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***Mound Laboratory
Isotopic Power Fuels Programs:
October-December 1973***

March 15, 1974

AEC Research and Development Report

Monsanto

MOUND LABORATORY

Miamisburg, Ohio
operated by

MONSANTO RESEARCH CORPORATION

a subsidiary of Monsanto Company
for the

U. S. ATOMIC ENERGY COMMISSION

U. S. Government Contract No. AT-33-1-GEN-53

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Foreword

This report presents the technological achievements of Mound Laboratory in its isotopic fuels programs during the past three months. The separate reports compiled here represent the work of the following sections of the Nuclear Operations Department (Director W. T. Cave): Heat Sources (Manager D. P. Kelly), and Technology Applications & Development (Manager R. E. Vallee).

This work is supported by the AEC Division of Space Nuclear Systems.

Summaries of all sections are compiled at the front of this report. Brief introductions to the work are included with each section.

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The molybdenum coating can be removed from ceramic particles by heating the particles to oxidize the molybdenum to the trioxide and then removing the molybdenum trioxide from the particles by washing the particles in alkali.

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The diffusion of oxygen into MHW fuel spheres was analyzed to determine a reasonable time required to oxidize the fuel form from $\text{PuO}_{1.85} \xrightarrow{\sim 1600 \text{ cm}^3 \text{ (STP) O}_2} \text{PuO}_{2.00}$. The bulk density of these

fuel spheres is 80-85% of the theoretical for $\text{PuO}_{2.00}$. Quantitative metallographic analysis (Classimet) of ThO_2 simulant spheres, produced identically to PPO spheres, showed that in extensive regions the porosity is about 20-30% or more. Porosity values above 10-12% in sintered ceramic structures are typically characterized by most of the pores being accessible to the sphere surface. Quantitative porosity data for ThO_2 spheres indicate that these surface-connected porous regions effectively reduce the length of the diffusion path for oxygen. Relatively small high density regions (up to 95% of theoretical) were also observed. Oxygen diffusion to the center of these regions is the rate-limiting step in the sphere oxidation process. For ThO_2 the maximum distance from a surface-connected porous region to the center of a typical high density region was observed to be $\sim 0.1 \text{ cm}$. Using a reasonable value of $D_0 = 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ at 800°C (the oxygen chemical diffusion coefficient in PuO_{2-x}) the observed high density regions in $\text{PuO}_{2.00}$ fuel spheres will be oxidized in 1 hr.

Acoustic emission (AE) measurements were made on PPO spheres during oxygen-16 treatment at 600-725°C with an oxygen-16 flow of about 500 cm³ min⁻¹. These data indicated that oxidation was completed after 30 min. Accompanying the AE activity an approximate 100°C increase was observed after the introduction of oxygen-16. This temperature excursion disappeared along with the AE activity after approximately 30 min.

Thus, the experimental results and the oxygen diffusion calculations clearly show that PPO fuel spheres will be oxidized to PuO_{2.00} at 800°C in 1 hr provided sufficient oxygen is available.

HEAT TRANSFER AND THERMAL CONDUCTIVITY OF MULTIHUNDRED WATT

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Analysis of limited radial temperature gradient data from PPO fuel spheres showed that the effective average thermal conductivity of the fuel can be calculated from such measurements. Also, the change of thermal conductivity with temperature can be readily determined. Heat transfer in the fuel spheres is controlled to a large extent by the gas phase present in the porosity, and in Ar-H₂O atmospheres it is controlled by a gas phase requiring a relatively large number of degrees of freedom. In helium atmospheres at high temperature and in vacuum from 705 to 1400°C, the fuel temperature dependence of the thermal conductivity is determined by helium with three degrees of freedom, as expected.

Heat transfer within the sphere is explained reasonably well by a slab model and series heat flow perpendicular to the slabs, rather than a parallel flow slab model. The fuel thus apparently behaves thermally as if it consists of fuel-helium-fuel layers in a radial direction, and the self-heat must flow successively through these layers to reach the sphere surface.

REMOVAL OF MOLYBDENUM FROM MOLYBDENUM-COATED CERAMIC PARTICLES

It is often desirable in manufacturing processes involving radioelements to coat the radioelement compound particles with a layer of nonradioactive material for such purposes as enhancing the thermal conductivity of the particles, or protecting the particles from breakage or chemical reaction. For heat sources employing plutonium-238 dioxide, it is sometimes useful to coat the oxide particles with molybdenum metal. Since the coating operation may not always lead to coated particles with a coating of proper thickness or integrity, it is occasionally necessary to remove the molybdenum from the plutonium-238 dioxide particles so that these particles may be recovered for later use. The removal of molybdenum coatings from ceramic oxide particles may be effected by fusing the particles in a bath of molten potassium hydroxide-potassium nitrate mixture, or with hydrogen peroxide.¹ However, these methods require the use of strongly oxidizing liquids which may be hazardous within the confines of an alpha box, or be undesirable for other reasons. It would, therefore, be desirable to have available a method for removing the molybdenum coating from ceramic particles which does not require strongly oxidizing liquids.

