer was partially broken. Pyrometer measurements were thus used as a check of the thermocouple temperatures at the higher temperatures. The refractory metal thermocouple and the pyrometer were calibrated to 1600 °C against a Pt/Pt-10%Rh thermocouple attached to a platinum disc set in the sample position. The platinum thermocouple had previously been calibrated at the gold point and against a reference platinum resistance thermometer. The estimated accuracy of the temperature measurement varied as a function of temperature. At 100 °C, the accuracy was ± 3 °C; at 800 °C, ± 2 °C; from 1000 to 1600 °C, ± 1 °C; from 1600 to 2200 °C, ± 2 °C; and ± 3 °C above 2200 °C.

HEATING CYCLES

The temperature of the furnace was raised in steps during thermal diffusivity measurements and was held near the desired temperature until the temperature was constant with time. Heating rates varied between 5 to 10 °C/min from room temperature to 1800 °C and from 20 to 25 °C/min above 800 °C and approximately 5 to 10 °C/min below 800 °C. (See Appendix A.)

Measurements were made in purified argon at a slightly positive pressure between 1 to 2 psi. The argon was passed

over 600 °C copper turnings and through a molecular sieve drier before introduction into the furnace. This gas contained 1 to 2 ppm oxygen and 3 to 7 ppm water. The flow rate into the 11 liter, water-cooled furnace shell was approximately 1 to 2 liter/min. The dew point of the furnace atmosphere was measured continuously using a hygrometer, and the oxygen content of the inlet gas was also continuously monitored using a solid electrolyte, electrochemical oxygen meter. The primary impurity in the gas was N₂ (<40 ppm).

The measurement conditions are summarized in Table 1. With the exception of RR-3, each sample was initially heated to 1000 to 1200 °C and cooled with measurements being made on heating. Subsequent cycles were made to higher temperatures, with measurements also being made both on heating and cooling. Generally, more data points were obtained on heating than on cooling. Samples were removed from the furnace after each cycle for examination to determine if the sample had changed or if experimental errors could be introduced by altering the position of the sample in the UO₂ holder.

TABLE 1. Thermal Cycling Conditions for "Round Robin" UO₂

Sample Thickness, cm	Temperatures, °C			
	Cycle 1	Cycle 2	Cycle 3	Cycle 4 and 5
RR-1 (0.081)	16-1208 ^(a)	94-1216	266-2012	1326-1336 1087-2111
RR-2 (0.127)	17-1200 ^(b)	400-1010	88-1487	
RR-3 (0.081- 0.076)	399-2500	16-1012 ^(c)	25-1519 ^(d)	

a. Because of instrument difficulties, precision of data was less than for other data.

b. No thermal diffusivity data obtained.

c. Sample surfaces coated with graphite (thickness 0.081).

d. Graphite coating removed mechanically (thickness 0.0761).

LASER PULSE

The samples were heated with a 3 to 5 J pulse from a 1.27 cm-diameter, 15.2 cm-long ruby laser ($\lambda = 6943 \text{ \AA}$). The laser pulse time was 0.00054 sec and approximated a square wave (Figure 2).

TRANSIENT TEMPERATURE MEASUREMENTS

The temperature rise on the back surface of the sample was measured with a liquid nitrogen-cooled, indium antimonide infrared detector. Operation at liquid nitrogen temperatures provided maximum sensitivity and optimum signal to noise ratio. The thermal radiation from the sample passed through a tungsten sight tube with a diameter less than the sample diameter to minimize impingement of extraneous radiation from other parts of the system (Figure 4). This allowed only the central area of the sample to be viewed by the detector.

A silicon lense was positioned near the detector to focus the radiation from the sample on the detector. This silicon window protected the detector from incidental irradiation from the laser beam, the flash tube, or other radiation with wavelengths less than 1μ . The Al_2O_3 window of the detector has a cutoff wavelength of approximately 5.5μ . Thus the detector was sensitive only to infrared radiation between 1 and 5.5μ .

The detector provided maximum sensitivity when the emf of detector was near zero, and the detector was biased before each measurement with an external voltage from a battery. At the higher temperatures, where the radiation energy from the sample was large, a neutral density filter(s) was placed between the sample and the detector to reduce the voltage necessary to null the detector.

The output from the detector was amplified, displayed on an oscilloscope, and photographed on film (Figure 5).

Time
RR-3, Cycle 1, 826 °C, 1.0 mv/cm
and 50 msec/cm

Time
RR-3, Cycle 2, 491 °C, 10 mv/cm
and 100 msec/cm

FIGURE 5. Examples of Oscilloscope Tracings of Temperature Transients on Rear Surface of RR-3 "Round Robin" UO_2

Measurements could be made to temperatures as low as 16 °C, although the signal to noise ratio was low making it difficult to accurately evaluate the tracing. Above 100 °C, the signal was of sufficient strength for accurate measurements to be made.

