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The Relationship of Fabrication Parameters to
Selected Properties of
 $^{238}\text{PuO}_2$ Radioisotopic Fuels

I. Dimensional Changes, Stoichiometries, and
Microstructural Features

by

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THE RELATIONSHIP OF FABRICATION PARAMETERS TO SELECTED PROPERTIES OF $^{238}\text{PuO}_2$ RADIOISOTOPIC FUELS

1. DIMENSIONAL CHANGES, STOICHIOMETRIES, AND MICROSTRUCTURAL FEATURES

by

T. K. Keenan, R. A. Kent, and R. W. Zocher

ABSTRACT

A study to examine the relationship of fabrication parameters to selected properties of $^{238}\text{PuO}_2$ has been initiated. The $^{238}\text{PuO}_2$ will be used in power sources for RTG's (Radioisotopic Thermal Generators) in space missions; therefore the response of the material to a wide variety of thermal and mechanical stresses must be understood. However, this response is partly a function of the processing of the $^{238}\text{PuO}_2$ into the specified geometry of the fuel module.

The initial phase of this study concentrated on the microstructural appearance of the fuel following its fabrication under varying conditions. The parameters examined included variations in (1) feed granule size ranges, (2) cold pressing pressures, (3) pre-press seasoning temperatures, (4) hot pressing pressures, and (5) post-press sintering temperatures. The resultant structural differences were correlated with these processing parameters.

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INTRODUCTION

The Los Alamos Scientific Laboratory has been involved for a number of years in a continuing program of development and characterization of $^{238}\text{PuO}_2$ radioisotopic fuels for The Space Nuclear Systems Division of the AEC. The half-life of ^{238}Pu ($t_{1/2}$), 2.77 Ga (87.7 yr), coupled with the available power, 0.4 J/s, and the reasonably low levels of penetrating radiation, make this an attractive isotope for space power applications. The ^{238}Pu as the dioxide, PuO_2 , is produced at the AEC Savannah River Plant. The dioxide is formed by calcining plutonium oxalate at moderate ($\sim 750^\circ\text{C}$) temperatures to yield a free-flowing powder of $\sim 6\mu$ size. Enrichment levels of 90 ± 2 atom percent ^{238}Pu are specified, the balance being

primarily ^{239}Pu with lesser amounts of other Pu isotopes and actinides, none of which contribute significantly to the thermal energy.

In the past, the LASL developmental studies have concentrated on pressing or forming appropriately treated feed powder into geometric shapes, some of which were prototypical flight modules, others were specimens required for specific testing. Both hot and cold pressing techniques were used for these fabrications. Many of the early efforts were directed toward a definite fabrication goal or test result. As deep space probe missions became more complex and elegant, additional requirements arose to know fuel behavior and properties under a wide variety of conditions. However, many operational thermophysical and thermochemical properties

can be affected by the previous thermal and mechanical history, not only of the fuel module but also of the feed used in its fabrication. Therefore, as the dependence of a particular property upon a known history becomes more clearly understood, it is possible to tailor the response of the fuel toward postulated or predicted environments.

Among the variables which constitute the thermal and mechanical history of a particular specimen are:

(1) treatment of feed powder prior to pressing (sizing, time and temperature of any thermal seasoning), (2) pressing parameters (time, temperature, and pressure), and (3) post-press sintering (time and temperature).

LASL has recently inaugurated a broad investigation of these variables and their resultant effect on fuel properties and behavior. This report is the first in a series which will describe and discuss these results. Subsequent reports will describe a variety of specific properties determinations.

EXPERIMENTAL

The Savannah River Plant $^{239}\text{PuO}_2$ was used without any further purification. The material was of high purity as received. Analytical samples were routinely taken from each batch of incoming oxide at LASL. In all cases, the LASL results adequately agreed with the impurity levels reported by Savannah River. A listing of spectroscopically determined trace impurities is shown in Table I.

