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Sintering Behavior of
Plutonium Dioxide

by

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ABSTRACT

Compacts of plutonium dioxide have been prepared and sintered in order to study the sinterability of PuO_2 powders prepared by various routes, and further, to study the effect of controlled impurity additions.

The plutonium dioxide was prepared by precipitation from nitrate solution of oxalate, hydroxide, and peroxide and subsequent conversion. Some powders were also prepared by direct oxidation of plutonium metal and by direct denitration of plutonium nitrate solution. Sintering was performed at 1600°C in both a reducing atmosphere, $\text{N}_2\text{-6\% H}_2$, and an oxidizing atmosphere, O_2 .

Generally, higher densities resulted from compacts sintered in oxygen as anticipated, since sintering in a reducing atmosphere tends towards the formation of lower density suboxides.

Sintered densities also tended to be higher for the oxalate derived material.

Controlled additions primarily of Y_2O_3 and SrO were studied as sintering aids. The results indicate that SrO addition in the range of 0.4 to 1.0 mol percent has a pronounced beneficial effect in increasing sintered density.

INTRODUCTION

Of all the ceramic oxides, only a relatively few crystallize in the fluorite structure and the majority of these are of great interest for nuclear applications. This interest is based mainly on three favorable physical characteristics:

(1) a fairly high melting point; (2) good resistance toward radiation damage; and (3) crystallographic stability over a wide temperature range. These oxides when listed in order of increasing lattice parameter, Table I, appear to fall into three distinct groups: (1) fluorite structure possible by impurity stabilization (no other oxidation states) as with the smaller cations, Zr and Hf; (2) fluorite structure stable with the tetravalent cation representing the highest oxidation state in a series as with Pr, Am, Cm, Pu, and Ce; and (3) fluorite structure stable with the tetravalent cation representing the lowest or only oxidation state as with Np, U, Pa, and Th.

An important area of ceramic fuel development is that concerned with one of these fluorite structural oxides, plutonium dioxide. While it is unlikely that pure PuO_2 will be utilized as a commercial reactor fuel, a complete ceramic evaluation of this material is essential since fuel compositions based on PuO_2 dispersed or dissolved in a fertile or an inert matrix will become of increasing importance. While most of the work to date has dealt with the UO_2 - PuO_2 system^(1,2,3,4,5,6), the investigations reported herein are limited to PuO_2 ; in particular to: (1) comparison of PuO_2 powders prepared by various methods; (2) evaluation of sintering behavior under different atmospheric conditions; and (3) study of the effect of various impurity additions upon the sintering behavior.

Table I

Properties of Fluorite Structured Oxides

<u>Compound</u>	<u>Lattice Constant Å</u>	<u>Cation Radius Å</u>	<u>Melting Point °C</u>	<u>Number of Lower Oxides</u>	<u>Number of Higher Oxides</u>
ZrO ₂	5.07	0.79	2700	None	None
HfO ₂	5.11	0.78	2810	None	None
PrO ₂	5.36	0.92	-	5	None
CmO ₂	5.37	-	-	1	None
AmO ₂	5.38	0.92	-	1	None
PuO ₂	5.39	0.93	2500	2 or 3	None
CeO ₂	5.41	1.07	2600	5	None
NpO ₂	5.42	0.95	-	None	1
UO ₂	5.47	0.97	2800	None	3
PaO ₂	5.50	0.98	-	None	-
ThO ₂	5.59	1.02	3050	None	None

EXPERIMENTAL PROCEDURE

Plutonium dioxide can be prepared by (1) direct oxidation of plutonium metal in air or steam; (2) direct ignition of plutonium nitrate solution; or (3) precipitation from nitrate solution as the oxalate, peroxide, or hydroxide followed by calcination to the oxide. These studies concentrated on the use of material prepared by the precipitation processes. The process parameters and particle characteristics of the various powders prepared by precipitation are presented in Table II.

The sintering behavior of the various powders was studied by the use of compacted right cylindrical pellets. The feed powders were compacted in hardened steel dies at pressures ranging from 10 to 40 TSI. An organic binder was never considered for experimental evaluation because of the known reaction between PuO_2 and carbon. A film of stearic acid solution was used as a die and punch lubricant. The compacts were sintered at 1600°C in molybdenum boats under flowing (4 cfh) nitrogen-6% hydrogen atmosphere or in platinum boats under flowing oxygen. The heating and cooling rates for all firings were approximately 350°C per hour. No detrimental interaction between PuO_2 and the boat materials was ever observed.

