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THERMAL EXPANSION OF $^{238}\text{PuO}_2$

by

J. F. Andrew, R. W. Zocher, and R. A. Kent

ABSTRACT

The linear thermal expansion of stoichiometric $^{238}\text{PuO}_2$ was measured over the range 25–1600°C. The value of $\Delta L/L_0$ per degree C, calculated from the data, is

$$\Delta L/L_0 = -2.249 \times 10^{-4} + 9.020 \times 10^{-6}T - 1.130 \times 10^{-9}T^2 + 1.525 \times 10^{-12}T^3.$$

I. INTRODUCTION

Isotopic heat sources, fueled with $^{238}\text{PuO}_2$ (80% ^{238}Pu), have been used in a number of space missions to supply the electrical energy required for on-board instruments. Although the thermal expansion of $^{238}\text{PuO}_2$ has been measured^{1,2} over the range 25–1400°C, that for $^{238}\text{PuO}_2$ (80% ^{238}Pu) has not been measured. Because the half-life³ of ^{238}Pu , 87.8 yr, is much shorter than that of ^{239}Pu , 24 390 yr, greater self-irradiation damage occurs to the $^{238}\text{PuO}_2$ lattice. In addition, self-heating problems associated with the ^{238}Pu are much greater than for ^{239}Pu . Finally, due to the α -decay of ^{238}Pu , ^{234}U grows into the $^{238}\text{PuO}_2$ lattice at the rate of about 0.5 wt% per yr. The thermal expansion of $^{238}\text{PuO}_2$ was measured in order to provide data for the actual fuel material used in thermal generators in space.

II. EXPERIMENTAL

A. Specimen Fabrication and Analyses

Three $^{238}\text{PuO}_2$ (80% ^{238}Pu) bar specimens, of the type shown in Fig. 1, were used in these experiments. Two lots of specimens were hot pressed in graphite dies from <125 μm PuO_2 granules that had been thermally seasoned for 3 h at 1150°C. During the hot pressing cycle,

Fig. 1. $^{238}\text{PuO}_2$ thermal expansion specimens.

plutonia is reduced so that as-pressed specimens have an O/Pu ratio of about 1.89. Therefore, the hot pressed specimens were reoxidized by heating them in flowing $\text{Ar-H}_2^{16}\text{O}$. The use of H_2^{16}O results in a conversion of the oxygen in the plutonia to ^{16}O , thereby reducing the neutron emission rate caused by (α, n) reactions with ^{17}O and ^{18}O . The specimens from lot HPZ-69 were heated for 6 h at 1350°C, those from lot HPZ-70 for 12 h at 1000°C, followed by 6 h at 1600°C. Fabrication data for

the $^{238}\text{PuO}_2$ specimens are listed in Table I. Spectrochemical data are listed in Table II for the feed material and for the specimens at the completion of the experiments. Additional analytical data are listed in Table III.

The platinum standard rod, 0.95-cm diam by 6-cm long, was fabricated at LASL. Spectrochemical data are listed in Table IV.

B. Thermal Expansion Experiments

The thermal expansion specimens, longer end up, were placed on a tungsten block that had been flame spray-coated with a 0.008-cm layer of thoria to prevent reactions between the tungsten and the plutonia. The block was grooved to accept two chromel-alumel thermocouples calibrated against NBS standards and was also provided with a blockbody hole for temperature measurement by means of an optical pyrometer, located outside the glovebox. The block was located within a tungsten-mesh horizontal tube furnace that could be programmed for heating cycles from 25 to 2500°C. All thermal expansion measurements were made with helium flowing through the furnace at the rate of 1.9 L/min and a pressure of 81 kPa. Air pressure at Los Alamos is about 80% that at sea level.

The thermal expansion of the specimens was measured by means of two precision telemicroscopes rigidly mounted to a stand located outside the glovebox. The telescopes were aligned with the sharp corners at the top of the specimens. Filar micrometer eyepieces calibrated with a fused silica scale at 25°C were used to measure the changes in length of the specimens at elevated temperatures. During the thermal expansion runs, the specimens were back-lighted with a tungsten lamp.