Molybdenum forms a variety of volatile compounds including the trioxide, MoO_3 , which is reported to melt at 795°C and to volatilize at 1155°C at 760 mm pressure. As molybdenum metal oxidizes in air at red heat, it would appear that molybdenum metal could be removed from ceramic oxide particles by oxidation and volatilization at high temperatures. An apparatus consisting of a hollow cup with a porous bottom enclosed within a gas transfer tube was constructed and placed within a tube furnace (inclined at 30° to the horizontal) to test this hypothesis. Molybdenum-coated ceramic thorium dioxide was placed into the cup (Figure 1). The average size of the particles was 53-177 μm and they contained about 15% molybdenum as coating by weight. The flow of air through the ceramic frit which formed the bottom of the cup was just sufficient to cause gentle agitation of the particles in the bed. When the apparatus was placed inside the inclined tube furnace (heated to $800\text{--}1000^\circ\text{C}$) along with 30 g of molybdenum-coated ThO_2 particles, white fumes of MoO_3 volatilized from the bed of hot particles. After several minutes, this volatilization of MoO_3 ceased. When the particles treated in this manner were cooled, it was observed that only the topmost layers of particles in the

FIGURE 1 - Apparatus for removing molybdenum from ceramic oxide particles.

particle bed had assumed a white color, i.e., the white color characteristic either of ThO_2 or MoO_3 . Not only had the treatment failed to remove most of the molybdenum from the particles in the particle bed, but it also allowed the particles in the bed to agglomerate into a solid mass which could be broken only with difficulty.

In order to overcome this shortcoming and to enhance the extent of molybdenum removal, a stirrup was attached to the top of the quartz cup so that the cup could be rotated inside the tube furnace, thereby providing the particle bed with constant agitation and motion so that agglomeration could not occur as readily as in an unagitated bed. A coupling was attached to the tube at the bottom of the cup to allow both free rotation and the unobstructed passage of air during the rotation. Small indentations or protrusions were forced into the sides of the cup so that the bed of particles would be broken and perturbed during rotation. When the cup was thus heated and rotated, while admitting air through the bottom, the molybdenum from 30-g samples of molybdenum-coated ThO_2 could be oxidized and volatilized without agglomeration of the particles into a single mass. This treatment effectively oxidized all of the molybdenum, although some agglomeration of particles into small mounds near the bases of the protrusions was generally observed. These were easily broken and dislodged, however, by tapping the mounds with a glass rod. Most of the particles remained free and unagglomerated, however. After a half hour treatment, as described above, 30-g samples of molybdenum-coated particles were rendered white. Typical conditions and analyses of heat treated particles are shown in Table 1.

Table 1

REMOVAL OF MOLYBDENUM FROM CERAMIC OXIDE
PARTICLES BY HEAT AND AIR

Sample	Initial Sample Weight (g)	Time in Furnace (hr)	Revolution Speed (rev/min)	Molybdenum (%)	
				Before Treatment	After Treatment
1	30	1/2	140	14.56	8.5
2	30	1/2	100	13.67	3.1
3	30	1/2	100	13.67	8.8
4	30	1/2	80	13.67	8.4

As can be seen from Table 1, much of the molybdenum is removed by volatilization by the treatment using heat and air. Sufficient molybdenum remains with the particles, however, to warrant either higher ignition temperatures to facilitate volatilization of the MoO_3 from the particle bed, or secondary chemical treatment to effect removal of the molybdenum from the ceramic oxide particles. As the tube furnace used in the experiments could not be heated much above 1000°C for prolonged treatment without significant risk of either destroying the furnace or the quartz particle cup, secondary chemical treatment took the form of boiling the heat treated particles in a beaker with 2M KOH: 60 ml of 2M KOH were used for each 15 g of heat treated particles, although the combination is not critical. Molybdenum trioxide is soluble in alkali to form alkali molybdate. Table 2 describes some results obtained by this sequential treatment, and the data in this table indicate that molybdenum may be effectively removed from ceramic particles by this process. The small amounts of molybdenum remaining in the ceramic oxide would cause no difficulty in most recovery processes. As most ceramic actinide oxide particles are neither soluble in 2M KOH nor degraded by heating to 1000°C , this method allows the removal of molybdenum from molybdenum-coated ceramic oxide particles without the use of strongly oxidizing or hazardous liquids. (G. L. Silver and D. E. Etter)

Table 2

REMOVAL OF MOLYBDENUM FROM CERAMIC OXIDE PARTICLES
BY HEAT, AIR AND SUBSEQUENT AQUEOUS ALKALI

<u>Sample</u>	<u>Initial Sample Wt (g)</u>	<u>Time in Furnace (hr)</u>	<u>Revolution Speed (rev/min)</u>	<u>Molybdenum (%)</u>		
				<u>Before Heat Treatment</u>	<u>After Heat Treatment</u>	<u>After Heat Treatment and Alkali Wash</u>
5	30	1/2	80	13.67	8.4	0.11
6	30	1/2	80	14.56	8.9	0.11
7	30	1/2	80	18.00	9.2	0.07

OXIDATION OF PPO FUEL SPHERES DURING OXYGEN-16 TREATMENT

INTRODUCTION

The oxidation state of MHW (Multihundred Watt) fuel in the form of PPO (pressed plutonium oxide) spheres has been the subject of recent concern as the result of the observation that some impacted spheres contained substoichiometric phases rather than $\text{PuO}_{2.00}$. The effect of these phases upon the impact behavior of fueled PICS (post impact containment shells) is unknown at present and, therefore, it is most desirable that the fuel spheres consist primarily of stoichiometric $\text{PuO}_{2.00}$. The fuel spheres are expected to be substoichiometric relative to $\text{PuO}_{2.00}$ after being fabricated by the standard procedure of hot pressing in graphite die components. However, after fabrication, the spheres are heated in oxygen enriched in oxygen-16 and this procedure is expected to re-oxidize the fuel so that the composition is near to $\text{PuO}_{2.00}$.