TABLE I

COMPARISON OF LASL AND SRP ANALYTICAL RESULTS OF $^{239}\text{PuO}_2$, SRP LOT 2041A399

Element	SRP Analysis ppm	LASL Analysis ppm
Al	< 10	13
B	< 20	< 1
Ba		20
Be	< 10	< 1
Bi		< 1
Ca	< 50	150
Cd	10	< 4
Co		< 1

TABLE I (cont)

Element	SRP Analysis ppm	LASL Analysis ppm
Cr	10	35
Cs		< 20
Cu	< 10	4
Fe	100	400
Hf		< 4
K	< 200	4
La		< 4
Li		< 4
Mg	< 10	< 2
Mn	< 50	15
Mo	< 10	5
Na	300	200
Nb		< 10
Ni	< 50	120
Pb	< 10	15
Rb		< 4
Re		< 4
Si	< 100	80
Sn	< 50	8
Sr		7
Ta		< 100
Ti		10
V		< 2
W		< 10
Y		< 4
Zn	< 200	10
Zr		8

The preliminary LASL processing of Savannah River feed was constant throughout all phases of effort described in this report. This ensured that any observed change in the developmental specimens would be a function only of a deliberately modified parameter. The invariant feed processing steps are listed in Table II.

TABLE II

CONSTANT FEED PROCESSING STEPS FOR DEVELOPMENTAL STUDIES

1. Receive SRP oxide, transfer into glovebox line
2. ^{16}O exchange at 775°C for 0.34 Ms (96 h) using Ar saturated in H_2^{16}O
3. Outgas at 1000°C for 3.6 ks (1 h)
4. Ball mill for 0.12 Ms (32 h)

The oxygen exchange step decreases the extent of the (α, n) nuclear reaction between the 5.48-Mev ^{239}Pu alphas and ^{16}O and ^{18}O in $\text{PuO}_2^{\text{nat}}$ ("nat" refers to oxygen of normal isotopic composition). While ^{16}O is present at 0.037 % and ^{18}O is present at 0.204 % in normal oxygen, the cross sections for the ^{16}O and ^{18}O (α, n) reactions are large enough to develop significant increases in neutron emission rates. For example, the reported spontaneous fission rate for SRP 80 at. % ^{239}Pu is 2260 n/s/g $\text{Pu}^{(2)}$. Typical $\text{PuO}_2^{\text{nat}}$ has an emission rate of $\sim 12\,500$ n/s/g Pu or an increase of $\sim 10\,000$ n/s/g Pu due to the contribution of ^{16}O and ^{18}O . The more abundant ^{16}O isotope does not undergo the (α, n) reaction. Therefore, if the isotopic content of oxygen in $\text{PuO}_2^{\text{nat}}$ could be enriched in ^{16}O , the overall emission rate would be decreased. Measured emission rates on $^{239}\text{PuO}_2$ after exchange indicate 6 000 - 8 000 n/s/g Pu . Note that the temperature, 775°C , barely exceeds that used for the calcination at Savannah River. Therefore, the feed undergoes no change due to thermal effects.

The exchange operation is carried out in a Pyrotube furnace with Ar saturated H_2^{16}O flowing at 1.7×10^{-3} m³/s. The outgassing step is done in the same furnace while maintaining the Ar/ H_2^{16}O flow. The short exposure time, 3.6 ks at 1000°C , does not induce any thermal effects.

The exchanged feed is then ball-milled in Type 440 S/S jars each containing 55 1.6-cm-diam Type 440 S/S balls. Milling is done batch-wise in ~ 70 g lots. The mills are rotated at 30 rpm for 0.12 Ms. Longer milling times achieved little further reduction in size. Figure 1 shows a typical ball mill and rollers. Particle size data from all lots show that the exchanged, milled feed is now

Fig. 1. Typical Ball Mill Apparatus.

of an identical, reproducible size ($\sim 2 \pm 1\mu\text{m}$) and thermal history for subsequent processing.

Following the milling operation, the feed is cold-pressed into a pellet of ~ 1.6 cm diam x 1.6 cm tall. This pressing is done in a Ferrotek die and punch assembly in a 30-ton American Steel Foundries press. No binder is used. The green pellet is crushed and screened to preselected size ranges. The screened granules are, of course, considerably larger than the 2μ material from the milling.

The screened granules are heated at preselected temperatures in an Astro Model 1000A furnace in an atmosphere of Ar/ H_2^{16}O at a flow rate of 8.5×10^{-4} m³/s. The heating reduces the mean diameter of the granules by $\sim 15\%$ but much more important, varying degrees of thermal seasoning are introduced depending upon the time and temperature selected. Table III lists particle size data for the two size ranges of feed granules used in these studies.

The screened and thermally seasoned granules are formed into the desired shape by a hot pressing operation. The hot press is 75-ton capacity with a 100-kVA MG set and a vacuum system capable of 1.3×10^{-4} Pa (10^{-6} torr). POCO AXM graphite is used for the die and punch assemblies. A prescribed time/temperature/pressure profile is followed during every pressing.