A number of pellet physical characteristics were determined subsequent to sintering. Geometric densities were calculated from the weight and external dimensions. The microstructures of mounted and polished sections were brought out by cathodic vacuum etching and examined with a Unitron metallographic unit using reflected light. Electrical resistance measurements were made at room temperature with a Wheatstone bridge. High surface resistance on the oxide shapes was overcome by the application of liquid In-Ga contacts. X-ray diffraction was used for phase identification and lattice parameter determination.

Table II

Preparation Conditions and PuO₂ Powder Characteristics

<u>Batch Designation</u>	<u>Calcination Temperature °C</u>	<u>Calcination Time Minutes</u>	<u>Surface Area M²/gm</u>	<u>Bulk Density gm/cc</u>	<u>Tap Density gm/cc</u>	<u>Average Particle Size Microns</u>
<u>Oxalate</u>						
Pu4-4	560	5	39	1.42	2.03	1.9
Pu5-2	420	5	69	1.55	2.00	2.2
Pu9-3	760	30	4.45	1.85	3.56	1.2
Pu38	760	30	4.88	1.53	2.70	1.4
Pu27	760	30	5.83	1.85	3.09	2.2
<u>Hydroxide</u>						
78-38-A	850	120	5.0	-	-	-
78-38-B	850	120	22.2	-	-	-
17-8-A	850	120	5.7	-	-	-
17-8-B	850	120	11.2	-	-	-
78-46-A	850	120	28.4	1.84	3.36	1.07
<u>Peroxide</u>						
Pu29	490	30	26.0	2.79	4.96	2.27
Pu30	490	30	19.5	1.85	3.79	1.06
Pu31	490	30	23.7	2.10	4.14	1.22

RESULTS AND DISCUSSION

Pertinent sintering data are presented in Table III for compacts sintered under both reducing ($N_2-6\% H_2$) and oxidizing (O_2) conditions. Certain general conclusions can be drawn from these data. In agreement with previous investigations^(3,6), higher sintered densities were obtained with oxalate derived powder. Final densities of pellets produced from this material are more often in excess of 90% of theoretical PuO_2 than is the case with hydroxide or peroxide derived material. The powders from nitrate ignition and metal oxidation sinter to relatively low density. It is to be noted that higher densities were generally obtained when sintering under oxidizing conditions. This is to be anticipated since sintering under such conditions would prevent the formation of suboxides having lower theoretical density. Gravimetric determinations made by reoxidation of reduction sintered pellets show that the final product is $PuO_{1.85}$ to $PuO_{1.95}$, which indicates a possible $\alpha-Pu_2O_3$ concentration in the range 10-40%. Due to the lower density of $\alpha-Pu_2O_3$ one would, therefore, expect the pellets sintered in an oxidizing atmosphere to have a 1-5% higher density than those sintered under reducing conditions. The data bear out this tendency.

Typical microstructures of the reduction sintered compacts are shown in Figures 1 and 2. The reduced second phase, $\alpha-Pu_2O_3$, is readily distinguishable in all cases. No $\beta-Pu_2O_3$ was detected by x-ray diffraction analysis. It is to be noted that the structure and location of the second phase material is dependent upon the precipitation route; the nature of the precursor, oxalate or hydroxide, obviously influences the structure of the final oxide product.

Sintering aids were investigated to improve sintered density, especially for the hydroxide and peroxide derived materials. Two possibilities exist for such an improvement of sinterability through impurity additions: (1) the impurity forms a reactive liquid surrounding the grains at the sintering temperature, or (2) the impurity goes into substitutional solid solution in the host lattice. The success of the solid solution process depends on the relative cation sizes and the creation of lattice defects by the difference in valence states associated with the cations.