The present oxygen-16 process uses the self-heat of a given sphere to raise its surface temperature to about 800°C while oxygen-16 enriched gas flows over the surface for approximately 1 hr. The oxidation of the fuel to $\text{PuO}_{2.00}$ will be dependent upon the initial O/Pu ratio, the availability of oxygen at the fuel surface, the oxygen chemical diffusion coefficient in PuO_{2-x} , and the time available for the diffusion to take place. The process will be discussed relevant to the known oxygen diffusion properties of PuO_{2-x} , the known microstructure of the fuel sphere, and the times required for chemical equilibrium to be attained in the fuel based on various assumed diffusion geometries.

MICROSTRUCTURE OF PPO FUEL SPHERES

All of the available metallographic data for fuel spheres produced by the standard fabrication process indicate that the porosity in the fuel is quite high, about 20 to 30% or more in extensive regions in a given sphere. Porosity values above 10-12% in a sintered structure are typically characterized by most of the pores being accessible to the surface.² Because of the relatively high porosity of MHW fuel, it is reasonable to expect that most of the porosity in the spherical fuel form will be open and, therefore, have gas phase contact with the atmosphere surrounding the sphere during the oxygen-16 treatment. High porosity will, therefore, provide ready access of the oxygen-16 gas to

most of the pore walls within the fuel and thereby greatly reduce the diffusion path length for oxygen ions in the fuel during the oxidation reaction. The actual availability of oxygen-16 at the pore walls deep within the fuel sphere will be determined by the permeability of the fuel to oxygen gas through the pore network and by the diffusion coefficient of gaseous oxygen. These various aspects will now be discussed in detail.

OXYGEN REQUIRED TO OXIDIZE A SUBSTOICHIOMETRIC FUEL SPHERE

The first requirement that obviously must be met by the oxygen-16 oxidizing treatment is that a sufficient amount of oxygen be delivered to the fuel in the available time. The present process consists of continuously flowing the gas about the sphere while its surface temperature is at about 800°C. The present process does not provide a quantitative measurement of the amount of oxygen that reacts with the sphere nor does it provide a measurement of the oxidation kinetics of the sphere. The latter would provide a means for actually determining the effective oxygen chemical diffusion coefficient of a PPO fuel sphere provided that the oxidation process for PuO_{2-x} is oxygen diffusion controlled. In the present case, it is not reasonable to assume that in the present flow-through system that every oxygen molecule that enters the oxygen-16 fixture will contact the fuel and react with it. The 100-W spheres now being produced contain about 0.94 mole of fuel. If the fuel sphere is initially $\text{PuO}_{1.85}$, the volume of oxygen that must react with the sphere at standard temperature and pressure is about 1580 cm^3 . The original oxygen-16 process developed at Mound to remove residual surface carbon and/or carbides consists of flowing oxygen-16 gas at 500 $\text{cm}^3 \text{ min}^{-1}$ into the oxidizing fixture for 1 hr; this flow rate will deliver about 19 times the minimum amount of oxygen required. On the other hand, a flow rate of 20 $\text{cm}^3 \text{ min}^{-1}$ for 1 hr will deliver only about 76% of the minimum required oxygen to the sphere.

OXYGEN DIFFUSION IN PuO_{2-x} FUEL

As noted previously, the reaction rate for the oxidation of PuO_{2-x} is dependent upon (1) the oxygen chemical diffusion coefficient, D_o , in PuO_{2-x} ; (2) the geometry of the diffusion system; and (3) the presence or lack of an interfering surface reaction on the fuel. An interference reaction is assumed to be absent for the cases being considered here. The only data available for D_o in PuO_{2-x} is for a temperature of 1080°C.³ Chereau and Wadier³ showed that, for PuO_{2-x} , D_o does not depend strongly upon composition, as shown in Figure 2. They also observed that D_o is relatively large for PuO_{2-x} at 1080°C, $D_o \approx 10^{-4} \text{ cm}^2 \text{ sec}^{-1}$, compared to Lay's⁴ value of $D_o \approx 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ for oxygen diffusion in UO_{2+x} at this temperature. The activation energy for oxygen diffusion in PuO_{2-x} and the pre-exponential term are unknown, and therefore, the value of D_o for PuO_{2-x} cannot presently be calculated as a function of temperature. However, values of D_o for PuO_{2-x} can be roughly estimated by assuming that the activation energy for oxygen chemical diffusion in PuO_{2-x} is the same as that for oxygen in UO_{2+x} . (Lay determined a value of 28,500 cal/mole for this process in UO_{2+x} .) Using this

FIGURE 2 - Oxygen chemical diffusion coefficient, D_o , in PuO_{2-x} at 1080°C (After Chereau and Wadier, 1973).

assumption, the pre-exponential term "A" in equation (1) can be calculated using the data for PuO_{2-x} of Chereau and Wadier³ at 1080°C .

$$D_o = A \exp(-28,500/RT) \quad (1)$$

where D_o = oxygen chemical diffusion coefficient
 R = gas constant
 T = Temperature in $^\circ\text{K}$.