TABLE III
TYPICAL SIZE RANGES FOR FEED GRANULES

A. 0 - 125 μ m Feed

Size, μ m	Wt. % In Listed Size Range After Pre-Press Thermal Seasoning			
	Green	1050 $^{\circ}$ C	1150 $^{\circ}$ C	1250 $^{\circ}$ C
105 - 125	44.1	16.4	4.4	2.9
63 - 105	44.8	65.5	46.0	45.0
44 - 63	7.5	9.8	27.5	26.2
< 44	3.6	8.3	22.1	25.9

B. 0 - 297 μ m Feed

250 - 297	11.6	10.8	5.2	7.0
210 - 250	23.3	15.8	18.9	6.3
177 - 210	18.4	26.7	16.2	23.3
125 - 177	9.6	9.2	15.3	20.9
105 - 125	5.9	2.8	5.7	7.6
63 - 105	18.0	17.5	17.2	15.8
44 - 63	11.6	8.2	8.6	9.3
< 44	1.5	9.0	12.9	9.8

The dies were designed so that 16 pellets could be fabricated simultaneously under identical conditions. The charge of $^{238}\text{PuO}_2$ to each die cavity and the material handling techniques were unchanged throughout all pressings. Figure 2 shows this "Gatling Gun" die and punch assembly.

Fig. 2. Gatling Gun Die Assembly.

More than 200 specimens were made during this study. The specimen size chosen for the developmental pressings was a right circular cylinder, 0.76 cm diam x 0.76 cm tall. Previous LASL studies had clearly demonstrated that analytical data from small specimens may be directly related to larger fuel modules typical of flight units. Therefore the utilization of economical 1.3 J/s pellets is satisfactory.

Following the fabrication, 12 of the formed pieces were subjected to a sintering operation in an Astro Model 1000A furnace under an atmosphere of flowing (8.5×10^{-9} m³/s) Ar/H₂¹⁶O. Three specimens were examined "As Pressed" and the last was used for analytical chemistry. This sample served as a control that no impurities were introduced during any pressing. None were detected in any run. Dimensional and weight data were recorded for all specimens. Analytical samples were removed as required. Records and documentation were maintained throughout the entire process so that any individual specimen could be traced to its parent Savannah River feed lot.

TABLE IV

VARIED PARAMETERS FOR INITIAL DEVELOPMENTAL STUDIES

1. Cold Pressing Pressures:	Two Pressures, 0.4 GPa (58 000 psi) and 0.8 GPa, (116 000 psi)
2. Feed Granule Size Ranges:	Two size ranges, 0 - 297 μm and 0 - 125 μm
3. Pre-Press Seasoning Temperatures*:	Four temperatures, 1050°, 1100°, 1200°, and 1250° at a constant time of 10.8 ks (3 h)
4. Hot Pressing Pressures:	Two Pressures, 20.7 MPa (3000 psi) and 34.5 MPa (5000 psi)
5. Post-Press Sintering Temperatures*:	Four temperatures, 1000°, 1200°, 1350°, and 1527° at a constant time of 21.6 ks (6 h)

DEVELOPMENTAL MATRIX

It is obvious that many parameters could be varied independently over rather wide ranges of experimental capability. These could include: (1) cold pressing pressures, (2) feed granule size ranges, (3) time/temperature thermal pre-press seasoning, (4) hot pressing time/temperature/pressures, and (5) post-press sintering time/temperature. Table IV lists the variables selected for the present study.

The matrix was structured so that only a single variable would be introduced at a time. The analytical methods used for evaluation included dimensional and weight change, chemical analyses, and detailed microstructural examination. The latter item included measurements of discrete grain sizes, porosities, and their distribution.

The assignment of the 16 simultaneously fabricated specimens is shown schematically in Fig. 3. Note that the "conditioned" feed for a particular pressing will vary from run to run.

*Strictly speaking, these temperatures were not "varied" in different runs. However, the simultaneously pressing of 16 specimens allowed replicate samples to be subjected to different thermal equilibrations. Their effects could therefore be evaluated with the selected variable parameter.

A total of 12 separate pressings were made according to the planned matrix. Appropriate analyses were carried out on all specimens.