III. RESULTS AND DISCUSSION

A. Platinum Specimen

The thermal expansion of the platinum bar was measured over the range 25 to 1500°C to test both the technique and the experimental equipment. Data are listed in Table V and plotted in Fig. 2. These data, corrected to the reference temperature, 25°C, lead to the equation

Fig. 2. Thermal expansion data for platinum.

where

$$\Delta L/L_0 = (L - L_0)/L_0 \text{ per degree C,}$$

L is the length at the experimental temperature and L_0 is the length at 25°C. Thermal expansion data calculated from Eq. (1) are compared to those obtained by Hahn and Kirby⁴ in Table VI. The agreement between the two sets of data indicate the accuracy of the experimental procedures and equipment.

B. $^{238}\text{PuO}_2$ Specimens

Specimen HPZ-69-1, sintered at 1350°C, was placed in the furnace and heated in stepwise fashion to 2000°C. Thermal expansion measurements were made under conditions of thermal equilibrium. The times required to obtain thermal equilibrium ranged from about 1 h at the lower temperatures to 15 min at the highest temperatures. Above 1600°C, the thermal expansion vs temperature curve began to break upward, presumably due to reduction of the PuO_2 , even in flowing helium. After the specimen was heated to 2000°C, it was cooled and reweighed in an inert atmosphere (1 ppm oxygen) glovebox. The weight loss corresponded to a residue stoichiometry of about $\text{PuO}_{1.94}$. The specimen was reoxidized by heating it in $\text{Ar-H}_2^{16}\text{O}$ for 6 h at 1200°C and the thermal expansion experiment was repeated. The specimen was heated to

$$\Delta L/L_0 = -2.35 \times 10^{-4} + 9.38 \times 10^{-6}T + 2.60 \times 10^{-10}T^2 + 6.25 \times 10^{-13}T^3 \quad (1)$$

1746°C and then held at that temperature for 15 min. During this hold, the measured thermal expansion increased by 47%. The residual stoichiometry was $\text{PuO}_{1.97}$. The relative increases in the thermal expansion values at the higher temperatures are very close to those noted for the lattice parameters as PuO_2 is reduced.⁵ After the second thermal expansion experiment, the specimen was sampled for metallographic analysis. The average grain size was found to be 36 μm . Data for specimen HPZ-69-1 are listed in Table VII and plotted in Fig. 3.

Specimen HPZ-69-3 was further sintered in $\text{Ar-H}_2^{16}\text{O}$ for 6 h at 1600°C and the thermal expansion was measured to 1500°C. The residual stoichiometry was $\text{PuO}_{1.99}$ and the average grain size was found to be 26 μm . Data for this specimen are also listed in Table VII.

Specimen HPZ-70-3, sintered at 1527°C, was placed in the furnace and heated in stepwise fashion to 1500°C. Again, thermal expansion measurements were made under conditions of thermal equilibrium. The residual stoichiometry was $\text{PuO}_{1.99}$. The specimen was re-oxidized by heating it in $\text{Ar-H}_2^{16}\text{O}$ for 6 h at 1000°C, followed by 6 h at 1600°C. The thermal expansion experiment to 1500°C was repeated, and again, the residual O/Pu ratio was found to be 1.99. The average grain size for this specimen, after the thermal expansion runs, was found to be 25 μm . Thermal expansion data for specimen HPZ-70-3 are listed in Table VIII.

All of the $^{238}\text{PuO}_2$ thermal expansion data, corrected to the reference temperature, 25°C, were combined to yield the following equation, in degrees C

$$\Delta L/L_0 = -2.249 \times 10^{-4} + 9.020 \times 10^{-6}T - 1.130 \times 10^{-9}T^2 + 1.525 \times 10^{-12}T^3. \quad (2)$$

Recommended values for the thermal expansion of $^{238}\text{PuO}_2$, calculated from Eq. (2), are listed in Table IX and all of the data are plotted in Fig. 4. Data were not obtained below 100°C because of the self-heating associated with ^{238}Pu .

