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PREPARATION, MICROSTRUCTURES, AND PROPERTIES OF PuO₂*

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ABSTRACT

PuO₂ pellets with controlled microstructures were fabricated to meet operational requirements for packaged heat sources. Size distributions, morphologies (forms and structures), and packing densities were measured on calcined and milled powders, slugged compacts, and presintered granules. These variables influence microstructure, porosity distribution, and fracture behavior of hot-pressed and sintered PuO₂.

INTRODUCTION

²³⁸PuO₂ generates 0.5 watt (thermal)/gram by alpha decay. Encapsulated ²³⁸PuO₂ heat sources have been used to power thermoelectric generators in Transit, Pioneer, Apollo, and Viking satellites and deep-space probes.¹ Advanced concept generator systems require fuel pellets that remain dimensionally stable at centerline temperatures exceeding 1400°C.² Dense, fully sintered pellets would not shrink; however, densities exceeding 90% theoretical are not currently practical because of swelling induced by decay helium at operating temperatures.³ Thus, typical fuel pellet densities are 80 to 90% of theoretical density.

Fuel pellets with microstructures that remain stable at operating temperatures can be fabricated by a granulation and hot-pressing process.⁴ Two interdependent factors that must be controlled for reproducible densities are particle characteristics (size, morphology, and agglomeration) after ball milling, and the thermal conditions (temperature and time) at

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which granules made from milled powder are presintered prior to hot pressing. Relationships are presented between these factors and their effect on the density and integrity of fuel pellets.

EXPERIMENTAL PROCEDURE

Two types of pellets were examined in these studies: one made by cold pressing and sintering relatively fine powders and one by hot pressing sized granules. The process flowsheets are shown in Table 1.

Table 1. Process for Fabricating PuO₂ Pellets

1) Precipitate plutonium oxalate	
2) Calcine to PuO ₂ (2 hr at 735°C in air)	
3) Simulate ¹⁶ O ₂ enrichment (8 hr at 700°C in air)	
4) Outgas (1 hr at 1000°C in air)	
Cold-Pressed Pellets	Hot-Pressed Pellets
5) Ball mill (8 hr in air) ^a	5) Ball or vibratory mill (varying periods in argon)
6) Cold press (58,000 psi, without binder)	6) Cold press (58,000 psi, without binder)
7) Sinter (3 hr at selected temperatures)	7) Crush (<125 μ)
	8) Presinter (3 hr at selected temperatures)
	9) Hot press (0.33 hr at 1530°C in graphite dies)
	10) Heat treat (12 hr at 1440°C in air)

^aStep omitted for some pellets.

Cold-Pressed Pellets

For the cold-pressed pellets, powder from sixteen separate precipitation batches was used. The powder was calcined and then reheated at 700°C for 8 hr in air to simulate a ¹⁶O₂-enrichment step to reduce neutron emission. It was then outgassed at 1000°C for 1 hr in air to remove helium decay gas and to reduce sinterability.⁵ Part of the outgassed powder was ball milled in argon for 8 hr. Portions of the outgassed powder with or without milling were cold pressed to form pellets, which were then sintered to increase density.

Hot-Pressed Pellets

Hot-pressed Pellets A through J were similarly made from powders ball milled from two precipitations with differing calcined particle sizes (Table 2). Equal amounts of powder were removed from the ball jar after 1, 4, 16, and 64 hr. Powders for hot-pressed Pellets K through O were vibratory milled in argon in two 12-g batches until the particle size mode was 1.3 to 1.35 μm ; this required 10 to 20 min.

Pellets representing each powder sample were cold pressed at 58,000 psi, without binder, and broken into granules by forcing the pellets through a 125- μm sieve. The granules were presintered in air at 1175°C for 3 hr in platinum crucibles.

Pellets were hot pressed, five at a time, in fixed-cavity-volume graphite dies at 1530°C for 20 min. The average hot-pressed stoichiometry was $\text{PuO}_{1.85}$. After hot pressing, the pellets were heat treated in air at 1440°C for 12 hr to adjust the stoichiometry to PuO_2 , and as a test of dimensional stability and pellet integrity.