RESULTS AND DISCUSSION

As noted in Table IV, a total of 5 separate parameters were examined during this study. The results of each and appropriate discussions will be tabulated separately. The following general remarks apply to all the data to be shown:

1. Admittedly, many of the conclusions are based on metallographic evidence for pore size, grain growth, structure "appearance," etc. Since it is impossible to guarantee complete and absolute sample homogeneity, some of the results may be partially biased by asymmetric grain growth, the particular surface exposed by the polishing or etching process, or the unavoidable occasional artifact which might appear. Therefore, the conclusions in this study should be regarded as an

Fig. 3. Assignments of Developmental Specimens.

establishment of behavioral trends, although additional corroborative evidence is anticipated.

2. "% T. D." stands for "Percent Theoretical Density" based on 11.46 g/cm^3 for PuO_2 .⁽³⁾ Limits of precision are ± 0.3 .
3. Average grain and pore sizes are accurate to a factor of two.
4. Volume (or Δ volumes) are accurate to ± 0.2 .

A. Effect of Varying Cold Pressing Pressure (Prior to Feed Granule Formation)

Constant Conditions

1. 0 - 125 μm feed granules
2. Pre-press thermal seasoning at 1050° and 1150°C for 10.8 ks
3. Hot pressing at 1490°C for 1.8 ks at 34.5 MPa
4. Post-press sintering of 3 each pellets at 1000° , 1200° , 1350° and 1527°C for 21.6 ks

Varied Conditions

1. Cold press at 0.4 GPa followed by crushing and screening
2. Cold press at 0.8 GPa followed by crushing and screening

The results are shown in Table V.

B. Effect of Varying Size Range of Feed Granules

Constant Conditions

1. Cold Pressing pressure of 0.4 GPa
2. Pre-press thermal seasoning at 1050° and 1150°C for 10.8 ks
3. Hot pressing at 1490°C for 1.8 ks at 34.5 MPa
4. Post-press sintering of 3 ea. pellets at 1000° , 1200° , 1350° , and 1527°C for 21.6 ks

Varied Conditions

1. Feed sized to 0 - 125 μm at 1650°C and 1150°C
2. Feed sized to 0 - 297 μm at 1050°C and 1150°C

The data from these pressings are shown in Table

VI.

a. 0.4 GPa Cold Press $\longleftrightarrow$
Run P-2 100 μm

b. 0.8 GPa Cold Press $\longleftrightarrow$
Run P-10 100 μm

Fig. 4. Comparison of microstructures with 0.4 GPa and 0.8 GPa cold pressing pressures. Pre-press seasoning temperature (1150°C) and post press sintering temperature (1527°C) are constant.

TABLE V
RESULTS OF VARYING COLD PRESSING PRESSURES

Run No.	Cold Press Pressure, GPa	Pre-Press Seasoning Thermal Temp., °C	Post-Press Sintering Temp., °C	Pellet Data			
				Density % T. D.	Avg Grain Size, μm	Avg Pore Size, μm	Δ Volume During Sintering, %
P-1	0.4	1050	"As Pressed"	87.6	5	2	-
	0.4	1050	1000	88.1	4	4	- 0.1
	0.4	1050	1200	89.1	7	3	- 0.7
	0.4	1050	1350	89.6	8	5	- 1.5
	0.4	1050	1527	90.8	26	4	- 2.8
P-11	0.8	1050	"As Pressed"	88.4	3	2	-
	0.8	1050	1000	89.3	4	1	- 0.3
	0.8	1050	1200	89.5	3	2	- 0.7
	0.8	1050	1350	90.5	10	2	- 1.7
	0.8	1050	1527	90.2	35	3	- 1.2
P-2	0.4	1150	"As Pressed"	86.3	4	4	-
	0.4	1150	1000	87.8	5	6	- 0.9
	0.4	1150	1200	87.6	7	6	- 0.6
	0.4	1150	1350	87.9	9	4	- 1.2
	0.4	1150	1527	89.6	14	6	- 2.9
P-10	0.8	1150	"As Pressed"	86.5	2	1	-
	0.8	1150	1000	87.1	4	1	-
	0.8	1150	1200	87.2	2	10	- 0.1
	0.8	1150	1350	88.7	11	5	- 1.8
	0.8	1150	1527	89.6	20	7	- 2.8

Conclusions

1. The lower pre-press seasoning temperature (1050°C) and the lower cold pressing pressure (0.4 GPa) allow enough residual specific surface activity in the feed granules to allow attainment of ~91% T. D. at 1527°C post-press sintering temperature.
2. Considerable growth in grain size at 1527°C post-press sintering temperature was noted; pore sizes remain rather constant.
3. Microstructures in Fig. 4 above show rather qualitative differences. The pores in those specimens from Run P-10 tend to be a bit more rounded and homogeneously distributed. Other parameters to be discussed will exert a more dominating influence on appearance.