From reference 3, $D_o = 10^{-4} \text{ cm}^2 \text{ sec}^{-1}$ at $T = 1353.2^\circ\text{K}$ (1080°C). Therefore, "A" ≈ 4 for PuO_{2-x} , compared to a value of 0.5 for UO_{2+x} (reference 4). The assumed activation energy and derived A are then used in Equation 1 to obtain a value of $D_o \approx 7 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$ for PuO_{2-x} at 800°C . Because of uncertainties in obtaining this value for D_o , values in the range of 10^{-5} to $10^{-6} \text{ cm}^2 \text{ sec}^{-1}$ appear to be reasonable for PuO_{2-x} at 800°C and will be used in the following illustrative diffusion calculations for PPO fuel.

SPECIFIC DIFFUSION CASES

Solid Fuel Sphere The most difficult case for obtaining complete oxidation of a fuel sphere in 1 hr at $T \approx 800^\circ\text{C}$ is that of a theoretically dense sphere having a homogeneous temperature. The core region of the sphere will actually be $100\text{-}150^\circ\text{C}$ hotter than the surface and diffusion will therefore occur more rapidly in the sphere center than indicated

by the homogeneous temperature assumption. This case was treated as that of constant oxygen surface concentration⁴ on the sphere equivalent to the composition $\text{PuO}_{2.00}$. In Figure 3 the radial composition of a sphere that was originally $\text{PuO}_{1.85}$ is shown for various values of D_0 and a period of 1 hr. From Figure 3, $D_0 \geq 10^{-4} \text{ cm}^2 \text{ sec}^{-1}$ is required in order to essentially oxidize the complete sphere to a composition near PuO_2 in 1 hr. If D_0 is $\lesssim 10^{-4} \text{ cm}^2 \text{ sec}^{-1}$, the sphere would have a reduced core after this reaction time. A temperature of about 1100°C would thoroughly oxidize such a solid sphere in an hour.

Porous Fuel Sphere Earlier, it was noted that PPO fuel spheres have a bulk density of about 80-85% of theoretical for $\text{PuO}_{2.00}$, and that in this density range, most of the porosity will be open to the sphere surface.

Quantitative metallographic measurements on ThO_2 simulant spheres by Dr. J. Selle of this laboratory provided information about the actual density distribution within a fuel sphere. This work showed that regions having densities of 85-100% of theoretical are relatively small in these spheres. It is the diffusion of oxygen into these dense regions during the oxidation process that will actually determine the time required for complete sphere equilibration in the oxygen-16 atmosphere, because the oxygen diffusion path length in the high porosity regions will be quite small relative to that in the denser regions.

FIGURE 3 - Radial O/Pu composition for MHW sphere of $\text{PuO}_{1.85}$ after 1 hour in oxygen.

Typical high density regions in the sphere were measured from the quantitative metallographic data and their dimensions are given in Table 3.

Table 3

DIMENSIONS AND GEOMETRY OF HIGH DENSITY
REGIONS IN A ThO_2 MHW SIMULANT SPHERE

Height (cm)	Width (cm)	General Shape
0.19	0.16	Spherical
0.19	0.80	Slab
0.13	1.46	Slab

Slab Shaped Regions For the slab shaped regions, diffusion into a plane sheet with constant oxygen surface concentration was assumed; i.e., no oxygen diffusion into the "edges" of these regions was acknowledged. This is a worse case assumption for this geometry. The completeness of oxygen diffusion into this type of region in a fuel sphere is shown in Figure 4, where the average O/Pu ratio in the slab is shown as a function of the diffusion parameter, $(Dt/\ell^2)^{1/2}$.

FIGURE 4 - Oxidation of a slab of PuO_{2-x} having thickness $T = 2\ell = 0.2$ cm in one hour.

The average slab composition is also indicated for two values of D_0 for a diffusion time of 1 hr. The half-slab thickness, l , is assumed to be approximately equal to 0.1 cm as deduced from the metallographic measurements. For $D_0 \approx 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$, in 1 hr $(Dt/l^2)^{1/2}$ equals 1.9, and from Figure 4, $O/Pu \approx 2.0$; i.e., the high density slab region is completely oxidized to $PuO_{2.0}$.

If D_0 is assumed to be $10^{-6} \text{ cm}^2 \text{ sec}^{-1}$ for these slab regions, a period of 1 hr gives $(Dt/l^2)^{1/2} = 0.6$, and from Figure 4, the slab region would have a composition of $O/Pu \approx 1.95$.

Spherical Shaped Regions For spherical high density regions, the time required for oxidation to $PuO_{2.0}$ can be estimated by assuming a radius for the spherical region and assuming that oxygen can be delivered to the surface of the high density region at a rate sufficient to satisfy the oxygen diffusion requirements.

If it is assumed that the radius of the largest of these regions is $\approx 0.25 \text{ cm}$ from the metallographic measurements, the O/Pu ratio for this case is shown in Figure 5, where for 1 hr, $(Dt/a^2)^{1/2} = 0.76$ and $O/Pu \approx 2.0$. If $D_0 \approx 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$, $O/Pu \approx 1.94$ in 1 hr.