IV. SUMMARY

The thermal expansion of stoichiometric $^{238}\text{PuO}_2$ (88-90% TD) has been measured over the range 25 to 1600°C. Operating temperatures for $^{238}\text{PuO}_2$ fuel in

Fig. 3. Thermal expansion of $^{238}\text{PuO}_2$ specimen HPZ-61-1.

spacecraft electric generators fall in the range 800 to 1500°C. While reentry temperatures may be higher, to 1850°C, reentry times are short compared to the times at high temperatures encountered during the thermal expansion measurements. Therefore, the values calculated from Eq. (2), and listed in Table IX are believed to be sufficiently accurate ($\pm 10\%$) for calculations involving current or planned flight fuels over the full operational temperature range, including reentry, likely to be encountered during mission lifetimes.

The effects of stoichiometry and density will be determined in future experiments.

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Fig. 4. Thermal expansion of $^{238}\text{PuO}_2$, all data.

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TABLE I
FABRICATION PARAMETERS FOR $^{238}\text{PuO}_2$ SPECIMENS

Feed Material	$< 125\mu\text{m PuO}_2$, thermally seasoned at 1150°C
Hot Pressing Parameters	31.1 MPa (4500 psi) for 20 min at 1530°C
Specimen Sintering	6-12 h at T in $\text{Ar-H}_2^{16}\text{O}$

Results

Specimen HPZ No.	Sintering		Dimensions (cm)			Weight (g)	Density (% TD)
	Time (h)	Temp. ($^\circ\text{C}$)	Width	Height	Top Length		
69-1	As Pressed		0.963	0.948	5.123	40.980	86 ^a
	6	1350	0.956	0.942	5.083	41.256	88
69-3	As Pressed		0.961	0.946	5.117	41.058	87
	6	1350	0.956	0.942	5.165	41.335	87
	6	1600	0.954	0.941	4.994	41.293	90
70-3	As Pressed		0.976	0.936	5.031	41.400	89
	12	1000	0.975	0.935	5.045	41.679	89
	6	1527	0.976	0.938	5.034	41.665	89

^aAs-pressed specimens are $\text{PuO}_{1.89}$, sintered specimens, $\text{PuO}_{2.00}$.

TABLE II
SPECTROCHEMICAL DATA FOR $^{238}\text{PuO}_2$ SPECIMENS
(ppm by weight)

Species ^a	$^{238}\text{PuO}_2$ Feed Material	Bar Specimens ^b	
		HPZ-69-3	HPZ-70-3
Al	35	20	15
Ba	4	10	10
Ca	530	500	500
Cr	55	15	30
Cu	5	10	6
Fe	300	190	260
K	4	50	50
Mg	3	7	5
Mn	4	4	4
Ni	75	10	25
Pb	5	15	70
Si	400	500	500
Sr	ND	7	9
Tl	20	20	50
Zn	10	8	50
Zr	ND	7	25

^aThe following impurities were not detected in either the feed or the bar specimens; B, Be, Bi, Cd, Co, Cs, Hf, La, Li, Mo, Na, Nb, Rb, Re, Sn, Ta, V, W, and Y.

^bThe bar specimens were analyzed at the end of the experiments.

TABLE III
ANALYTICAL DATA FOR $^{238}\text{PuO}_2$ SPECIMENS

Species	Specimen ^a	
	HPZ-69-3	HPZ-70-3
Pu (wt%)	85.3	85.3
U (wt%)	1.40 ^b	1.40
Th (wt%)	0.05	0.09
Np (wt%)	0.21	0.20
Am (wt%)	0.11	0.11
O (wt%)	11.83	11.78
C (wt%)	0.02	0.02
Neutron Emission (n/s-g sample)	4580	3780

^aData are for bars at end of experiments.

^b ^{234}U grows in due to alpha-decay of ^{238}Pu .

TABLE IV

SPECTROCHEMICAL DATA FOR PLATINUM SPECIMEN

Species (ppm by weight)	
Au	5
Fe	40
Pd	10
Si	15

1. No other cation impurities were detected.
2. Values correspond to Pt purity of 99.993 wt%.

TABLE VI

COMPARISON OF THERMAL EXPANSION DATA FOR PLATINUM

Temp. (°C)	$(\Delta L/L_0) (\times 10^3)$	
	Hahn and Kirby (Ref. 4)	This Work Eq. (1)
38	0	0
100	0.78	0.70
200	1.68	1.64
300	2.61	2.62
400	3.59	3.60
500	4.59	4.60
600	5.63	5.63
700	6.68	6.67
800	7.77	7.76
900	8.89	8.88
1000	10.06	10.03
1100	11.26	11.23
1200	12.50	12.48
1300	13.78	13.78
1400	15.11	15.13
1500	16.51	16.54
1600	17.88	(18.01) ^a

^aExtrapolated.