The first process, reactive liquid, has been observed in the case of hydroxide derived material which had high impurity levels of Fe, Cr, and Ni. As shown in Figure 2(a), a considerable liquid phase is observed along the grain boundaries and this particular preparation (78-38-B) sintered to a higher density than the other hydroxide batches. For the solid solution process with PuO_2 , the selected cations should have an atomic radius close to $0.93\text{\AA}$ and be a stable mono-, di-, or tri-valent species. With this combination, such a solid solution would produce oxygen vacancies as the lattice defect and the oxygen mobility during sintering would then be enhanced. Extensive investigation^(7,8,9,10,11) of Ca^{+2} substituting for Zr^{+4} in the fluorite oxide

Table III

Sintering Characteristics of PuO₂
(Sintered at 1600°C for 1 Hour in N₂-6% H₂ or O₂)

Powder Preparation Route	Batch Designation	Compaction Pressure TSI	Green Density gm/cc	Fired Density gm/cc		Fired Density Percent of Theoretical PuO ₂	
				N ₂ -6% H ₂	O ₂	N ₂ -6% H ₂	O ₂
Oxalate	Pu4-4	38	6.36	10.34	10.94	90.4	95.6
	Pu5-2	38	5.85	10.35	10.90	90.5	95.2
	Pu9-3	38	7.51	10.33	10.60	90.1	92.6
	Pu38	40	7.25	9.58	10.55	83.6	92.1
	Pu27	10	6.50	9.93	10.49	86.6	91.5
	Pu27	20	7.01	10.21	10.70	89.1	93.4
Hydroxide	78-38-A	32	8.08	9.94	9.92	86.7	86.6
	78-38-B	32	5.95	10.34	10.71	90.2	93.5
	17-8-A	32	7.81	9.50	9.57	82.9	83.5
	17-8-B	32	6.90	9.70	9.85	84.6	85.9
	78-46-A	32	5.75	10.36	10.35	90.4	90.3
Peroxide	Pu29	20	6.60	9.24	9.45	80.6	82.5
	Pu29	40	7.04	9.26	9.87	80.8	86.1
	Pu30	20	6.20	9.75	10.07	85.1	87.9
	Pu30	40	6.73	10.28	10.51	89.7	91.7
	Pu31	20	7.10	10.21	10.49	89.1	91.5
	Pu31	40	7.57	10.12	10.71	88.3	93.4
Denitration	-	12	6.85	9.32	10.30	81.3	89.9
Metal Oxidation-Air	Pu59A	40	8.87	9.05	9.04	79.0	78.9
Metal Oxidation-Steam	Pu59B	40	7.88	9.64	9.09	84.0	79.4

(a)

Pu38
Sintered for 64 Hours

Neg. 891

200X

(b)

Pu9-3
Sintered for 4 Hours

Neg. 32C

400X

(c)

Pu4
Sintered for 1 Hour

Neg. 111

400X

(d)

Pu4
Sintered for 1 Hour

Neg. 106

400X

Figure 1

Microstructures of PuO₂ - Oxalate Derived
Sintered in Nitrogen-6% Hydrogen at 1600°C
Cathodic Vacuum Etched

(a)

78-38-B

Neg. 328

400X

(b)

78-46-A

Neg. 330

400X

(c)

78-38-A

Neg. 331

400X

(d)

17-8-A

Neg. 414

400X

Figure 2

Microstructures of PuO_2 - Hydroxide Derived
Sintered in Nitrogen-6% Hydrogen at 1600°C for 1 Hour
Cathodic Vacuum Etched

has shown that the oxygen vacancy concentration is strictly controlled by composition. The sintering behavior of ThO_2 with Ca^{+2} substitution has been studied⁽¹²⁾, and sintered densities in excess of 98% theoretical were obtained in this manner. With PuO_2 , the cations which were selected along with their associated characteristics are shown in Table IV. Strontium and magnesium were added as the carbonate, yttrium as Y_2O_3 , and calcium as CaF_2 .

The results of sintering trials involving the use of controlled impurity additions are presented in Tables V, VI, and VII. From these data, it is seen that strontium additions have a marked beneficial effect upon the sintering behavior in oxygen while the other additions lead to an equivalent or lower density. Improvement is noted only under oxidizing sintering conditions, as expected, since the formation of oxygen vacancies, as such, could not be expected under reducing conditions. The situation, when a reducing atmosphere is utilized, becomes further complicated by the behavior of the impurity compound and by the formation of trivalent plutonium. The beneficial effect of SrO is illustrated in Figure 3. Both the physical density relationship, percent of theoretical $\text{PuO}_2 + \text{SrO}$ density for the mixture, and the PuO_2 density relationship, 1 percent of theoretical density of PuO_2 , are shown. The physical density of a PuO_2 preparation (Pu29) which sintered to a rather low density (83%), without additives, was increased by 10% with a 1.29 m/o strontium addition. With a more sinterable grade PuO_2 , the percent density increase was smaller but still significant. Microstructure was also observed to be affected by the strontium addition as shown in Figure 4.