The oscilloscope tracing was analyzed with an optical comparator with an accuracy of ± 0.005 cm. With a sweep time of 50 msec/cm, times can be determined to within $\pm 0.5\%$. However, the error in reading the tracings is in determining the position of the line on the photograph due to line width and noise. The precision of this measuring technique was estimated to be within $\pm 1\%$ using a sweep time of 50 msec/cm. The overall accuracy for measuring the tracing from the photograph is estimated to be $\pm 2\%$.

CALIBRATION OF APPARATUS

The thermal diffusivity apparatus was calibrated using ARMCO iron. The thermal diffusivity results for the iron are in satisfactory agreement with the reported values. Details of these calibrations have been reported elsewhere.⁽⁹⁾

CALCULATION OF THERMAL DIFFUSIVITY/CONDUCTIVITY

The thermal diffusivity (cm^2/sec) value was calculated from relationship

$$\alpha = \frac{d^2}{t_c \pi^2} \quad (5)$$

The sample thickness (d) was corrected for thermal expansion using the data reported by Conway, Fincel and Hein⁽¹⁰⁾ which had been extrapolated to 2500 °C by Conway and Feith.⁽¹⁾ The correction is

$$d = d_o \left(1 + \frac{\Delta L}{L_o} \right) \quad (6)$$

where $\frac{\Delta L}{L_0}$ is the fractional thermal expansion at temperature $T(^{\circ}\text{C})$.

L_0 is the sample length at 16°C .

d_0 is the sample thickness at 16°C .

The thermal conductivity (λ , W/cm- $^{\circ}\text{C}$) was calculated from the relationship

$$\lambda = 4.186 \alpha \cdot C_p \cdot \rho \quad (7)$$

where C_p (cal/g- $^{\circ}\text{C}$) is the heat capacity.

ρ (g/cm³) is the sample density at 16°C .

Both C_p and ρ are functions of temperature, and values must correspond to the temperature used to measure α .

The density correction was calculated from the expansion

$$\rho = \frac{\rho_0}{(1 + e \frac{\Delta L}{L_0})} \quad (8)$$

where ρ_0 is measured density at room temperature.

ρ is density at temperature, T .

This approximation assumes the thermal expansion of UO_2 to be isotropic.

The polynomial expression for $\frac{L}{L_0}$ used to calculate sample thickness and density changes as a function of temperature was

$$\begin{aligned} \frac{L}{L_0} = & - 2.0701 \times 10^{-4} + 8.4051 \times 10^{-6} T \\ & + 1.6502 \times 10^{-9} T^2 + 2.6128 \times 10^{-13} T^3 \end{aligned} \quad (9)$$

with T in $^{\circ}\text{C}$. This equation is valid only from 16 to 2500°C .

Heat capacity values were those suggested by Conway and Feith.⁽¹⁾ The original values were obtained from combined

data of Kelley⁽¹¹⁾ and Hein and Flagella⁽¹²⁾ in which the intermediate values from 1200 to 1800 °K are averages of the two data. The polynomial expression for C_p used to calculate the thermal conductivity was

$$C_p = 5.4662 \times 10^{-2} + 9.2506 \times 10^{-5} T - 1.9890 \times 10^{-7} T^2 \\ + 2.5575 \times 10^{-10} T^3 - 1.8582 \times 10^{-13} T^4 + 6.9070 \\ \times 10^{-17} T^5 - 9.7477 \times 10^{-21} T^6$$

with T expressed in °C. This equation is valid only from 27 to 2527 °C.

URANIUM DIOXIDE SAMPLES

Measurements were made on sintered UO_2 discs, 0.635 cm in diameter and 0.0760 ± 0.0005 and 0.127 ± 0.0005 cm thick. The sample discs were fabricated and machined by the GE-SNP. The fabrication technique and the sample properties have been reported.^(1,2) The samples were designated as RR-1 (0.077 cm), RR-2 (0.127 cm), and RR-3 (0.081 cm). Some comparative analytical evaluation was made at BNW, and these results are summarized in Table 2 and are compared with the data reported by GE-NSP.

The microstructures of the samples were studied before and after the thermal diffusivity measurements (Figures 6 through 8). The average grain size was between 41 and 50 μ . The larger pores were found principally at grain boundaries, and the small pores were concentrated within the grains. The as-received pellets contained a metallic second phase which was found principally at the grain boundaries, especially at the intersection of grain boundaries or at the pores. Electron microprobe analysis showed these metallic inclusions to contain primarily iron with lesser amounts of chromium, nickel, and uranium.

TABLE 2. Properties of "Round Robin" UO_2

	BNW	G.E.	
Density	10.79 g/cm ³ ^(a) (98.4% TD)	10.72 - 10.87 g/cm ³ (97.72 - 99.1% TD)	
O/U	2.000 ± 0.002 ^(b)	2.003 - 2.007 ± 0.003	
Average Grain Size			
a. Before measurements	100-250	41 to 50 μ	
b. After measurements	100-250	----	
Uranium Content	----	87.57%	
Total Impurity content	----	322 to 487 ppm	
Sample Dimensions (after measurements) (cm)			
	Diameter	Thickness	Weight ^(c)
RR-1	0.634 ± 0.001	0.0775 ± 0.006	0.2532 g
RR-2	0.632 ± 0.001	0.1283 ± 0.0006	0.4316 g
RR-3			
(a) Initially	0.636 ± 0.001	0.0810 ± 0.0006	0.2631 g
(b) Uncoated	0.636 ± 0.001	0.1281 ± 0.0006	---

a. Measured by mercury displacement.

b. Measured by a modified gravimetric technique. ⁽¹³⁾

c. No significant weight change occurred within experimental limit.

