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***A High-Temperature X-Ray
Study of $^{238}\text{PuO}_2$ Plasma-
Formed Microspheres***

*R. J. DeSando, W. C. Wyder,
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SUMMARY

A high-temperature x-ray study of $^{238}\text{PuO}_2$ microspheres (50-250 μm in diameter) produced from an rf induction-coupled plasma torch has been conducted in the temperature interval of 14-1505°C. The lattice parameters obtained at 22 different temperatures exhibit linearity up to about 675°C and expand in a normal fashion up to 1137°C. The expansion curve undergoes anomalous behavior at 1137°C, which is attributed to a major fraction of helium (produced from alpha emission) being released and removal of configurational defects by annealing. The lattice parameters of the $^{238}\text{PuO}_2$ microspheres are slightly larger than the parameters of $^{238}\text{PuO}_2$ powder because of radiation damage and helium entrapment. Fourth-degree polynomial expressions as functions of temperature for the lattice parameter (a), instantaneous coefficient of thermal expansion (α_i), and fractional changes in the lattice parameter ($\Delta a/a$) are presented. Mean square atomic vibrational amplitudes were computed from the thermal expansion data using Grüneisen's theory, and exhibit an increase with temperature as expected. The root-mean-square vibrational amplitudes, $\langle u^2 \rangle_{\text{av}}^{1/2}$, at 50°C and 1137°C are 0.037 Å and 0.20 Å, respectively.

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INTRODUCTION

Refractory compounds of fissile materials are of interest as potential nuclear fuels. Microspheres¹ of $^{238}\text{PuO}_2$ have a specific power of 0.40 W/g or 12.1 Ci/g (based on 80% plutonium-238 in the element plutonium) and a power density of 2.5-2.8 W/cm³. An accurate knowledge of the thermal expansion coefficients of the material relative to suitable containers is necessary since the rate of heat transfer from the material is a function of the magnitude of the space between the material and the container at operating temperatures. Microspheres having nominal diameters between 50 and 250 μm were obtained by passage of polycrystalline $^{238}\text{PuO}_2$ (under a partial pressure of oxygen) through an rf induction-coupled plasma torch. It was deemed highly desirable to undertake a high-temperature x-ray study of the oxide to obtain thermal expansion data, to determine anomalous discontinuities (if any) in the expansion curve, and also to observe whether the oxide undergoes any phase transformations at elevated temperatures.

Previous thermal expansion measurements have been conducted on $^{238}\text{PuO}_2$ by bulk methods up to 1000°C,^{2,3} and by x-ray methods up to 980°C.⁴ The present study on $^{238}\text{PuO}_2$ microspheres was conducted in the temperature interval of 14-1505°C.

It has been established that factors other than temperature effects produce changes in the lattice parameter. They consist of the variable oxygen-to-plutonium ratio,^{4,5} self-irradiation damage resulting in the displacement of ions from their lattice sites and the formation of uranium-234 recoil nuclei,⁶⁻⁸ and interstitial effects due to helium production from alpha emission. The samples (typical production batches) employed in the thermal expansion measurements were stoichiometric, corroborated

by thermal gravimetric analyses and x-ray data. Lattice parameters of plasma-fired microspheres have consistently exhibited larger values than does the polycrystalline oxide; this phenomenon is attributed to self-irradiation damage and helium retention. Measurements of the release of helium from plasma-formed microspheres, conducted over the temperature range of 600 to 1200°C, indicate that most of the helium is released between 1000 and 1200°C.⁹

EXPERIMENTAL WORK

The $^{238}\text{PuO}_2$ microspheres were placed in quartz capillaries (0.3-mm inside diameter and 0.02 to 0.03-mm wall thickness) and sealed in an oxygen atmosphere in order to prevent loss of oxygen. The high-temperature camera (Debye-Scherrer type) used in the x-ray study was designed after the one of Edwards, Speiser and Johnston.¹⁰ The camera, capable of attaining temperatures in excess of 2000°C, is situated on top of and open to a glove box in order to contain radioactive materials; it can be operated in either a vacuum or an inert atmosphere. The upper and lower furnace elements consist of two hollow tantalum foil cylindrical resistance heaters; the sample sits in a tantalum holder and is radiantly heated. The heaters are surrounded by tantalum foil radiation shields, which in turn are surrounded by water-cooled copper jackets.