FIGURE 5 - Oxidation of dense spherical region of PuO_{2-x} having $a = 0.25 \text{ cm}$, in one hour.

OXYGEN DIFFUSION INTO THE OPEN POROSITY OF THE FUEL

As stated earlier, the rapid oxidation of dense fuel regions within a porous MHW sphere requires that oxygen rapidly reach the boundaries of the region through the open porosity. An estimate of the rate of gaseous oxygen diffusion along a MHW sphere radius can be made by examining the diffusion in a semi-infinite medium having a constant surface concentration and using the diffusion coefficient for gaseous oxygen. This model has the solution:

$$C/C_0 = \operatorname{erfc} (x/2\sqrt{Dt}) \quad (2)$$

where C = concentration at distance x from the reference origin
 C_0 = constant surface concentration
 D = oxygen binary diffusion coefficient, and $\approx 0.2 \text{ cm}^2 \text{ sec}^{-1}$
 t = time of diffusion
 erfc = complement of the error function

For the case of C_0 at the sphere surface equivalent to the oxygen potential in $\text{PuO}_{2.0}$ at time $t=0$, after 60 sec the oxygen concentration at the sphere center will be $\sim 72\%$ of that at the surface. At 180 sec, $C \approx 0.78 C_0$. Therefore, oxygen gas diffusion will occur quite rapidly into the open porosity and thus should not limit the availability of oxygen at the boundaries of the dense regions in the fuel sphere.

ACOUSTIC EMISSION DATA ON MHW PPO SPHERES DURING THE OXYGEN-16 TREATMENT

Extensive acoustic emission (AE) data were obtained on PPO spheres during oxygen-16 treatments by Dr. J. D. Hastings of this laboratory during the original process development for the fuel form. Acoustic emissions are produced by brittle solids when they are stressed either by mechanically applied loads or by rapid temperature changes. Various phase transformations also produce copious amounts of acoustic activity. The oxidation of PuO_{2-x} in the reaction

results in a contraction of the fuel and the fuel would be expected to generate acoustic emissions during this reaction. The AE activity of spheres was studied using the apparatus shown in Figure 6, where the MHW fuel sphere is shown within the oxygen-16 fixture along with the acoustic emission contact probe. The sphere surface temperature was monitored continuously via a thermocouple from the moment that the fixture was assembled. The time at completion of the assembly was designated $t=0$ on Figures 7, 8, and 9. At $t=0$, the sphere temperature began to increase from self-heat as shown. At a sphere surface temperature of about 600°C , the oxygen-16 was turned on at a rate of $500 \text{ cm}^3 \text{ min}^{-1}$ (STP) and was left on for about an hour. As soon as the oxygen-16 gas reached the sphere, the sphere temperature increased abruptly and this

FIGURE 6 - Acoustic emission apparatus and instrumentation for plutonia spheres.

FIGURE 7 - Acoustic emission of plutonia sphere SPO-21.

FIGURE 8 - Acoustic emission of plutonia sphere SPO-25.

FIGURE 9 - Acoustic emission of plutonia sphere SPO-22.

increase was accompanied by a sharp rise in the acoustic emissions. This is shown in Figure 7 for sphere SPO-21 and in Figure 8 for sphere SPO-25 where the cumulative acoustic emissions are plotted as a function of time. The excess heating of the sphere during oxidation is due to the enthalpy change associated with Equation (3).

From work on other spheres such as SPO-22 (shown in Figure 9) it was possible to identify fuel spheres which had reoxidized in storage prior to the oxygen-16 treatment. It was therefore, quite evident that the large number of acoustic emissions accompanying the introduction of oxygen-16 were due to oxidation and not thermal stress cracking caused by sudden cooling of the sphere surface by the gas. These data and other metallographic data indicated that oxidation was essentially completed in about 30 min. The oxygen-16 gas was typically allowed to flow through the fixture for twice this time to ensure completeness of the oxidation reaction. (V. J. Tennery)

HEAT TRANSFER AND THERMAL CONDUCTIVITY OF MULTIHUNDRED WATT FUEL SPHERES

INTRODUCTION

Recent measurements of interior and surface temperatures in both 100- and 50-W spheres of $^{238}\text{PuO}_2$ at LASL⁶ in gaseous atmospheres and at Mound Laboratory in vacuum indicated that the radial temperature profiles in these fuel forms are quite different from those expected. Because the reported thermal conductivity of PuO_2 decreases with increasing temperature, it was expected that the temperature difference between the core and surface of a fuel sphere would increase with the average temperature of the sphere. The opposite behavior has been observed in both the 100- and 50-W spheres that have been studied. This result indicates that, under the experimental conditions used, the effective thermal conductivity of the fuel increased with increasing temperature.

An investigation was made in an effort to explain the experimental results available on fuel spheres to date as well as to develop a reasonable model to describe the heat transfer in the fuel.

EXPERIMENTAL RESULTS

Data available at this time are for LASL⁶ spheres SPP-59, with a power of 100 W, and SPP-60, with a power of 50 W, and Mound sphere SPO-71 with a power of 100 W. These spheres were fabricated with one hole running from the center to the surface. The LASL spheres were placed in a tube furnace with one thermocouple in the center of the sphere and one in contact with the sphere surface. The sphere temperature was increased by heating the furnace. During these measurements on SPP-59, an atmosphere of argon-water vapor was passed through the furnace. During measurements on SPP-60, atmospheres of argon-water vapor and helium were passed through the furnace in order to determine the effects of furnace atmosphere on the radial temperature gradient.