The extent and ease of solid solution formation between Y_2O_3 or SrO and PuO_2 can be ascertained from electrical resistivity measurements, the results of which are presented in Figure 5. With an addition of only two mol percent, SrO or Y_2O_3 , the electrical resistivity at room temperature decreased four to six orders of magnitude. In the analogous system of calcium substitution in ZrO_2 ⁽⁷⁾, the resistivity at 1000°C decreased only slightly more than one order of magnitude with 12 mol percent impurity. The similarity in the resistivity relationship for both Sr^{+2} and Y^{+3} in PuO_2 is expected since for an equivalent molar addition of each oxide, the same number of oxygen vacancies are formed. Actual differences in values for a specific impurity level are probably insignificant since that much difference has been observed in the unaltered PuO_2 material.

The empirical results of enhancements of sinterability with concurrent decrease in electrical resistivity as SrO is added to PuO_2 allow one to conjecture about the basic processes.

For example, the controlled strontium addition can enter the PuO_2 fluorite lattice either substitutionally by replacing a plutonium ion at a normal cation site or interstitially by filling in a normal vacant site. The second case involving interstitial cations has not been observed with other impurities in fluorite structured oxides^(8,10,13) and is most likely precluded by the energy relationship to form and maintain such an arrangement. While an increase

Table IV

Properties of Selected Cations

<u>Element</u>	<u>Valence State</u>	<u>Ionic Radius Å</u>	<u>Thermal Neutron Cross-Section Barns</u>	<u>Melting Point of Oxide °C</u>
Pu	+3	1.08	270	2085
Pu	+4	0.93	270	2400
Ca	+2	0.99	0.43	2572
Sr	+2	1.12	1.30	2430
Y	+3	0.92	1.30	2410
Mg	+2	0.67	0.06	2800

Table V

Effect of Various Impurities on SinteringBehavior of PuO₂

(Compacted at 20 TSI)

(Sintered at 1600°C for 1 Hour in O₂)

<u>Composition</u>	<u>Impurity Addition</u>	<u>Impurity Content m/o</u>	<u>Green Density gm/cc</u>	<u>Fired Density gm/cc</u>	<u>Fired Density Percent of Theoretical PuO₂</u>
Pu29 (Hydroxide)	-	0	6.58	9.54	83.2
	SrO	1.29	6.57	10.62	93.4
	CaO	2.37	6.55	8.97	79.6
	MgO	3.27	6.49	9.18	82.0
	CaF ₂	1.71	6.59	9.03	79.8

Table VI

Effect of SrO Additions on Sintering
Behavior of PuO₂
 (Compacted at 40 TSI)
 (Sintered at 1600°C for 1 Hour)

Composition SrO Content in mol/o	Green Density gm/cc	Flowing Oxygen Atmosphere			Nitrogen-6% Hydrogen Atmosphere		
		Fired Density			Fired Density		
		gm/cc	Percent of Theoretical PuO ₂ +SrO Density	Percent of Theoretical PuO ₂ Density	gm/cc	Percent of Theoretical PuO ₂ +SrO Density	Percent of Theoretical PuO ₂ Density
Pu29=0	6.58	9.54	83.2	83.2	10.07	87.9	87.9
Pu29=1.29	6.57	10.62	93.4	92.1	10.23	89.9	88.7
Pu30=0	6.73	10.51	91.7	91.7	10.28	89.7	89.7
Pu30=1.29	6.72	10.95	96.3	95.0	-	-	-
Pu38=0	7.25	10.55	92.1	92.1	9.58	83.6	83.6
Pu38=0.4	7.27	11.06	96.7	96.3	-	-	-
Pu38=0.8	7.24	11.02	96.6	95.8	-	-	-
Pu38=1.29	7.25	10.95	96.3	95.0	10.23	89.9	88.8
Pu38=2.55	7.21	10.70	94.7	92.3	9.27	82.1	80.0
Pu38=3.78	7.03	10.57	94.2	90.7	9.77	87.1	83.8
Pu38=4.97	6.96	10.33	92.7	88.1	9.41	84.5	80.3

Table VII

Effect of Y_2O_3 Additions on Sintering
Behavior of PuO_2
 (Compacted at 40 TSI)
 (Sintered at 1600°C for 1 Hour in O_2)