A beryllium vapor shield protects the beryllium camera window. The film sits in a 114.6-mm cassette on the outside of the camera. The data were taken with filtered $\text{CuK}\alpha$ radiation using a General Electric high-intensity tube. Temperature measurements up to 900°C were determined by measuring the lattice parameters of annealed platinum powder on the surface of the capillary; the thermal expansion data of Campbell¹¹ were utilized, with the accuracy of the temperature

measurements being $\pm 5^\circ\text{C}$. Temperatures from 800 to 1505°C were measured by means of a Leeds and Northrup optical pyrometer of the disappearing filament type calibrated with the system and considered reliable to within $\pm 10^\circ\text{C}$. The final lattice parameters of platinum and plutonium oxide from two samples were obtained by subjecting the data to a full matrix least-squares program.^{1,2}

RESULTS AND DISCUSSION

The lattice parameters at 22 different temperatures from 14 to 1505°C were obtained and are tabulated in Table 1 and shown in Figure 1. In the temperature range studied no phase changes were observed. The thermal expansion data are linear up to approximately 675°C and deviate from a straight line above 675°C to the maximum temperature recorded (1505°C). At 1137°C the expansion curve undergoes anomalous behavior in that the lattice parameters level off and then increase up to 1505°C . We attribute this behavior (at 1137°C) to a major fraction of helium being released from the spheres and removal of configurational defects by annealing. Helium release rate studies on $^{238}\text{PuO}_2$ microspheres conducted at Mound

Table 1
LATTICE PARAMETERS OF $^{238}\text{PuO}_2$ PLASMA-FORMED MICROSPHERES AT VARIOUS TEMPERATURES

Temperature ($^\circ\text{C}$)	Lattice Parameter ($\text{\AA}$)
14	5.4158(9) ^a
65	5.4180(8)
235	5.4235(7)
429	5.4303(5)
555	5.4339(5)
623	5.4365(4)
702	5.4388(4)
812	5.4440(6)
837	5.4455(6)
924	5.4497(4)
962	5.4534(3)
1031	5.4566(6)
1137	5.4657(8)
1290	5.4694(5)
1345	5.4724(7)
1390	5.4748(8)
1455	5.4788(7)
1505	5.4800(7)

^aNumbers in parentheses are standard deviations.

FIGURE 1 - Lattice parameter of stoichiometric $^{238}\text{PuO}_2$ plasma-formed microspheres as a function of temperature.

Laboratory indicate that most of the helium produced from alpha emission is retained until temperatures of 1000-1200°C are attained.⁹ The magnitude of helium retention is greatly enhanced in the oxide microspheres relative to powdered $^{238}\text{PuO}_2$. The surfaces of oxide microspheres as obtained from the plasma torch exhibit a glassy-like texture which may result from high electrical pressures and the extremely rapid quenching effect. It is conceivable that the immediate surface possesses a highly disordered structure relative to the powder and thereby inhibits the release of helium gas. Above 1137°C the lattice parameters then increase with temperature in a normal fashion. PuO_2 , possessing the fluorite structure, has crystallographically favorable sites for the entrapment of helium atoms. At room temperature the interstitial hole along the body diagonal (111) at position $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ (or its equivalent site at the midpoint along an edge), surrounded by eight oxygen ions at 2.34 Å and six plutonium ions octahedrally at 2.7 Å, has a diameter of about 1.9 Å, slightly smaller than the diameter of a helium atom at 2.4 Å. The diameter of an alpha particle or helium ion at its inception would be considerably smaller than the diameter of the interstitial hole, so that a helium atom or ion could easily be contained in the cavity and maintain this metastable configuration until higher temperatures are attained. We attribute a major fraction of the increase in cell size of $^{238}\text{PuO}_2$ plasma-formed microspheres to the above phenomenon.