TABLE VI
RESULTS OF VARYING FEED GRANULE SIZE

Run No.	Feed Granule Size, μm	Pre-Press Seasoning Thermal Temp., $^{\circ}\text{C}$	Post-Press Sintering Temp., $^{\circ}\text{C}$	Pellet Data			
				Density % T. D.	Avg Grain Size, μm	Avg Pore Size, μm	Δ Volume During Sintering, %
P-1	0-125	1050	"As Pressed"	87.6	5	2	-
	0-125	1050	1000	88.1	4	4	+0.1
	0-125	1050	1200	89.1	7	3	-0.7
	0-125	1050	1350	89.6	8	5	-1.5
	0-125	1050	1527	90.8	26	4	-2.8
P-2	0-125	1150	"As Pressed"	86.3	4	4	-
	0-125	1150	1000	87.8	5	6	-0.9
	0-125	1150	1200	87.6	7	6	-0.6
	0-125	1150	1350	87.9	9	4	-1.2
	0-125	1150	1527	89.6	14	6	-2.9
P-4	0-297	1050	"As Pressed"	87.7	3	10	-
	0-297	1050	1000	88.4	3	11	-0.1
	0-297	1050	1200	88.7	7	9	-0.4
	0-297	1050	1350	89.9	9	8	-1.7
	0-297	1050	1527	90.4	19	6	-2.3
P-5	0-297	1150	"As Pressed"	85.9	3	11	-
	0-297	1150	1000	86.5	4	7	+0.1
	0-297	1150	1200	87.3	7	5	-0.9
	0-297	1150	1350	87.2	9	8	-0.7
	0-297	1150	1527	88.5	19	7	-2.2

Conclusions

1. Considerable grain growth at highest sintering temperature; pore size remains rather constant.
2. Photomicrographs in Figs. 5 and 6 below show tendency toward more evenly distributed porosity in the specimens made from the 0 - 125 μm feed granules.
3. Feed granule size range of 0 - 125 μm preferred over 0 - 297 μm .

C. Effect of Varying Feed Granule Pre-Press Seasoning Temperature on Different Sized Feed Granules

Constant Conditions

1. Cold pressing pressure of 0.4 GPa
2. Hot pressing at 1490°C for 1.8 ks at 34.5 MPa
3. Post-press sintering of 3 each pellets at 1000°, 1200°, 1350°, and 1527°C

Varied Conditions

1. Feed sized to 0 - 125 μ m with pre-hot press seasoning at 1050°, 1150°, 1200°, and 1250°C (i.e., 4 runs)
2. Feed sized to 0 - 297 μ m with pre-press seasoning at 1050°, 1150°, 1200°, and 1250°C (i.e., 4 runs)

The data from this series of pressings are shown in Tables VII and VIII.

D. Effect of Varying Hot Pressing Pressure

Constant Conditions

1. Cold press pressure of 0.4 GPa
2. Pre-press seasoning temperatures of 1050° and 1150°C
3. Feed granule size of 0 - 125 μ m
4. Post-press sinter 3 each pellets at 1000°, 1200°, 1350°, and 1527°C

Varied Conditions

1. Hot press at 1490°C for 1.8 ks at 20.7 MPa and 34.5 MPa

The data for this series are shown in Table IX.

a. 0 - 125 μ m Feed, Run P-1 50 μ m

b. 0 - 297 μ m Feed, Run P-4 50 μ m

Fig. 5. Comparison of microstructures of 0 - 125 μ m and 0 - 297 μ m feed granules. Cold pressing pressure of 0.4 GPa, pre-press seasoning temperature (1050°C) and post-press sintering temperature (1527°C) are constant.