100X

250X

Before Measurements

100X

250X

After Measurements

FIGURE 6. Microstructure of "Round Robin" UO₂ - RR-1, Before and After Thermal Diffusivity Measurements

100X

250X

Before Measurements

10M - IC

100X

250X

After Measurements

FIGURE 7. Microstructure of "Round Robin" UO_2 - RR-2, Before and After Thermal Diffusivity Measurements

FIGURE 8. Microstructure of "Round Robin" UO_2 -RR-3, After Thermal Diffusivity Measurements

A similar metallic second phase was seen in the typical microstructures for the "round robin" UO_2 samples 4-2 and 18-3 reported by Conway and Feith.⁽¹⁾ The presence of the iron, nickel, and chromium is traceable to the starting UO_2 powder which contained 100 ppm iron, 25 ppm Chromium, and 45 ppm nickel.

The measured O/M ratio of a larger sibling sample* was 2.000 ± 0.002 . This is lower than the reported $2.003 - 2.007 \pm 0.003$ reported by GE-NSP. No O/M measurements were made after thermal diffusivity measurements.

* This O/M was determined using a modified gravimetric analysis developed by McNeilly and Chikalla.⁽¹³⁾ The accuracy of this technique is reported to be ± 0.002 .

RESULTS AND DISCUSSION

The thermal diffusivity and conductivity of the "round robin" UO_2 are summarized in Figures 9 through 11. The data is tabulated and graphically illustrated in detail in Appendix A.

The data for all three specimens are the same only after the samples had been heated from 1200 to 1500 °C. The thermal diffusivity values between room temperature and 1200 °C are higher during the first cycle. The diffusivity decreased during subsequent heating cycles and attained a reproducible value only after prolonged heating at 1200 °C or after heating to 1500 °C or higher for shorter periods. For example, the diffusivity of RR-1 at 400 °C decreases from 0.0200 to 0.0188 after heating to 1200 °C and decreased to approximately 0.0174 after a second heating to 1200 °C. This latter value was reproduced during the third and fourth cycles (Figure 9). The diffusivity of RR-3 at 400 °C decreased from 0.0190 to 0.0176 during the first cycle on cooling after heating to 2500 °C. In all instances, the diffusivity approached a common value after heating to 1500 °C.

It was evident that the as-received sample was changing during thermal diffusivity measurements. This change resulted in a decrease in the thermal diffusivity and is attributed to an increase in stoichiometry from a starting hypostoichiometric sample. The O/U ratio of the as-fabricated samples was reported to be between 2.002 to 2.007. ⁽¹⁾ In the argon atmosphere and temperatures (1200 °C) used to measure the diffusivity, these stoichiometries should not change. However, if the samples were hypostoichiometric initially, the initial thermal diffusivity could be higher than for stoichiometric oxide. Exposure to the argon containing 1 to 2 ppm O_2 and 3 to 5 ppm H_2O at 1200 °C would have oxidized the samples to a final, nearly stoichiometric composition resulting in a decrease in diffusivity. Ross, (14)

FIGURE 9. Thermal Diffusivity of RR-1 Showing Decrease in Conductivity During Heating Cycles

FIGURE 10. Thermal Diffusivity of All "Round Robin" UO₂ Specimens After Initial Heat Treatment to 1500 °C

FIGURE 11. Thermal Conductivity of "Round Robin" UO₂ Compared to Conductivity of UO₂ Reported by Godfrey et al. and Stora et al., and Showing Decrease in Conductivity During Initial Thermal Cycles (RR-1 and RR-3)

Howard and Gulvin,⁽¹⁵⁾ and May,⁽¹⁶⁾ have reported hypostoichiometric UO_2 to have a higher thermal conductivity at low temperatures. Similar effects have been noted by the author for single crystal UO_2 .

Ceramographic examination of the "round robin" UO_2 before and after thermal diffusivity measurements (Figure 6 through 8) shows that the metallic iron, chromium, nickel, and uranium phase was no longer present in the samples after measurement, suggesting a possible change in stoichiometry and/or composition. Similar unidentified metallic phases can be seen in the microstructures of "round robin" samples reported by Conway and Feith.⁽¹⁾ However, it is difficult to see how free Fe-Ni-Cr-U could be retained during the fabrication process which involved presintering to 1700 °C and final sintering to 2250 °C in hydrogen, followed by a final heat treatment at 1700 °C in wet hydrogen designed to make the oxide stoichiometric. Yet a treatment in argon during the thermal diffusivity measurement with oxygen pressures of approximately 10^{-7} atmospheres did remove or dissolve the alloy.