TABLE V

THERMAL EXPANSION DATA FOR PLATINUM

Temp. (°C)	$\Delta L/L_0$ ($\times 10^3$)
16 ^a	0
222	1.92
326	2.81
411	3.81
515	4.91
618	5.91
703	6.85
780	7.60
875	8.72
1013	10.32
1078	11.18
1202	12.59
1328	14.42
1433	15.76
1493	16.71

^aTemperatures for first eight points measured with thermocouple, remainder with optical pyrometer.

TABLE VII

THERMAL EXPANSION DATA FOR SPECIMEN LOT HPZ-69

HPZ-69-1 ^a				HPZ-69-3 ^c	
Run 1		Run 2 ^b			
Temp. (°C)	$\Delta L/L_0$ ($\times 10^3$)	Temp. (°C)	$\Delta L/L_0$ ($\times 10^3$)	Temp. (°C)	$\Delta L/L_0$ ($\times 10^3$)
100	0.65	116	0.80	150	1.15
200	1.55	200	1.83	315	2.66
320	2.60	310	2.63	425	3.74
425	3.45	408	3.34	495	4.30
505	4.20	508	4.09	600	5.34
600	4.85	605	5.03	720	6.24
695	5.70	715	5.87	800	7.40
795	6.65	785	6.71	900	8.42
810	7.75	880	7.39	958	9.31
1000	9.05	980	8.35	1061	10.16
1100	10.35	1073	9.51	1148	11.70
1200	11.25	1148	10.61	1222	13.06
1365	12.40	1212	11.23	1318	14.28
1400	13.70	1360	12.76	1396	15.66
1504	14.70	1535	14.88	1493	17.24
		1636	17.02		
		1746	20.46		
		hold 15 min			
		1746	20.10		

^aValues $\Delta L/L_0$ corrected to 25°C reference temperature.

^bAfter first run to 2000°C, O/Pu ratio was 1.94. Specimen was reoxidized and used again. After second run, O/Pu ratio was 1.97.

^cAfter run, O/Pu ratio was 1.99.

TABLE VIII

THERMAL EXPANSION DATA FOR SPECIMEN HPZ-74-3

Run 1 ^a		Run 2 ^b	
Temp. (°C)	$\Delta L/L_0$ ($\times 10^3$)	Temp. (°C)	$\Delta L/L_0$ ($\times 10^3$)
110	0.65	130	0.70
295	2.66	285	1.81
430	4.03	415	2.92
525	5.10	525	4.05
625	6.05	555	4.43
710	6.81	640	5.00
810	7.75	680	5.18
914	8.76	780	5.92
1013	9.88	875	6.78
1126	11.35	956	7.60
1222	12.41	1030	8.60
1280	13.36	1170	10.80
1362	14.32	1260	12.02
1465	15.34	1310	12.82
1493	15.72	1384	14.22
		1482	15.44

^aValues of $\Delta L/L_0$ corrected to 25°C reference temperature.^bAfter first run, O/Pu ratio was 1.99. Specimen was re-oxidized and used again. After second run, O/Pu ratio again was 1.99.

TABLE IX

THERMAL EXPANSION OF STOICHIOMETRIC ²³⁸PuO₂

RECOMMENDED VALUES

Temp. (°C)	$\Delta L/L_0$ ($\times 10^3$)
25	0
50	0.23
100	0.67
200	1.55
300	2.42
400	3.30
500	4.19
600	5.11
700	6.09
800	6.99
900	7.89
1000	9.19
1100	10.36
1200	11.61
1300	12.94
1400	14.37
1500	15.91
1600	17.56
1700	(19.33) ^a
1800	(21.24)
1900	(23.29)
2000	(25.49)

^aValues in parentheses are extrapolated.