TABLE VII
RESULTS OF VARYING PRE-PRESS SEASONING TEMPERATURE, 0-125 μ m FEED

Run No.	Granule Feed Size, μ m	Pre-Press Seasoning Temp., °C	Post-Press Sintering Temp., °C	Pellet Data			Δ Volume During Sintering, %
				Density % T. D.	Avg Grain Size, μ m	Avg Pore Size, μ m	
P-1	0-125	1050	"As Pressed"	87.6	5	2	-
	0-125	1050	1000	88.1	4	4	+0.1
	0-125	1050	1200	89.1	7	3	-0.7
	0-125	1050	1350	89.6	8	5	-1.5
	0-125	1050	1527	90.8	26	4	-2.8
P-2	0-125	1150	"As Pressed"	86.3	4	4	-
	0-125	1150	1000	87.8	5	6	-0.9
	0-125	1150	1200	87.6	7	6	-0.6
	0-125	1150	1350	87.9	9	4	-1.2
	0-125	1150	1527	89.6	14	6	-2.9
P-7	0-125	1200	"As Pressed"	85.8	3	2	-
	0-125	1200	1000	86.6	4	2	-0.3
	0-125	1200	1200	87.2	6	2	-1.1
	0-125	1200	1350	88.3	12	2	-2.2
	0-125	1200	1527	89.6	27	3	-3.7
P-3	0-125	1250	"As Pressed"	80.6	4	5	-
	0-125	1250	1000	81.1	6	6	+0.2
	0-125	1250	1200	81.1	7	6	0.0
	0-125	1250	1350	81.6	9	4	-0.5
	0-125	1250	1527	83.0	18	7	-2.2

TABLE VIII
RESULTS OF VARYING PRE-PRESS SEASONING TEMPERATURE, 0-297 μ m FEED

Run No.	Granule Feed Size, μ m	Pre-Press Thermal Seasoning Temp., $^{\circ}$ C	Post-Press Sintering Temp., $^{\circ}$ C	Pellet Data			
				Density % T. D.	Avg Grain Size, μ m	Avg Pore Size, μ m	Volume During Sintering, %
P-4	0-297	1050	"As Pressed"	87.7	3	10	-
	0-297	1050	1000	88.4	3	11	- 0.1
	0-297	1050	1200	88.7	7	9	- 0.4
	0-297	1050	1350	89.9	8	8	- 1.7
	0-297	1050	1527	90.4	18	6	- 2.3
P-5	0-297	1150	"As Pressed"	85.9	3	11	-
	0-297	1150	1000	86.5	4	7	+ 0.1
	0-207	1150	1200	87.3	7	5	- 0.9
	0-297	1150	1350	87.2	9	8	- 0.7
	0-297	1150	1527	88.5	16	7	- 2.2
P-8	0-297	1200	"As Pressed"	85.8	3	2	-
	0-297	1200	1000	86.7	3	1	- 0.3
	0-297	1200	1200	87.1	3	3	- 0.9
	0-297	1200	1350	88.2	13	4	- 2.0
	0-297	1200	1527	89.5	22	5	- 3.6
P-6	0-297	1250	"As Pressed"	82.4	4	6	-
	0-297	1250	1000	83.1	4	8	- 0.1
	0-297	1250	1200	83.0	4	8	+ 0.1
	0-297	1250	1350	83.3	6	16	- 0.4
	0-297	1250	1527	85.8	27	8	- 3.3

Conclusions (Both 0 - 125 and 0 - 297 μ m Feed Granules)

1. A very striking lack of sinterability (or density increase) is apparent in those runs in which the feed granules were pre-press seasoned at 1250 $^{\circ}$ C. Note that the same trend is evidenced by both the 0 - 125 and 0 - 297 μ m granules. Figure 7 compares the corresponding microstructures from both sizes of feed granules; in particular Fig. 7.d shows the more uneven and irregular porosity distribution following the pre-press seasoning at 1250 $^{\circ}$ C.
2. Graphical displays of the attainable densities are shown in Figs. 8 and 9. For clarity, the curves showing the changes in densities following sintering at 1000 $^{\circ}$ C and 1350 $^{\circ}$ C are omitted; however, they exhibit the same trend. Therefore, it is obvious that densities > 86% cannot be attained if the feed granules are pre-press seasoned at >1200 $^{\circ}$ C.
3. Grain growth increases sharply with sintering temperatures > 1350 $^{\circ}$ C although the pore sizes remain rather constant.