The O/M of the sibling samples was very near to stoichiometry and less than that reported by GE-SNP.

Thus, the variation in the diffusivity values of the as-received "round robin" UO_2 and the slightly higher thermal diffusivity values at low temperature may well be related to stoichiometric differences in the oxide. The fact that the data did approach the reported values of other "round robin" UO_2 investigators would also fortify this conclusion.

It was evident that the meaningful results for stoichiometric UO_2 should include data obtained only after the oxide had been heated to higher temperatures. Therefore, the data from Cycles 1 and 2 for RR-1 and the heating portion of Cycle 1 for RR-3 are not considered further in evaluating these data

for the stoichiometric "round robin" UO_2 . These results do support other evidence⁽¹⁴⁻¹⁶⁾ that the lower temperature (<1200 °C) diffusivity and conductivity of UO_2 increases as the O/U ratio of UO_2 decreases below 2.00.

The thermal diffusivity for all three "round robin" UO_2 samples after heat treatment are the same over the entire temperature range within the experimental error (Figure 10). The corresponding calculated thermal conductivity values are shown in Figure 11. These latter results are compared with the data of Godfrey et al⁽¹⁷⁾ and Stora et al⁽¹⁸⁾ (Figure 12). These values were recommended by the 1965 IAEA Panel⁽¹⁹⁾ on Thermal Conductivity to be the most reliable for UO_2 at that time. The data for "round robin" UO_2 measured in this study are approximately 10% higher than the recommended data at 400 °C but agree very well within experimental error at temperatures above 800 °C. However, the values above 1800 °C appear to be slightly lower than the data of Stora et al.⁽¹⁸⁾ However, the difference is still within the +5% experimental error. The difference becomes more pronounced near room temperature; however, this is also the temperature range where the experimental error is the highest and diffusivity measurements are most difficult. It is also the temperature range where stoichiometric effects are most pronounced.

Previous studies⁽²⁰⁾ have shown that single crystal UO_2 is, to a small degree, translucent to the ruby laser beam at room temperatures. Because of the large grain size of these samples, any penetration of the laser beam into the sample could influence the thermal diffusivity results. Two tests were made to determine if this problem was resulting in an error in the thermal diffusivity. Any error would result in an apparent higher thermal diffusivity.

- The first was measurements on two sample thicknesses, (RR-1,3 and RR-2). If the absorption was not occurring at or very near the sample surface, the thicker sample would show substantially lower thermal conductivity values.
- The second was to cover the sample surfaces with an opaque coating of graphite to ensure that the laser pulse was absorbed at the surface. A coating of graphite was applied by painting successive coats of a graphite - water emulsion on both back and front surfaces of the sample until an opaque coating was developed. This would prevent any radiation from the laser beam to pass beyond the sample surface and to ensure that the infrared detector did not see beyond the sample surface. This technique had been successfully used in coating transparent oxide materials. RR-3 was coated after the initial high-temperature measurements. Measurements were made with the coating to approximately 1000 °C. The coating was removed mechanically, and the sample diffusivity measured to 1500 °C.

The thermal diffusivity was the same for both the thick and the thin samples. This does not agree with the reports by other investigators⁽¹⁾ of the "round robin" UO_2 using the same "flash" technique, who have indicated that thicker (0.127 cm) samples had a higher thermal diffusivity than thinner (0.076 cm) samples. No mention was made of coating the samples, and no explanation was given for the 2 to 17% difference in thermal diffusivity.

The diffusivity values for the coated and the uncoated samples were the same within experimental error. Although there was some indication that the values for coated samples were lower, below 100 °C, the experimental errors in this temperature range make it difficult to determine if this difference was real. Therefore, the transmission of the laser beam into the sample does not appear to influence the thermal diffusivity results.

One of the purposes of this "round robin" UO_2 program was to determine whether or not thermal conductivity of UO_2 exhibits a minimum value near 1500 °C. This can best be evaluated by plotting $1/\lambda$ or $1/\alpha$ versus T and determining the deviation from linearity

$$1/\lambda = A + BT \quad (10)$$

where A and B are constants. This equation also provides a convenient comparison between data from different investigators if the standard deviation and error are known.

Figure 12 shows a plot of thermal resistivity ($\text{W/cm} \cdot ^\circ\text{C}$)⁻¹ versus T , °C for all specimens. The results indicate that between 100 and 1600 °C, the data can be fitted to a straight line expressed by the equation

$$1/\lambda = 8.687 + 0.02516 T. \quad (11)$$

The standard deviations for any single measurement is 1.321; for the slope (A) is 1.725×10^{-5} and for the intercept (B) is 0.0160. Above 1600 °C, the data depart from this linear relationship indicating that the conductivity does reach a maximum and increases at the higher temperatures. Below 100 °C, the data suggest that the conductivity does not increase with decreasing temperature as fast as the T^{-1} relationship predicts.