RESULTS AND DISCUSSION

Density Variations in Cold-Pressed and Sintered Pellets

Pellets with the desired density (~82% theoretical) can be made by cold pressing and sintering the processed powder (Figure 1), but fabricated dimensions are difficult to control. The pellets shrink at operating temperatures, which are higher than sintering temperatures.

Low temperature sintering has been proposed as a way of stabilizing pellet microstructure to prevent grain growth and shrinkage at high temperatures.⁸ Presintered pellet dimensions show unacceptable variation when sintered at higher temperatures (see Points A, B, and C in Figure 1).

Pellets cold pressed from as-calcined powder had densities with larger standard deviations than similar pellets made from milled powder. Additional density variations occur during sintering, and the sintered densities of neither type of pellet are acceptable.

Pellet microstructure coarsens with increasing sintering temperature. At 1050°C, pellets retain much of the structure of the cold-pressed powder, with some rounding-of-grains, grain growth, and elimination of fine particles (Figure 2). Although pellets sintered at 1175°C show an apparent equiaxed structure on the fracture surface, the structure actually contains many irregular strings of elongated crystal clusters, the result of non-reproducible alignment of fractured laths in the cold-pressing operation. This type of structure causes the ratio of diametral-to-axial shrinkage to vary from pellet to pellet between 0.5 and 2.

Table 2. Hot Pressed Pellet Experimental Data

Pellet	Calcined Powder			Milled Powder				
	Mode, ^a μm	Thickness, μm	Tap Density, ^b % theo- retical	Time, hr	Method	Mode, ^a μm	Particle Size Standard Deviation, μm	Tap Density, ^b % theo- retical
A	2.3	0.15	23	0	-	2.3	9.6	23
B				1	BM	1.5	7.2	36
C				4	BM	1.2	7.1	38
D				16	BM	1.2	5.8	41
E				64	BM	0.7	10.0	47
F	5.0	0.75	21	0	-	5.0	7.1	21
G				1	BM	2.8	4.1	37
H				4	BM	1.8	8.9	42
I				16	BM	1.8	5.1	40
J				64	BM	1.2	5.9	42
K	7.9	1.1	22	0.33	VM	1.35	3.9	46
L				0.33	VM	1.35		46
M	1.9	0.15	14	0.17	VM	1.3	8.5	41
N				0.17	VM	1.3		41
O				0.17	VM	1.3		41

HOT PRESSED PELLET EXPERIMENTAL DATA

Pellet	Cold-pressed Pellet Density, ^c % theo- retical	Presintered Granules <125 μm		Hot-pressed Pellet Density, ^c % theo- retical	Heat-Treated Pellet		
		Tap Density, ^b % theo- retical	Mean Grain Size, ^d μm		Density, ^c % theo- retical	Grain Size, ^e μm	Condition
A	58.6	37	-	85.4	85.8	8.0	C
B	57.8	35	0.8	85.3	87.5	9.1	C
C	62.2	40	1	85.0	87.2	10.4	CF
D	65.2	45	1.3	83.5	86.5	9.8	CF
E	64.7	47	2.3	82.7	85.3	10.1	C
F	63.2	39	-	88.8	90.6	13.8	C
G	64.3	44	0.8	85.0	87.8	10.5	C
H	66.9	42	1	84.7	87.3	10.7	CF
I	68.8	46	1	84.5	87.1	9.8	CF
J	69.4	48	1.9	84.4	87.6	8.9	CF
K	68.3	49	-	83.9	85.2	9.7	CF
L	68.3	49	-	84.3	85.2	11.0	CF
M	64.9	46	-	84.7	85.8	12.4	CF
N	64.9	46	-	84.5	85.6	13.4	CF
O	64.9	46	-	84.1	85.2	11.1	CF

^aCoulter Counter Model TAI1, Coulter Electronics Co., Hialeah, Florida, after 10 minutes ultrasonic dispersion.

^bTap-Pac Volumeter, Shandon Scientific Co., Sewickley, Pennsylvania.

^cGeometric density, actual densities may be higher for cracked pellets.

^dAverage caliper diameter of 100 grains on fracture surface.

^eHilliard's intercept method⁶ multiplied by Fullman's factor⁷ for equiaxed grains.

BM = ball mill; VM = vibratory mill; C = cracked; CF = crack free.