The Mound sphere was studied while under vacuum. These data, although preliminary, are included for completeness. Results available to date are given in Tables 4 and 5 for these spheres.

Table 4

CORE AND SURFACE TEMPERATURES
IN PPO FUEL SPHERES *

Temperature of 100-W SPP-59 in Ar-H ₂ O Atmosphere		Temperature of 50-W SPP-60		
at Surface	at Core	in Ar-H ₂ O Atmosphere	in He Atmosphere	
(°C)	(°C)	at Core	at Surface	at Core
		(°C)	(°C)	(°C)
400	646	497	300	460
500	700	562	400	534
600	760	626	500	615
700	828	702	600	702
800	905	786	700	794
900	990	875	800	889
1000	1080	968	900	986
1100	1174	1063	1000	1084
1200	1270			
1300	1368			
1400	1467			

*Personal Communication, T. K. Keenan, LASL

Table 5

RADIAL TEMPERATURE GRADIENT
IN 100-W SPHERE SPO-71

Temperature at Polar Surface	Core-Pole Temperature Difference
(°C)	(°C)
550	277
583	244
702	223
800	205
800	207
900	196
1000	183
1000	186
1200	165
1400	163

ANALYSIS OF EXPERIMENTAL RESULTS

In order to interpret the results of temperature measurements in self-heating spheres, the Laplace heat flow equation for the case of a self-heating sphere for the steady state was solved for the case of linear heat transfer at the sphere surface and with an incident radiant flux on the sphere.

For the case of a homogeneous self-heating sphere with heat flow only along the radius, the heat flow equation is

$$\frac{1}{r^2} \frac{d}{dr} r^2 \frac{dT}{dr} = - \frac{A_0}{K_0} \quad (1)$$

where T = temperature

r = radial distance in the sphere

A_0 = self-heat generation rate for the fuel sphere

K_0 = thermal conductivity of the fuel.

For the case of a sphere in which the thermal conductivity varies along the radius, a suitable function $K(r)$ is substituted into Equation (1) and Equation (1) can be solved.

For MHW (Multihundred Watt) spheres fabricated by hot pressing, the microstructure varies from the core to the sphere surface and it is expected that the thermal conductivity will not necessarily be constant along the sphere radius. Solutions of Equation (1) with assumed functions for $K(r)$ or $K_0(1+\beta r)$ and $K_0(1+\beta r^2)$ were obtained and will be given subsequently.

For the case of a real MHW sphere, it is expected that A and K will vary approximately in the same manner as a function of the porosity and thus the radial dependence of A and K will tend to cancel each other as evident in Equation (2):

$$\frac{1}{r^2} \frac{d}{dr} r^2 \frac{dT}{dr} = - \frac{A(r)}{K(r)} = - \frac{A_0}{K_0} \quad (2)$$

For these conditions with a sphere in a medium at temperature T_0 and having an incident flux F , the steady state temperature at a radius r is given by

$$T = \frac{A_0}{6hK} \left\{ h(a^2 - r^2) + 2a \right\} + T_0 + F/H \quad (3)$$

where T = temperature in $^{\circ}\text{C}$

K = thermal conductivity of the sphere in $\text{cal sec}^{-1}\text{cm}^{-1}\text{C}^{-1}$

a = sphere radius in cm

r = radial position from the core in cm

T_0 = temperature of medium surrounding sphere in $^{\circ}\text{C}$

F = Incident flux

H = surface heat transfer coefficient at the sphere surface
in $\text{cal cm}^{-2} \text{sec}^{-1} \text{C}^{-1}$

$h = H/K = \text{surface coefficient in cm}^{-1}$

$A_0 = \text{self-heat generation rate of the fuel in cal cm}^{-3} \text{ sec}^{-1}.$

The temperature difference between the core and surface of the sphere is given by subtracting T for $r = 0$ from the value for $r = a$ and is found as follows:

$$\begin{aligned} T_{r=0} - T_{r=a} = \Delta T &= \frac{A_0}{6hK} \left\{ h(a^2 - 0) + 2a \right\} + T_0 + F/H \\ &\quad - \left[\frac{A_0}{6hK} \left\{ h(a^2 - a^2) + 2a \right\} + T_0 + F/H \right] \\ &= \frac{A_0}{6hK} \left\{ h a^2 + 2a - 2a \right\} + T_0 + F/H - T_0 - F/H \\ &= \frac{A_0}{6hK} \left\{ h a^2 \right\} = \frac{A_0 a^2}{6K} \end{aligned} \quad (4)$$

where ΔT = the temperature difference between the core and surface of the sphere.

The factors associated with heat transfer to and from the sphere all cancel out from the expression for the radial ΔT and therefore this measurement allows a direct calculation of the thermal conductivity of the sphere material. The calculated thermal conductivity is the mean along the radius if the conductivity varies significantly between the temperatures $T_{(\text{core})}$ and $T_{(\text{surface})}$.