A similar relationship was determined for the diffusivity where

$$1/\alpha = 22.11 + 0.09311 T \quad (12)$$

(See Appendix B). The standard deviation for any single point is 4.053, for A is 0.04900, and for B is 5.369×10^{-5} .

However, both $1/\lambda$ and $1/\alpha$ versus T plots indicate that the curve is S-shaped with lower values of resistivity near 500 and 1600 °C and higher values near room temperature and 1200 °C. This conclusion is reinforced in a plot of percent

FIGURE 10. Thermal Resistivity ($1/\lambda$) of "Round Robin" UO_2 Versus Temperature Between 16 and 1600 °C

deviation of $1/\lambda$ versus temperature for Equation (12), Figure 13. This was true for all three samples and for all heating cycles. Similar deviations in linearity of $1/\lambda$ have been observed for $(U_{0.8}Pu_{0.2})O_2$ with maximum and minima at the same temperatures.⁽²¹⁾

The thermal resistivities of the form in Equation (11) reported by other investigators for UO_2 and corrected to 98% TD are compared below.

CEN ⁽¹⁾	$\lambda^{-1} = 10.28 + 0.0228 T$
IAEA ⁽¹⁹⁾	$\lambda^{-1} = 11.16 + 0.0222 T$
Godfrey et al. ⁽¹⁷⁾	$\lambda^{-1} = 11.14 + 0.0223 T$ (± 3 -95% probability)
Bates, this study	$\lambda^{-1} = 8.51 + 0.0247 T$ (± 10 -95% probability)

The values for A are less than those of the other investigators because of the nonlinearity, the values for A and B depend upon the temperature range used to determine the equation. For example, from 100 to 1200 °C, the values approach

$$\lambda^{-1} = 11.05 + 0.0222 T$$

which agree very well with the CEN or Godfrey data.

Thus, because of the nonlinearity of the $1/\lambda$ versus temperature relationship of the data, it is somewhat different to exactly compare the results with other investigators. However, the results are not significantly different and agree within the limits of error, i.e., the $\pm 10\%$ error to 95% probability. Although the error is large when fitting a thermal resistivity versus temperature relationship, the error at any one temperature is $\pm 5\%$, well within the estimated accuracy of the technique (Figure 13).

FIGURE 13 The Percent Deviation of Thermal Resistivity Data From Least Squares Equation

CONCLUSION

The thermal diffusivity of "round robin" UO_2 was measured from 16 to 2500 °C using the "flash" thermal diffusivity technique. The samples were received and showed evidence of high thermal diffusivity values at low temperature until heated above 1200 °C. At these temperatures and at the measuring oxygen pressure, the samples oxidized to nearly-stoichiometric UO_2 with a corresponding decrease in the thermal diffusivity at lower temperatures. Assuming the final reproducible values to represent nearly-stoichiometric UO_2 , corresponding calculated thermal conductivity values agree within experimental error to the values of other reported "round robin" UO_2 conductivities and with the other accepted conductivity values. The values were slightly higher at lower temperatures and slightly lower at higher temperatures but agreed very well at the intermediate temperatures. The data indicate that thermal conductivity reaches a minimum at 1600 °C and increases with the higher temperatures.

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APPENDIX A

THERMAL DIFFUSIVITY/CONDUCTIVITY DATA
FOR SAMPLE RR-1

APPENDIX A

THERMAL DIFFUSIVITY DATA
FOR RANGE (R-1)

FIGURE A.1. Heating Cycles for Thermal Diffusivity Measurements of "Round Robin" UO_2 Sample RR-1

TABLE A.1. RR-1 Data

<u>Temp, °C</u>	<u>Thermal Diffusivity, cm²/sec</u>	<u>Thermal Conductivity, W/cm-°C</u>
<u>Cycle 1</u>		
16	0.0357	0.0902
16	0.0383	0.0966
204	0.0274	0.0824
196	0.0285	0.0852
194	0.0282	0.0843
398	0.0205	0.0657
399	0.0200	0.0640
398	0.0200	0.0640
599	0.0153	0.0504
603	0.0149	0.0491
600	0.0157	0.0518
604	0.0145	0.0478
795	0.0115	0.0387
799	0.0116	0.0390
1003	0.00995	0.0337
1004	0.00983	0.0333
1004	0.0100	0.0340
1003	0.00967	0.0327
1203	0.00732	0.0249
1202	0.00740	0.0252
1208	0.00825	0.0281
<u>Cycle 2</u>		
94	0.0297	0.0825
85	0.0294	0.0809
203	0.0262	0.0790
203	0.0261	0.0784
205	0.0241	0.0724
293	0.0217	0.0677
287	0.0222	0.0693
291	0.0219	0.0682
393	0.0182	0.0583
400	0.0181	0.0580
501	0.0167	0.0546
501	0.0160	0.0524
494	0.0167	0.0543
494	0.0164	0.0536
503	0.0164	0.0534
602	0.0146	0.0484
599	0.0146	0.0484
596	0.0154	0.0508
705	0.0134	0.0448

TABLE A.1. (contd)