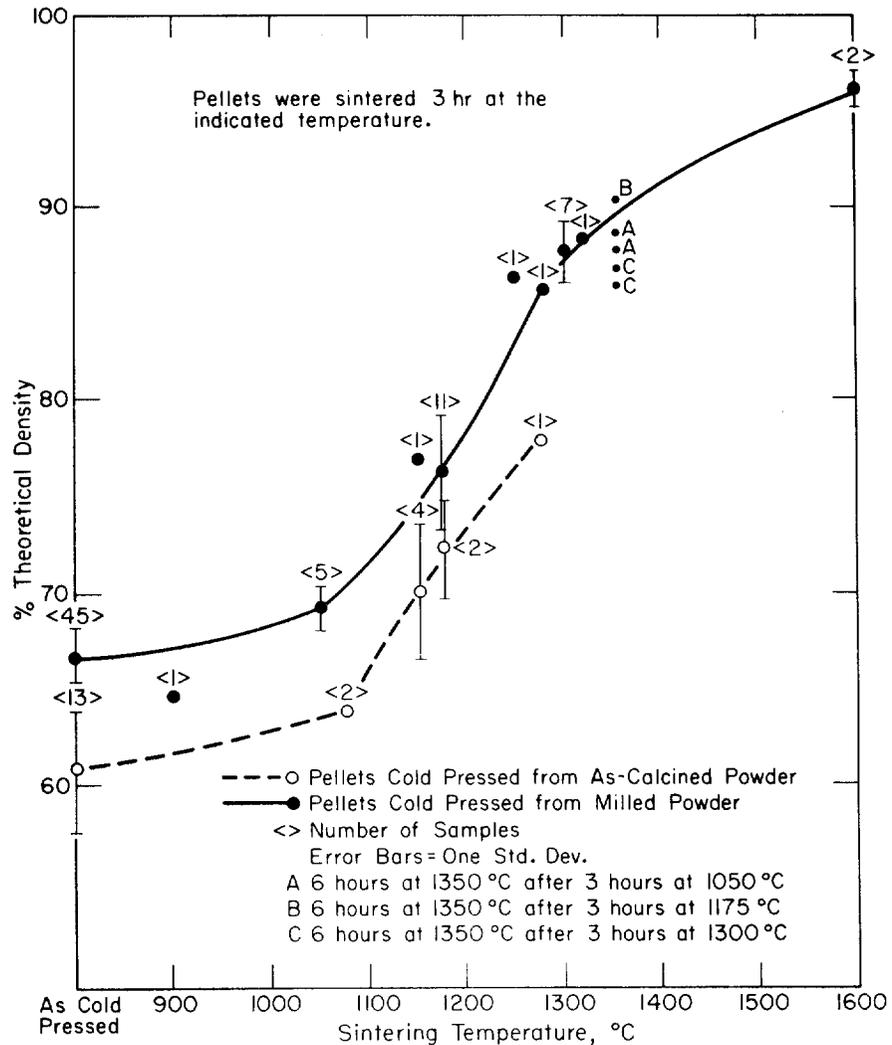


Fig. 1. Effect of sintering temperature on densities of cold-pressed pellets

No elongated crystal clusters were observed after sintering at 1300°C; instead extensive necks formed. At ~85% theoretical density, fracture mode appears to have changed from intergranular (across necks) to mixed inter- and transgranular as shown by the corresponding fractograph.

Thus, cold-pressed and sintered microstructures, from the milled or unmilled powder, are neither sufficiently stable nor reproducible to meet dimensional requirements.