Lattice parameters obtained from numerous diffraction patterns of freshly prepared $^{238}\text{PuO}_2$ microspheres over a period of several years have consistently corresponded to a cell size of approximately 5.4100 Å, whereas powdered $^{238}\text{PuO}_2$ samples have yielded values between 5.3960 and 5.4000 Å. As previously mentioned, the increase in cell size would not be attributed to deviations in stoichiometry since thermal gravimetric analyses coincide with stoichiometric PuO_2 . Self-irradiation damage with time⁸ may have contributed to an increase in cell size; however, this effect would be minimal considering the brief time that elapsed between sample preparation and recording of x-ray data.

The variation of the lattice constant in the temperature interval of 14-1137°C is represented by the following quartic expression from a least-squares analysis:

$$a_t = 5.4153 + 4.1066 \times 10^{-5} t - 2.4149 \times 10^{-8} t^2 + 1.5254 \times 10^{-11} t^3 + 7.4714 \times 10^{-15} t^4 \quad (1)$$

where t is the temperature in °C.

The fractional change in the cell size with temperature is shown in Figure 2 and can be given by:

$$\Delta a/a = -4.7451 \times 10^{-5} + 6.7755 \times 10^{-6} t - 1.8181 \times 10^{-9} t^2 - 5.3255 \times 10^{-13} t^3 + 2.8329 \times 10^{-16} t^4 \quad (2)$$

FIGURE 2 - Fractional change in lattice parameter of stoichiometric $^{238}\text{PuO}_2$ plasma-formed microspheres as a function of temperature.

Coefficients of thermal expansion of stoichiometric $^{238}\text{PuO}_2$ plasma-formed microspheres in the temperature interval of 14 to 1137°C were determined from the temperature dependence of their lattice parameters. The mean linear thermal expansion coefficient is given by

$$\langle \alpha \rangle = \frac{a(t) - a_0}{a_0(t - t_0)} \quad (3)$$

where a_0 is the lattice parameter at the reference temperature t_0 (14°C), and a is the lattice parameter at the specified temperature. The instantaneous thermal expansion coefficient is defined as

$$\alpha_i = \frac{1}{a_0} \left(\frac{\partial a}{\partial t} \right)_p \quad (4)$$

when the measurements are made at constant pressure. The instantaneous coefficient of thermal expansion data from 50 to 1137°C are given in Table 2 and shown in Figure 3; the analytical expression in this temperature interval can be represented by

$$\begin{aligned} \alpha_i = & 5.1688 \times 10^{-6} + 1.3499 \times 10^{-8} t \\ & - 5.2779 \times 10^{-11} t^2 + 7.0996 \times 10^{-14} t^3 \\ & - 2.4375 \times 10^{-17} t^4 \end{aligned} \quad (5)$$

The mean thermal expansion coefficient for $^{238}\text{PuO}_2$ microspheres as obtained from Equation 3 is $6.8 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$; the x-ray value of $\langle \alpha \rangle$ between 0 and 500°C for polycrystalline $^{238}\text{PuO}_2$ is $9.0 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$.¹³

FIGURE 3 - Instantaneous coefficient of thermal expansion of stoichiometric $^{238}\text{PuO}_2$ plasma-formed microspheres as a function of temperature.