Likewise, a linear radial dependence of the thermal conductivity along the sphere radius gives the expression

$$\Delta T = \frac{A_0}{3K_0} \left[\frac{1}{\beta^2} \left\{ 3a - \ln(1 + \beta a) \right\} \right] \quad (5)$$

where β = parameter having units of cm^{-1} in the expression

$$K = K_0 (1 + \beta r)$$

ΔT = the temperature difference between the core and surface.

A parabolic dependence of the thermal conductivity results in the expression:

$$\Delta T = \frac{A_0}{6K_0 \beta} \ln(1 + \beta a^2) \quad (6)$$

where β is a parameter with units of cm^{-2} in the expression

$$K = K_0 (1 + \beta r^2)$$

ΔT = the temperature difference between the core and surface.

In all cases, ΔT is related to the thermal conductivity by a relatively simple expression. Equation (4) was used to calculate the effective thermal conductivity of spheres SPP-59, SPP-60, and SPO-71 as a function of temperature. From Equation (4) and the data in Tables 4 and 5, it is apparent that the effective thermal conductivity of these spheres increases with temperature, because the radial temperature difference

decreases as the sphere temperature increases. An increasing thermal conductivity with temperature cannot be due to the fuel because the temperatures involved are well above the Debye temperature of PuO_2 and therefore the conductivity of the fuel must vary essentially with the reciprocal of its temperature. The thermal conductivity of the oxide fuel therefore must decrease with increasing temperature.

There are two known processes of heat transfer in electrically insulating materials which are characterized by an increase in the effective thermal conductivity with temperature. One involves thermal conduction in gases where the thermal conductivity varies as

$$K_g = \frac{fk}{6S} \sqrt{\frac{3RT}{M}} \quad (7)$$

where f = number of degrees of freedom for the gas molecule
 k = Boltzmann's constant
 S = collision area for the molecule
 R = gas constant
 T = temperature of the gas in $^{\circ}\text{K}$
 M = molecular weight of the gas in atomic mass units

when the gas is essentially ideal. Examination of Equation (7) shows that the thermal conductivity of gases increases linearly with the square root of the absolute temperature.

The second process involves heat transport by radiation through the material or across pores within the material. Both of these mechanisms depend on the cube of the absolute temperature. The contribution across pores is given by

$$K_r = 4\sigma n^2 \epsilon T^3 g L \quad (8)$$

where K_r = effective radiation thermal conductivity due to pores
 σ = Stefan-Boltzmann constant
 n^2 = square of the index of refraction of material filling the pore
 ϵ = effective emittance of the pore boundary
 T = absolute temperature of pore wall
 g = geometric factor dependent on pore shape
 L = pore size in the direction of heat flow.

For most ceramic oxides, values of $L \geq 0.1$ cm must be invoked in order to obtain K_r values that are significant fractions of the inherent thermal conductivity of the oxides.

Presently available data for fuel spheres SPP-59, SPP-60, and SPO-71 were analyzed using Equation (4) to compute the average effective thermal conductivity of the fuel as a function of the average of the measured core and surface temperatures. The values of $A = 0.9056 \text{ cal cm}^{-3} \text{ sec}^{-1}$ for SPP-59 and SPO-71 and $A = 0.835 \text{ cal cm}^{-3} \text{ sec}^{-1}$ for SPP-60 were used with appropriate sphere radii.

These data and other material to be discussed subsequently are shown in Figure 10. The agreement between the calculated thermal conductivity of the two different sized spheres in an Ar-H₂O atmosphere lend support to the validity of Equation (4) since very similar conductivity values are derived from the LASL spheres having significantly different sizes. The linear dependence of the calculated conductivity with $T^{1/2}$ for the spheres in Ar-H₂O atmospheres indicates that the heat transfer in the fuel spheres was controlled by a gas phase rather than the fuel phase up to at least 1200°C. The published thermal conductivity of PuO₂ having 82% of the theoretical density is also shown in Figure 10. Analysis of the slope of the conductivity curve for SPP-59 indicates that the gas phase dominating the heat transfer has ≈ 50 degrees of freedom if the gas behaves reasonably classically. The calculated conductivity values for SPP-60 measured in a helium atmosphere indicates a change in the mode of heat transfer at $T > 600^\circ\text{C}$, and the slope of the conductivity curve decreases to essentially agree with that of helium for $T > 600^\circ\text{C}$ as shown in Figure 10. Therefore, it seems reasonable to assume that the thermal conductivity in SPP-60 measured in a helium atmosphere is controlled by helium in the temperature range 600-1000°C. The slope of the helium and argon conductivity curves in Figure 10 can be accounted for by employing three degrees of freedom as would be expected for these noble gases. The steeper slopes observed for the Ar-H₂O atmospheres and the He atmosphere below 600°C require many degrees of freedom. Available thermal conductivity data for water vapor are also shown in Figure 10. In Figure 10, the thermal conductivities of argon and H₂O are multiplied by 10 in order to make the shapes of the curves easily perceptible. The sharp upturn in the published thermal conductivity of water vapor near 500°C indicates that there are significant increases in the number of degrees of freedom available for water vapor at high temperature. This conclusion is also supported by the increases in the specific heat of water vapor between 25 and 1200°C. The thermal conductivity data for SPP-59 and SPP-60 in an Ar-H₂O atmosphere cannot be adequately explained at this time, however, because of the large number of degrees of freedom that must be invoked to explain the slope of the appropriate curves in Figure 10. The results may, however, be due predominantly to water vapor.