Hot-Pressed Pellets with Stabilized Densities

Attempts to stabilize the as-pressed dimensions or eliminate

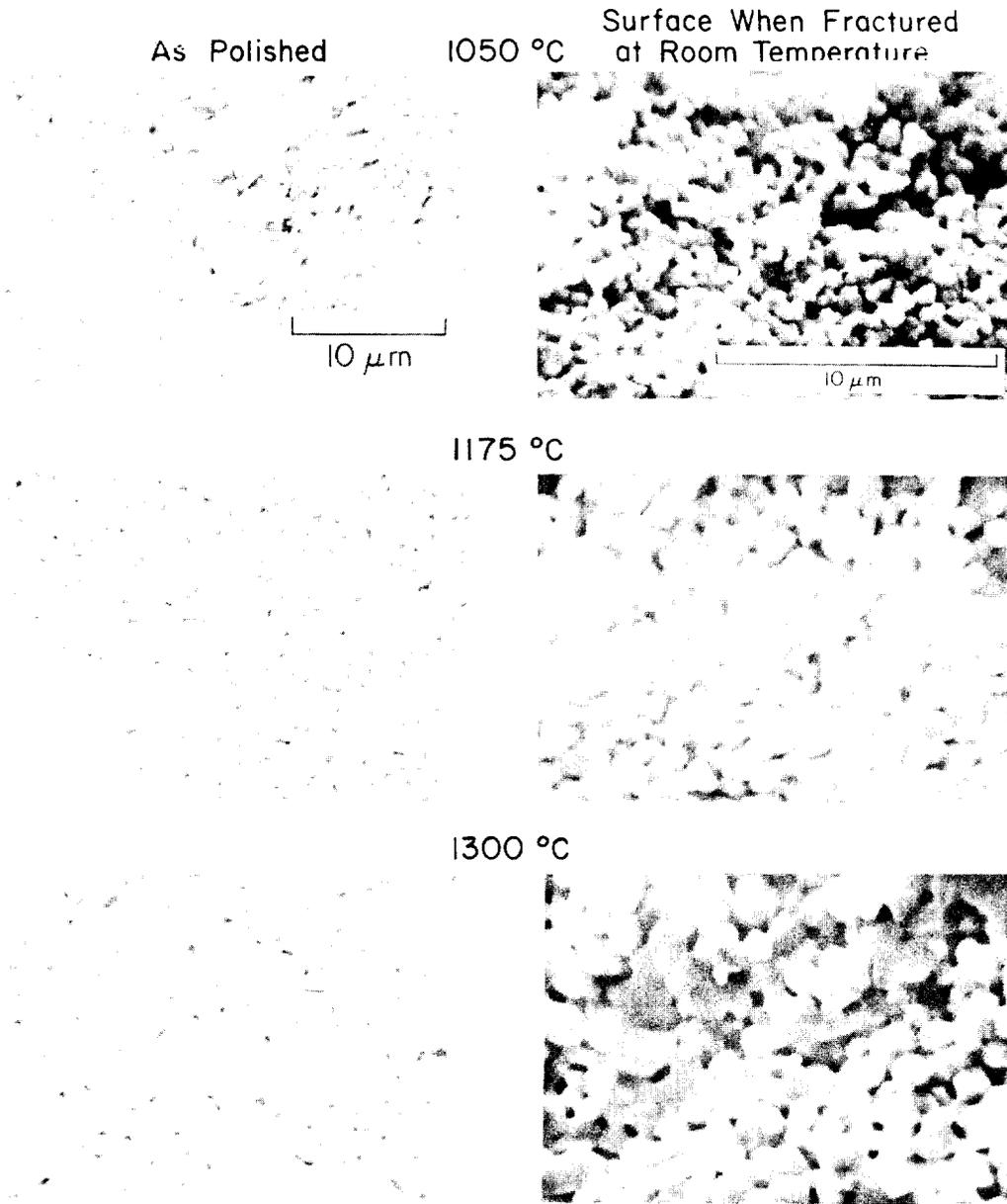


Fig. 2. Effect of sintering temperature on the microstructures of cold-pressed pellets

residual shrinkage of PuO_2 fuel forms by directly hot pressing milled oxalate based powder were unsuccessful. Densities could not be reproduced due to variable shrinkage away from the confining dies.⁹ Prolonged periods at operating temperatures caused networks of surface cracks to develop due to nonuniform shrinkage.¹⁰

However, a process was developed to fabricate pellets with the required dimensional stability and reproducibility by hot pressing granules rather than powder.⁴ Stability is achieved by presintering the granules to redistribute the porosity. For a given density, when moderately dense granules are hot-pressed, coarse pores (between granules) replace most of the fine porosity between grains normally observed in hot-pressed powders (Figure 3). Further work was undertaken to evaluate the effects of variables in this process on the stability and microstructure of the pellets.