<u>Composition</u>	<u>Y_2O_3 Content m/o</u>	<u>Green Density gm/cc</u>	<u>Fired Density gm/cc</u>	<u>Fired Density Percent of Theoretical PuO_2</u>	<u>Electrical Resistivity ohm-cm</u>
Pu38 (Oxalate)	0	7.32	10.69	93.3	1.77×10^6
	0.5	7.40	10.69	93.6	1.35×10^4
	1.0	7.31	10.65	93.5	1.29×10^3
	1.5	7.31	10.55	93.0	6.35×10^2
	2.0	7.37	10.43	93.0	3.80×10^2

EFFECT OF SrO ADDITION ON SINTERED PROPERTIES OF PuO₂

(SINTERED AT 1600°C FOR 1 HOUR IN O₂)

Figure 3

EFFECT OF SrO ADDITION ON SINTERED
PROPERTIES OF PuO₂

(SINTERED AT 1600°C FOR 1 HOUR IN O₂)

Figure 3

PuO₂-0.4 M/o SrO

Neg. 852

400X

PuO₂-0.8 M/o SrO

Neg. 857

400X

PuO₂-1.29 M/o SrO

Neg. 862

400X

Figure 4

Microstructures of PuO₂ with SrO Additions
Sintered at 1600°C in Oxygen for 1 Hour
Cathodic Vacuum Etched

ELECTRICAL RESISTIVITY vs IMPURITY CONTENT

FOR SrO AND Y₂O₃ IN PuO₂

(SINTERED AT 1600 °C FOR 1 HOUR IN O₂)

Figure 5

in the lattice density and a decrease in electrical resistivity would be expected in the interstitial model, a mode for increasing sintered density would be difficult to visualize. On the other hand, the substitutional model can be utilized to satisfactorily explain the observed behavior but it in itself could have two configurations. The more logical of these is the formation of oxygen vacancies according to the general formula, $\text{Sr}_x^{+2}\text{Pu}_{1-x}^{+4}\text{O}_{2-x}$. The electrical resistivity would decrease by changes in the conduction mechanism and the sintering behavior would be enhanced by the increased oxygen mobility due to the formation of the oxygen vacancies. One should not assume that the conduction is entirely ionic in nature since there appears to be a considerable difference in the resistivity value for the controlled impurity material, 10^3 ohm-cm for $\text{Sr}_{.02}\text{Pu}_{.98}\text{O}_{1.98}$, as compared to reported⁽¹⁴⁾ values for reduced PuO_2 of 10^5 ohm-cm for $\text{PuO}_{1.72}$ to 10^8 ohm-cm for $\text{PuO}_{1.96}$. If anything, the reduced phases should have a lower resistivity based on the existence of oxygen vacancies and Pu^{+3} species. The other possibility for the substitutional case involves the formation of Pu^{+6} to maintain the electro-neutrality of the lattice, resulting in a general formula such as $\text{Sr}_x^{+2}\text{Pu}_{1-2x}^{+4}\text{Pu}_x^{+6}\text{O}_2$. The higher valence state (+6) for plutonium has been well established in the liquid state but not in solids. The formation of such a mixed valence state would certainly give rise to a decrease in the electrical resistivity but would offer little reason for improvement in sinterability. One particular aspect associated with the sintering behavior which should not be overlooked is the dynamic situation occurring at the sintering temperature between the individual oxides during solid solution formation. Enhanced sintering may or may not be observed with preformed solid solution material. Without more specific knowledge, the most logical explanation for both the decrease in electrical resistivity and the improvement in sinterability with the impurity additions is the substitutional solid solution model with associated formation of oxygen vacancies.

SUMMARY AND CONCLUSIONS

1. Plutonium dioxide, PuO_2 , made via Pu-IV oxalate precipitation and conversion appears to be the most sinterable powder.
2. Higher PuO_2 densities are obtained by sintering under oxidizing conditions. Most of the observed increase over reduction sintering is due to the elimination of lower density suboxides.
3. The microstructure of reduction sintered PuO_2 is quite variable and the texture is more dependent upon the precipitation process than the sintering conditions.
4. Impurity additions of SrO in the range 0.4 to 1.0 mol percent increase the sintered densities by as much as 10%. This is attributed to the formation of a solid solution with PuO_2 in which oxygen vacancies were created. Electrical resistivity data indicate solid solution formation between PuO_2 and both Y_2O_3 and SrO .

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