Temp, °C	Thermal Diffusivity, cm ² /sec	Thermal Conductivity, W/cm-°C
702	0.0134	0.0448
701	0.0132	0.0439
800	0.0125	0.0420
801	0.0120	0.0401
803	0.0119	0.0400
899	0.0104	0.0349
1001	0.00967	0.0327
1005	0.00921	0.0312
1006	0.00948	0.0321
1102	0.00875	0.0297
1101	0.00812	0.0276
1102	0.00916	0.0311
1100	0.00886	0.0301
1216	0.00797	0.0272

Cycle 3

266	0.0212	0.0657
266	0.0215	0.0664
483	0.0150	0.0489
488	0.0156	0.0509
622	0.0126	0.0416
618	0.0133	0.0440
721	0.0116	0.0387
722	0.0118	0.0395
907	0.00978	0.0330
912	0.00932	0.0315
1052	0.00842	0.0285
1052	0.00852	0.0289
1216	0.00730	0.0249
1218	0.00752	0.0253
1393	0.00684	0.0236
1382	0.00677	0.0233
1505	0.00624	0.0219
1507	0.00593	0.0208
1590	0.00600	0.0214
1593	0.00600	0.0214
1704	0.00555	0.0205
1699	0.00592	0.0219
1820	0.00562	0.0229
1829	0.00569	0.0222
1901	0.00555	0.0225
1914	0.00548	0.0224
2100	0.00551	0.0255

TABLE A.1. (contd)

<u>Temp,</u> <u>°C</u>	<u>Thermal</u> <u>Diffusivity,</u> <u>cm²/sec</u>	<u>Thermal</u> <u>Conductivity,</u> <u>W/cm-°C</u>
2100	0.00583	0.0270
2007	0.00532	0.0231
2012	0.00559	0.0244
1326	0.00682	0.0234
1328	0.00714	0.0245
1336	0.00668	0.0229

Cycle 4

1087	0.00832	0.0283
1180	0.00708	0.0241
1289	0.00715	0.0245
1376	0.00678	0.0233
1477	0.00670	0.0234
1634	0.00575	0.0208
1732	0.00552	0.0206
1734	0.00607	0.0227
1836	0.00550	0.0216
1831	0.00574	0.0224
1922	0.00569	0.0234
2022	0.00571	0.0250
2111	0.00532	0.0248

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APPENDIX B

THERMAL DIFFUSIVITY/CONDUCTIVITY DATA
FOR SAMPLE RR-2

FIGURE B.1. Heating Cycles for Thermal Diffusivity Measurements of "Round Robin" UO₂ Sample RR-2

TABLE B.1. RR-2 Data

Temp, °C	Thermal Diffusivity, cm ² /sec	Thermal Conductivity, W/cm-°C
<u>Cycle 2</u>		
88	0.0296	0.0818
89	0.0306	0.0845
191	0.0235	0.0702
196	0.0232	0.0694
191	0.0246	0.0733
298	0.0185	0.0579
304	0.0195	0.0610
304	0.0199	0.0623
388	0.01687	0.0540
409	0.0165	0.0548
513	0.0138	0.0454
511	0.0137	0.0451
512	0.0143	0.0460
593	0.0128	0.0420
594	0.0125	0.0420
688	0.0113	0.0377
688	0.0110	0.0367
688	0.0120	0.0401
796	0.0101	0.0338
798	0.00997	0.0334
796	0.0105	0.0354
898	0.00908	0.0306
901	0.00917	0.0309
900	0.00968	0.0326
997	0.00833	0.0281
996	0.00851	0.0288
997	0.00834	0.0282
1088	0.00751	0.0255
1088	0.00776	0.0263
1087	0.00762	0.0259
1088	0.00776	0.0263
1198	0.00741	0.0252
1199	0.00752	0.0265
1196	0.00658	0.0224
1296	0.00692	0.0237
1298	0.00695	0.0238
1296	0.00708	0.0243
1410	0.00663	0.0229
1410	0.00674	0.0233
1485	0.00644	0.0225
1483	0.00611	0.0214
1487	0.00639	0.0223

TABLE B.1. (contd)

<u>Temp, °C</u>	<u>Thermal Diffusivity, cm²/sec</u>	<u>Thermal Conductivity, W/cm-°C</u>
<u>Cycle 3</u>		
400	0.0175	0.0561
1010	0.0814	0.0276
400	0.0171	0.0549

FIGURE B.2. Thermal Conductivity of "Round Robin" UO_2 Sample RR-2

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APPENDIX C

THERMAL DIFFUSIVITY/CONDUCTIVITY DATA
FOR SAMPLE RR-3

1941-1942

APPENDIX C

FIGURE C.1. Heating Cycles for Thermal Diffusivity Measurements of "Round Robin" UO_2 Sample RR-3