Effect of Varying PuO₂ Particle Size. Feed powders with four different sizes were fabricated into pellets (Table 2, Figure 3). Sizes between 2 and 8 μm represent the range of sizes previously produced in the ²³⁸PuO₂ powder production. The calcined PuO₂ particles consist of monoclinic laths with dimensions dependent upon precipitation parameters. As described in a companion paper,¹¹ methods have been developed to control particle size and morphology of the precipitated powder and, consequently, its milling response.

Crack-free pellets with controlled density were fabricated from all powder milled to a mass mode particle size between 1.2 and 1.7 μm . Pellet density was insensitive to calcined particle size when size variation was accommodated by varying milling time. For example, the mode of calcined powder used to make Pellets K and L was 7.9 μm , whereas Pellets M, N, and O had a nearly equal density but were made from feed with a mode size of 1.9 μm (Table 2).

With granules made from suitably milled powder, densities can be systematically controlled in the range from 82% to 88% theoretical density by controlling the hot-press die dimensions and the weight charged to the die. However, either the size of the feed powder must be controlled or milling time varied to obtain the proper milled size.

Density versus milled size. An inverse relationship between powder particle size and pellet density would normally be expected for sintered bodies. However, the granulation and heat treatment process reverses this, causing a direct relationship between particle size and pellet density. For a given powder batch, the density of the hot-pressed pellets decreases with decreasing particle size (obtained by milling for longer times) (Table 2). This relationship was observed in data for various Savannah River feed batches fabricated at LASL.¹²

The density of granules increases during presintering at 1175°C as the particles of milled powder decrease in size and