The data for SPO-71 indicate that the temperature dependence of the thermal conductivity in this fuel sphere is also dominated by a gas phase, at least during the initial heating cycle. The slope of the data for this sphere in Figure 10 agrees qualitatively with that for SPP-60 in helium above $\approx 600^\circ\text{C}$ and is approximately equal to that of helium.

The data for SPP-60 in helium indicate that water vapor or some other gas phase common to the Ar-H₂O atmosphere measurements controls the thermal conductivity below about 600°C. Above this temperature this sphere apparently consists of porous PuO₂ with helium in the porosity.

Sphere SPO-71 apparently consists of porous PuO₂ with helium at least in the closed porosity over the entire measured temperature range.

FIGURE 10 - Calculated thermal conductivities of fuel spheres, porous PuO₂, and various gases.

This hypothesis was tested using two different thermal conduction models for the fuel. The simplest heat flow models for two-phase materials are the parallel and series slab models. The solid is assumed to consist of a series of layers of the two phases, and the effective thermal conductivity of the material for heat flow parallel and perpendicular to the slabs is derived on the basis of the known conductivities of the two phases and their known volume fractions.

For heat flow parallel to the slabs in this model, the effective thermal conductivity of the composite solid⁷ is given by

$$K_{\text{eff}} = v_1 K_1 + v_2 K_2 \quad (9)$$

where K_{eff} = effective thermal conductivity of the composite
 v_1 = volume fraction of phase 1
 K_1 = thermal conductivity of phase 1
 v_2 = volume fraction of phase 2
 K_2 = thermal conductivity of phase 2.

For heat flow across the slabs in the series model, the effective thermal conductivity of the composite solid⁷ is given by

$$K_{\text{eff}} = \frac{K_1 K_2}{v_1 K_2 + v_2 K_1} \quad (10)$$

where these quantities have the same definitions as in Equation (9).

Equations (9) and (10) were used in testing the parallel and series flow models by using the calculated thermal conductivity for SPP-60 above 600°C. Data for SPO-71 have not yet been analyzed using these models. It was assumed that under these conditions the porosity was filled with helium. The results using the parallel flow model are shown in Figure 11 in which the calculated thermal conductivity of the fuel phase is shown for various fuel volume fractions. Also shown are available literature values of the thermal conductivity of theoretically dense PuO_2 .⁸ Since MHW fuel is approximately 85% of theoretical density, the curve for $v_f = 0.85$ (0.85 volume fraction of fuel) should agree approximately with the data for PuO_2 . Since it does not, the parallel flow model for heat conduction does not seem to apply to this case. Also, for reasonable values of v_f , the temperature coefficient for the conductivity of the fuel is positive for this model rather than negative.

Results using the series heat flow model are shown in Figure 12. This model gives very reasonable values for the thermal conductivity of the fuel phase for the fuel volume fractions that are applicable for MHW fuel. This model also provides the proper sign of the temperature coefficient for the thermal conductivity of the fuel phase. The thermal conductivities of helium which were used in these calculations are shown in Figure 13 and these were obtained from Reference 9.

FIGURE 11 - Calculated thermal conductivity of fuel vs. fuel volume fraction for parallel flow model.

FIGURE 12 - Calculated thermal conductivity of fuel vs. fuel volume fraction for series flow model.

FIGURE 13 - Thermal conductivity of helium.

CONCLUSIONS

Analysis of limited radial gradient data from PPO fuel spheres showed that the effective average thermal conductivity of the fuel can be calculated from such measurements. Also, the change of thermal conductivity with temperature can be readily determined. Heat transfer in the fuel spheres is controlled to a large extent by the gas phase present in the porosity, and in Ar-H₂O atmospheres it is controlled by a gas phase requiring a relatively large number of degrees of freedom. In helium atmospheres at high temperature and in vacuum from 705 to 1400°C, the fuel temperature dependence of the thermal conductivity is determined by helium with three degrees of freedom, as expected.

Heat transfer within the sphere is explained reasonably well by a slab model and series heat flow perpendicular to the slabs, rather than a parallel flow slab model. The fuel thus apparently behaves thermally as if it consists of fuel-helium-fuel layers in a radial direction, and the self-heat must flow successively through these layers to reach the sphere surface. This is reasonable, since the fuel contains numerous pores, cracks, and channels having limited access to the core and sphere surface and these being filled with helium will approximate the series flow model.

If the fuel sphere approximated the parallel flow model with helium in the pores then the temperature dependence of the thermal conductivity of the fuel would control the situation and the radial thermal gradient in a fuel sphere would increase with temperature. In the series model, the poorer thermal conductor essentially controls the heat flow and, as shown in Figure 1, the gas phase controls the temperature dependence of the conductivity.

Measurements of this type on MHW spheres in vacuum should provide information on the role of trapped helium in the fuel on the heat transfer within the fuel. Presumably, a sphere completely depleted of helium should have a completely different radial temperature gradient (ΔT) vs temperature relationship than the data shown in Tables 4 and 5. Such a dependence upon gas phase heat transfer will have profound effects upon the thermal stresses present in spheres having different gases within their porosity when they are subjected to similar heat transfer conditions.

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