TABLE C.1. RR-3 Data

<u>Temp,</u> <u>°C</u>	<u>Thermal</u> <u>Diffusivity,</u> <u>cm²/sec</u>	<u>Thermal</u> <u>Conductivity,</u> <u>W/cm-°C</u>
<u>Cycle 1</u>		
399	0.0187	0.0600
400	0.0190	0.0612
400	0.0187	0.0599
397	0.0193	0.0620
605	0.0153	0.0505
604	0.0154	0.0511
604	0.0148	0.0491
604	0.0148	0.0491
815	0.0116	0.0390
815	0.0115	0.0385
815	0.0113	0.0379
815	0.0113	0.0379
998	0.00949	0.0321
1001	0.00921	0.0312
995	0.00951	0.0322
994	0.00953	0.0323
1205	0.00743	0.0253
1208	0.00747	0.0255
1213	0.00735	0.0251
1212	0.00743	0.0253
1399	0.00637	0.0220
1404	0.00631	0.0218
1399	0.00646	0.0223
1386	0.00651	0.0225
1593	0.00557	0.0199
1603	0.00559	0.0200
1608	0.00557	0.0200
1603	0.00615	0.0220
1788	0.00545	0.0209
1804	0.00543	0.0210
1801	0.00552	0.0213
2003	0.00523	0.0227
2005	0.00528	0.0229
2252	0.00533	0.0275
2259	0.00481	0.0249
2500	0.00425	0.0293
827	0.0100	0.0363
816	0.0102	0.0343
817	0.0106	0.0357
826	0.0102	0.0344
540	0.0149	0.0492
524	0.0148	0.0486

TABLE C.1. (contd)

<u>Temp,</u> <u>°C</u>	<u>Thermal</u> <u>Diffusivity,</u> <u>cm²/sec</u>	<u>Thermal</u> <u>Conductivity,</u> <u>W/cm-°C</u>
<u>Cycle 2 (Coated)</u>		
16	0.0328	0.0827
28	0.0347	0.0891
32	0.0334	0.0863
59	0.0312	0.0835
121	0.0288	0.0819
107	0.0286	0.0804
193	0.0240	0.0718
199	0.0247	0.0739
314	0.0208	0.0654
310	0.0206	0.0648
403	0.0171	0.0549
406	0.0173	0.0559
490	0.0156	0.0508
491	0.0159	0.0520
600	0.0138	0.0455
603	0.0131	0.0434
706	0.0120	0.0399
708	0.0120	0.0400
792	0.0113	0.0377
799	0.0111	0.0372
915	0.00945	0.0319
914	0.0100	0.0338
1004	0.00908	0.0310
1012	0.00943	0.0320
1011	0.00961	0.0329
798	0.0112	0.0373
607	0.0140	0.0462
606	0.0138	0.0457
606	0.0138	0.0457
405	0.0165	0.0541
276	0.0206	0.0641
191	0.0238	0.0710
187	0.0239	0.0711
126	0.0276	0.0787
124	0.0279	0.0794
79	0.0278	0.0761
<u>Cycle 3 (Uncoated)</u>		
25	0.0360	0.0920
104	0.0308	0.0864
201	0.0232	0.0697
200	0.0230	0.0688

TABLE C.1. (contd)

<u>Temp, °C</u>	<u>Thermal Diffusivity, cm²/sec</u>	<u>Thermal Conductivity, W/cm-°C</u>
300	0.0200	0.0625
310	0.0190	0.0596
407	0.0169	0.0544
408	0.0165	0.0532
405	0.0168	0.0540
503	0.0152	0.0495
502	0.0152	0.0501
618	0.0128	0.0422
622	0.0130	0.0435
695	0.0121	0.0402
700	0.0120	0.0400
814	0.0104	0.0348
808	0.0105	0.0351
899	0.00967	0.0326
900	0.00944	0.0318
1019	0.00841	0.0285
1018	0.00829	0.0281
1104	0.00778	0.0264
1107	0.00771	0.0262
1200	0.00738	0.0252
1204	0.00754	0.0257
1305	0.00663	0.0227
1311	0.00705	0.0242
1400	0.00633	0.0219
1406	0.00624	0.0216
1496	0.00583	0.0204
1519	0.00623	0.0219
1513	0.00609	0.0214
1322	0.00707	0.0243
1323	0.00693	0.0238
1127	0.00766	0.0260
1126	0.00749	0.0255
893	0.00981	0.0331
806	0.0103	0.0347
812	0.0105	0.0353
574	0.0136	0.0448
574	0.0137	0.0451
304	0.0193	0.0605
280	0.0202	0.0629

FIGURE C.2. Thermal Conductivity of "Round Robin" UO_2 Sample RR-3

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APPENDIX D

ALL ROUND ROBIN $\underline{UO}_2$ DATA.