Table 2

INSTANTANEOUS COEFFICIENTS OF THERMAL
EXPANSION OF PLASMA-FORMED $^{238}\text{PuO}_2$
MICROSPHERES AT VARIOUS TEMPERATURES

Temperature (°C)	Expansion Coefficient $\times 10^6$ (°C ⁻¹)
50	6.10
100	6.05
150	6.19
200	6.13
250	6.28
300	6.28
350	6.28
400	6.28
450	6.28
500	6.28
550	6.28
600	6.28
650	6.28
700	7.39
750	7.76
800	8.49
850	9.23
900	10.16
950	11.82
1000	12.48
1050	13.85
1100	15.33
1137	17.43

CALCULATION OF MEAN SQUARE ATOMIC
VIBRATIONAL AMPLITUDE FROM
THERMAL EXPANSION DATA

Grüneisen¹⁴ developed the following relationship between the mean square atomic vibrational amplitude and the thermal expansion for cubic solids:

$$\langle u^2 \rangle_{av} = \left(\frac{3r_o^3}{8\pi^2 \gamma Z^2} \right) \left(\frac{\Delta V}{V_o} \right) \quad (6)$$

where: $\langle u^2 \rangle_{av}$ = mean square thermal
atomic vibrational
amplitude

r_o = atomic radius

γ = Grüneisen constant

Z^2 = constant for a given
material, calculated
from a central force
model

$\frac{\Delta V}{V_o}$ = fractional increase in
volume

Equation 6 can also be expressed in terms
of the thermal expansion:¹⁵

$$\langle u^2 \rangle_{av} = \left(\frac{9r_o^3}{8\pi^2 \gamma Z^2} \right) \left(\frac{\Delta a}{a_o} \right) \quad (7)$$

with $r_o^3 = 5.58 \text{ Å}^3$ and using γZ^2 as a
constant at 0.145. In Grüneisen's deri-
vation γ and Z^2 can have a range of values
but their product is constant when the
slope of $\langle u^2 \rangle_{av}$ is relatively constant.

At room temperature and below, different
vibrational amplitudes would exist for
each atom. However, at higher tempera-
tures a common isotropic amplitude can
be used as there are generally small
variations in the Debye temperature for
high-melting compounds¹⁶ ($^{238}\text{PuO}_2$ melts
at approximately 2200°C). In Table 3
are the values of $\langle u^2 \rangle_{av}$ calculated from

Table 3

VARIATION OF MEAN SQUARE
VIBRATIONAL AMPLITUDE WITH TEMPERATURE
FOR $^{238}\text{PuO}_2$ PLASMA-FORMED MICROSPHERES

Temperature (°C)	Mean Square Vibrational Amplitude $\times 10^4$ (Å ²)
50	13.8
100	26.7
150	39.7
200	52.7
250	67.3
300	80.2
350	93.2
400	106.9
450	119.1
500	132.9
550	145.1
600	159.7
650	172.6
700	187.2
750	205.0
800	222.9
850	242.3
900	265.0
950	290.9
1000	317.7
1050	347.7
1100	380.1
1137	404.4

Equation 7 and shown as a function of temperature in Figure 4. The root-mean-square vibrational amplitudes, $\langle u^2 \rangle_{av}^{1/2}$, at 50°C and at 1137°C are 0.037 Å and 0.20 Å, respectively, which correspond to 0.016 of the Pu-O distance (2.34 Å) at 50°C and 0.085 of the Pu-O distance (2.37 Å) at 1137°C. These numbers give some idea of the displacements due to thermal vibrations in $^{238}\text{PuO}_2$. It would be interesting to compare the data in Table 3 with experimental data obtained from x-ray diffraction integrated intensities and observe whether the $\langle u^2 \rangle_{av}$ values differ appreciably for each atom, as this would indicate whether the atoms are equally bound to their equilibrium positions.

We are presently engaged in obtaining thermal expansion data via high-temperature x-ray techniques of powdered $^{238}\text{PuO}_2$. It is expected that the latter results will more closely resemble $^{239}\text{PuO}_2$ data as the effect of the magnitude of radiation damage and helium retention will be less severe.

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FIGURE 4 - Mean square atomic vibrational amplitude of $^{238}\text{PuO}_2$ microspheres from thermal expansion data using Grüneisen's theory.

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