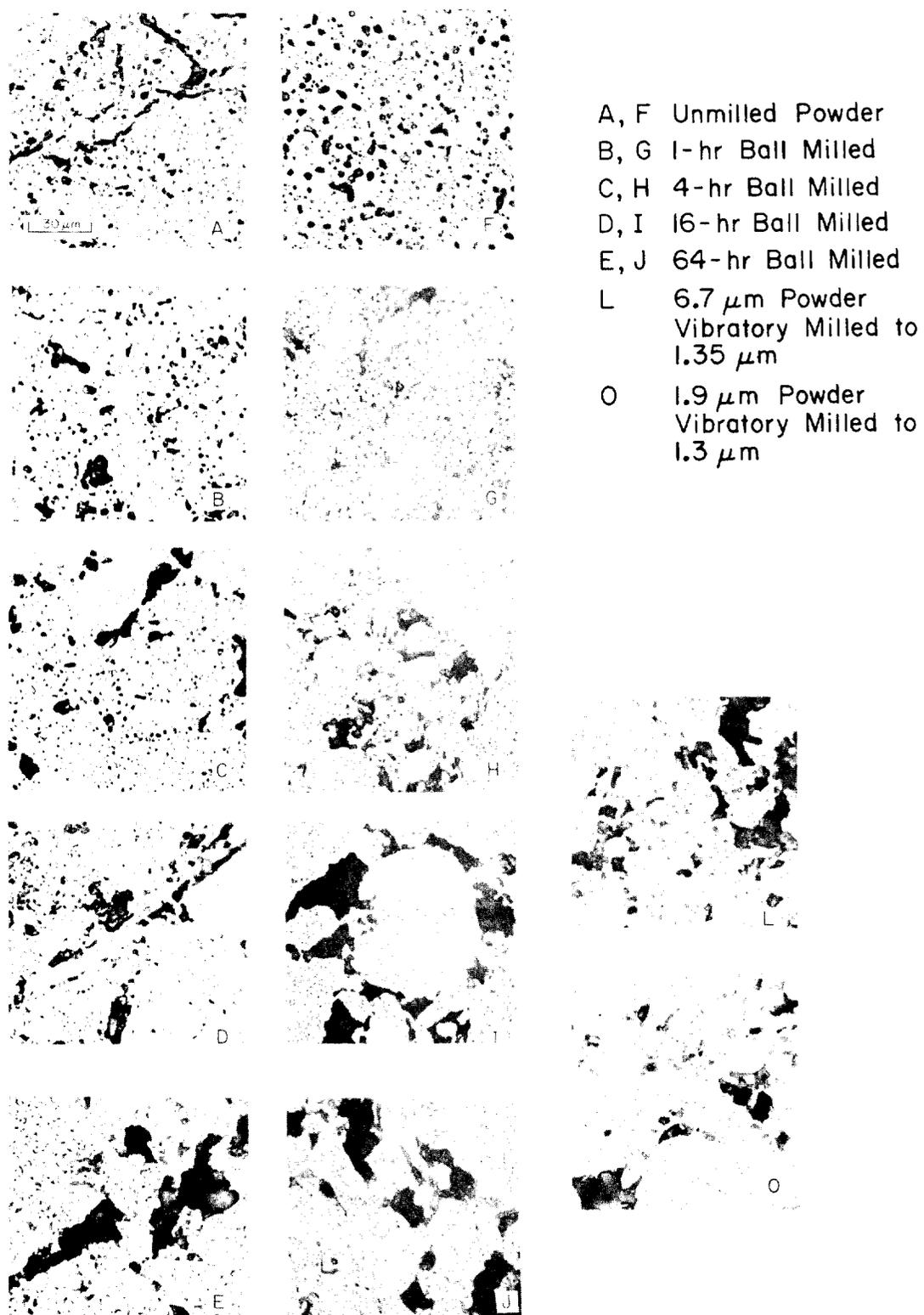


Fig. 3. Effect of milling on heat treated microstructure of hot-pressed pellets

become more uniform. Denser granules have reduced residual sinterability. Consequently, lower densities and coarser microstructures are obtained during hot pressing and subsequent heat treatment (Figure 3). These trends in density for cold-pressed pellets and heat-treated granules are shown in Table 2. For constant presintering conditions, the grain size and density of the presintered granules increase as the milled powder size decreases, i.e., at longer milling times.

Effect of granule presintering temperature. Final pellet density and potential for cracking can be controlled within certain limits by selecting a granule presintering temperature between 1050 and 1250°C. Granule density increases as presintering temperature increases between 1000 and 1300°C (Figures 1 and 2 and Table 2). An increase in presintering temperature, therefore, has a similar effect on density as longer milling. Pellets with lower densities and coarser microstructures are obtained as the granule presintering temperature is increased

Fracture versus milled size. Cracking of the fabricated fuel forms is also attributed to variations in the size and morphology of the milled powder. Microcracking occurs in pellets made from unmilled powder and powder that has been ball milled for 1 hr (Figure 3). With little or no milling, relatively little sintering occurs during granule presintering because of large size, elongated lath shape, and non-uniform packing of the powder. Thus, some granules shrink more than others during the final heat treatment causing the granules to separate.

Pellets made from powder milled to 1.2 to 1.7 μm mode size were not cracked (Table 2, Figure 3). Scanning electron microscope studies have shown that with these intermediate milling times, the powder particles are reduced in size and become equiaxed. This morphological change causes higher density and more uniform packing. Under these conditions, enough sinterability is removed during presintering of granules to prevent microcracking, but sufficient sinterability is retained to permit strong bond formation between granules during hot pressing.

Over-milling (64 hr) also causes cracking. The resulting high density granules form strong bridges internally, which cause non-uniform transmission of pressing forces within the pellet. This causes density variations and possibly residual stresses. Since these granules sinter readily in the presintering step, little sinterability is retained to bond the granules to one another. This relatively weak and inhomogeneous structure is more susceptible to cracking from thermal

or mechanical shock during hot pressing and subsequent heat treatment.

CONCLUSIONS

1. Sintered granules made from cold-pressed milled powder can be hot pressed into ~85% dense pellets with low residual sinterability and good mechanical integrity. In contrast, pellets made either by cold pressing and sintering (this work), or by hot pressing as-calcined or milled PuO₂ powders (previous work)^{9,10} are not dimensionally stable at elevated temperatures because of residual sinterability. Sintering at moderate temperatures and times does not significantly stabilize pellet density at higher temperatures.
2. Density and integrity of pellets hot-pressed from sintered granules are sensitive to properties that affect the internal density of the granules, such as particle size and agglomeration of milled powder and granule presintering temperature. Pellet density is directly proportional to the milled particle size of powder used in making the granules.
3. Calcined powder with a mode size between 2 and 8 μm requires milling to a mode size between 1.2 and 1.7 μm to produce granules for hot-pressed pellets which are crack free with controllable densities.

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