TABLE IX
RESULTS OF VARYING HOT PRESSING PRESSURE, 0-125 μ m GRANULES

Run No.	Hot Press Pressure, GPa	Pre-Press Thermal Seasoning Temp., °C	Post-Press Sintering Temp., °C	Pellet Data			
				Density % T. D.	Avg Grain Size, μ m	Avg Pore Size, μ m	Δ Volume During Sintering, %
P-13	20.7	1050	"AS Pressed"	86.8	4	1	-
	20.7	1050	1000	87.6	3	1	- 0.2
	20.7	1050	1200	88.7	3	2	- 1.4
	20.7	1050	1350	88.8	7	1	- 1.5
	20.7	1050	1527	91.2	24	3	- 4.2
P-1	34.5	1050	"AS Pressed"	87.6	5	2	-
	34.5	1050	1000	88.1	4	4	+ 0.1
	34.5	1050	1200	89.1	7	3	- 0.7
	34.5	1050	1350	89.6	8	5	- 1.5
	34.5	1050	1527	90.8	26	4	- 2.8
P-12	20.7	1150	"As Pressed"	85.8	6	2	-
	20.7	1150	1000	86.6	5	1	- 0.2
	20.7	1150	1200	87.5	5	2	- 1.1
	20.7	1150	1350	88.3	6	1	- 2.2
	20.7	1150	1527	90.6	21	3	- 4.7
P-2	34.5	1150	"As Pressed"	86.3	4	4	-
	34.5	1150	1000	87.8	5	6	- 0.9
	34.5	1150	1200	87.6	7	6	- 0.6
	34.5	1150	1350	87.9	9	4	- 1.2
	34.5	1150	1527	89.6	14	6	- 2.9

Conclusions

1. The attainable densities are quite similar again indicative that the pre-press seasoning temperature is the overriding factor.
2. The relatively large (>4%) shrinkage in the runs carried out at 20.7 MPa and subjected to the 1527°C post-press sintering temperature suggests that a larger specimen (representative of a more massive current operational fuel module) might not withstand a shrinkage of this magnitude.
3. Therefore, if operational temperatures in the $\geq 1350^\circ\text{C}$ range are anticipated, more thermal shock resistance will result from hot pressing at >30 MPa. If lower operational temperatures are anticipated and higher geometric and power densities are desired, lower hot pressing pressures could be considered.

a. 0 - 125 μ m Feed, $\leftarrow \rightarrow$
Run P-2 50 μ m

b. 0 - 297 μ m Feed, $\leftarrow \rightarrow$
Run P-5 50 μ m

Fig. 6. Comparison of microstructures of 0 - 125 μ m and 0 - 297 μ m feed granules. Cold press pressure of 0.4 GPa, pre-press seasoning temperature (1150°C), and post-press sintering temperature (1527°C) are constant.

a. Pre-Press Seasoning Temperature: 1050°C $\leftarrow \rightarrow$
Run P-1 50 μ m

Run P-4

Run P-2

b. Pre-Press Seasoning Temperature: 1150°C $\leftarrow \rightarrow$
50 μ m

Run P-5

Run P-7

Run P-8

c. Pre-Press Seasoning Temperature: 1200°C $\leftarrow$ 50 μm

Run P-3

0 - 125 μm Feed

Run P-6

0 - 257 μm Feed

d. Pre-Press Seasoning Temperature: 1250°C $\leftarrow$ 50 μm

Fig. 7. Comparison of microstructures showing effects of pre-press seasoning temperatures. Feed granule size (0 - 125 μm), cold pressing pressure (0.4 GPa), and post-press sintering temperature (1527°C) are constant.

E. Stoichiometric Effects

While these studies were in progress, some additional results were noted concerning stoichiometric effects in PuO_2 as a function of processing and environments. Since the hot pressing itself is done in graphite dies under reducing (vacuum) conditions, it was not surprising that some reduction of the dioxide took place. Examination of a microstructure of a typical pellet in the "as pressed" condition indicated considerable amounts of the reduced phase, PuO_{2-x} , as illustrated in Fig. 10a. Visual suggestions of this second phase persisted in microstructures of

comparison specimens which had been sintered as 1000° and even traces were evident after sintering at 1200° , both in the oxidizing environment of $\text{Ar}/\text{H}_2^{18}\text{O}_2$, as noted in Figs. 10b and 10c.

However, other diagnostics, including TGA analysis and X-ray diffraction, indicated only PuO_2 in these specimens. The visual appearance of the reduced phase following the 1200° and 1250° post-press sintering has not been completely explained. It may be that 1000° or 1200°C , while indeed oxidizing all of the plutonium in

Fig. 1. Product densities vs seasoning temperatures for 125µm feed granules.

Fig. 2. Product densities vs seasoning temperatures for 297µm feed granules.

$\text{PuO}_{2.00}$ leaves the lattice in some distorted or disordered form which could give the appearance of reduced phase in photomicrographs.

It also became apparent, based on weight change and TGA data, that the "as pressed" pellets would slowly oxidize over a period of several hours due to reactions with oxidizing components in the glovebox atmosphere. Nevertheless, the visual indications of reduced phase in photomicrographs persisted. All of the studies described in this report were carried out in "Argon Flush" gloveboxes. It is estimated that the $\text{O}_2/\text{H}_2\text{O}$ content was ≈ 0.10 or ≈ 10 ppm Fe (10^{-4} atm). Thermodynamically, this is sufficient to carry out the oxidation to $\text{PuO}_{2.00}$ even at room temperature.