1881-1882

1881-1882

TABLE D.1. Polynomial Fitting of Thermal Diffusivity Data [Except RR-1 (Cycles 1 and 2) and RR-3 (Cycle 1 on Heating <1500 °C)]

$$\lambda = A + BT + CT^2 + DT^3 + ET^4$$

Sample	Cycle	A	B	C	D	E
RR-1	1	3.7920×10^{-2}	-5.5633×10^{-5}	2.2812×10^{-8}	1.7775×10^{-11}	-1.3017×10^{-14}
	2	3.5750×10^{-2}	-6.6721×10^{-5}	7.9569×10^{-8}	-5.3206×10^{-11}	1.4278×10^{-14}
	3-5	3.2078×10^{-2}	-5.0325×10^{-5}	4.0699×10^{-8}	-1.6334×10^{-11}	2.6723×10^{-15}
RR-2	2,3	3.6032×10^{-2}	-7.8956×10^{-5}	9.9033×10^{-8}	-6.3540×10^{-11}	1.5927×10^{-14}
RR-3	1	3.1143×10^{-2}	-3.8084×10^{-5}	1.9588×10^{-8}	-3.7168×10^{-11}	1.0429×10^{-15}
	2	3.4873×10^{-2}	-6.8092×10^{-5}	8.1694×10^{-8}	-5.5000×10^{-11}	1.5968×10^{-14}
	3	3.7854×10^{-2}	-8.9887×10^{-5}	1.2263×10^{-7}	-8.2846×10^{-11}	2.1124×10^{-14}
RR	A11 ^(a)	3.4372×10^{-2}	-6.0327×10^{-5}	5.3241×10^{-8}	-2.2177×10^{-11}	3.4845×10^{-15}

a. Except RR-1 (Cycles 1 and 2) and RR-3, Cycle 1 (heating <1500 °C).

See Figure 10 in text for Figure illustrating all data.

TABLE D.2. Polynomial Fitting of Thermal Conductivity Data [Except RR-1, Cycles 1 and 2) and RR-3 (Cycle 1 on Heating <1500 °C)]

$$\lambda = A + BT + CT^2 + DT^3 + ET^4$$

Sample	Cycle	A	B	C	D	E
RR-1	1	9.3865×10^{-2}	-1.2895×10^{-5}	-2.6445×10^{-7}	3.5060×10^{-10}	-1.3361×10^{-13}
	2	8.9537×10^{-2}	-6.9606×10^{-5}	-3.4736×10^{-8}	8.3476×10^{-11}	-3.5556×10^{-14}
	3,4,5	9.3275×10^{-2}	-1.2434×10^{-4}	8.8897×10^{-8}	-3.4396×10^{-11}	6.1621×10^{-15}
RR-2	2,3	9.4130×10^{-2}	-1.4119×10^{-4}	1.2832×10^{-7}	-7.0384×10^{-11}	1.7614×10^{-14}
RR-3	1	9.1495×10^{-2}	-8.8260×10^{-5}	2.4833×10^{-8}	4.3053×10^{-12}	-1.6315×10^{-15}
	2	8.7802×10^{-2}	-7.5837×10^{-5}	-5.2000×10^{-8}	1.3655×10^{-10}	-6.4695×10^{-14}
	3	9.6787×10^{-2}	-1.5731×10^{-4}	1.6430×10^{-7}	-9.9086×10^{-11}	2.4798×10^{-14}
RR	All ^(a)	9.0482×10^{-2}	-1.1011×10^{-4}	6.3835×10^{-8}	-1.7120×10^{-11}	2.1933×10^{-15}

a. Except RR-1 Cycles 1 and 2 and RR-3 Cycle 1 (heating <1500 °C)

FIGURE D.1. Thermal Conductivity of All "Round Robin" UO₂ Data (Except RR-1, Cycles 1 and 2 and RR-3, Cycle 1 on Heating <1500 °C)

TABLE D.3. Thermal Resistivity ($1/\alpha$) for "Round Robin" UO_2 (Exception RR-1, Cycles 1 and 2 and RR-3 on Heating $<1500^\circ\text{C}$)

$$1/\alpha = A + BT$$

Sample	Cycle	A	B	Single Measurement	A	B
RR-1	1	20.376	0.080279	2.9006	0.27954	4.1765×10^{-4}
	2	22.127	0.080299	3.1389	0.19843	2.9051×10^{-4}
	3-4-5	33.810	0.078798	8.2057	0.52687	3.6040×10^{-4}
RR-2	All Data	24.415	0.092175	4.1932	0.20675	2.2981×10^{-4}
RR-3	1	18.127	0.091586	7.7767	0.44101	3.5027×10^{-4}
	2	26.625	0.078248	1.8342	0.088369	1.5914×10^{-4}
	3	21.503	0.094383	3.1987	0.16297	1.8044×10^{-4}
All*		22.11	0.093112	4.0529	0.049903	5.3688×10^{-5}
<hr/>						
*		8.6872	0.025158	1.3305	0.016008	1.7247×10^{-5}

FIGURE D.2. Thermal Resistivity ($1/\alpha$) for "Round Robin" UO₂
(Except RR-1, Cycles 1 and 2 and RR-3, Cycle 1 on
Heating <1500 °C)

FIGURE D.3. Thermal Resistivity ($1/\lambda$) for "Round Robin" UO₂ (Except RR-1, Cycles 1 and 2, and RR-3, Cycle 1 on Heating <1500 °C)

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