Definitive reproducible tests, involving immediate transfers of "as pressed" pellets in a protecting atmosphere of pure Ar (< 1 ppm $\text{O}_2/\text{H}_2\text{O}$) for analyses, established the "as pressed" stoichiometry as $\text{PuO}_{2.00}$. Metallography, TGA analysis, X-ray, and weight change data all corroborated this value. Except for the metallographic evidence, reoxidation at 1000° indicated $\text{PuO}_{2.00}$. Therefore, while equilibration at 1000° or 1200° in an oxidizing atmosphere is sufficient to chemically transform $\text{PuO}_{2.00}$ to $\text{PuO}_{2.00}$, some structure defects persist.

It should be noted that reoxidation at $\approx 1250^\circ$ in Ar/ H_2O for < 1 h not only removes all optical traces of reduced phases but also encourages grain growth to a more ordered structure (see Fig. 10d and 10e).

a. "As Pressed" $\overline{\text{K}} \rightarrow$
Run P-4 20 μm

d. Post Press Sinter at 1350°C $\overline{\text{K}} \rightarrow$
Run P-4 20 μm

b. Post Press Sinter at 1000°C $\overline{\text{K}} \rightarrow$
Run P-4 20 μm

e. Post Press Sinter at 1527°C $\overline{\text{K}} \rightarrow$
Run P-4 20 μm

c. Post Press Sinter at 1200°C $\overline{\text{K}} \rightarrow$
Run P-4 20 μm

Fig. 10. Comparison of microstructures showing effect of post press sintering temperatures on elimination of reduced phase and enhanced grain growth. Cold press pressure (0.4 GPa), feed granule size (0 - 125 μm), and pre-press seasoning temperature (1050°C) are constant.

SUMMARY

The results obtained in the studies to date may be summarized as follows:

1. Cold pressing pressures of 0.4 GPa and 0.8 GPa were compared. Cold pressing pressures of 0.8 GPa do yield structures of slightly higher homogeneity; however, other parameters are more important.

2. Feed granules sized to 0 - 125 μ m lead to a more even and balanced porosity distribution than those sized to 0 - 297 μ m.
3. Pre-press seasoning temperatures should not exceed 1200°C to maintain sufficient surface activity to promote grain coalescence. Pre-press seasoning in excess of 1200°C results in a more uneven and non-reproducible structure even after sintering at 1527°C. All evidence to date indicates that the pre-press seasoning temperature is the overriding factor in attainment of high densities and well-ordered structures.
4. Hot pressing pressures should be as high as possible consistent with die design and specimen geometry. Pressing at lower pressures leaves considerable sinterability in the ceramic with potentially large shrinkage factors.
5. The $^{239}\text{PuO}_2$ specimens regardless of size, if fabricated under the conditions described in this report, will have an "as pressed" stoichiometry of $\text{PuO}_{1.89}$. This may be reoxidized to PuO_2 in various ways including several hours exposure to 10 Pa (10^{-4} atm) $\text{O}_2/\text{H}_2\text{O}$ environments. Re-oxidizing at 1350°C will ensure total oxidation and will promote grain growth.
6. Grain sizes in the "as pressed" state average 5 - 6 μ . Post-press sintering at temperatures $\leq 1200^\circ\text{C}$ does little to enhance grain growth while sintering at $> 1200^\circ$ shows a marked increase. Figure 11 shows the average grain growth for all twelve runs.
7. As the densities and grain size increase with high sintering temperatures, there is a tendency for the intragranular pores to migrate toward the grain boundaries. However, this seems to take place to a relatively less degree than would be expected from classic (non-radioactive) ceramic processing considerations. The presence of He from the decay of ^{239}Pu may tend to stabilize the pore configuration.

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Fig. 11. Grain growth vs post hot press sintering temperature -- averages of all runs.

Other studies are currently in progress at LASL to expand and refine these results. New parameters under investigation include the use of 44 - 125 μ m feed granules, and further variation in hot pressing times and temperatures. These results, coupled with those of the present study, will then be related to changes in mechanical properties (ultimate strength, tensile strength, etc.) of the fuel specimens as a function of processing parameters. Other operational properties such as thermal expansion, rates of He migration, etc. will be factored into future test matrices.

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