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Refractory Plutonium Fuel Materials

by

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The plutonium carbides PuC_{1-x} , Pu_2C_3 , $(\text{U}, \text{Pu})\text{C}$, and $(\text{U}, \text{Pu})_2\text{C}_3$ have been prepared as single phase powders and as dense bodies suitable for fuels. Sintering studies on PuO_2 in inert and in oxidizing atmospheres indicate that dense bodies were produced in either case. However, when an inert atmosphere was used, the less dense b.c.c. form of Pu_2O_3 was produced when the sintering temperature was high. Stoichiometric PuN powders were produced by reaction of $\text{PuH}_{0.04}$ with N_2 . Densification by sintering in N_2 at 1600°C was trivial. When PuN was cosintered with PuO_2 in N_2 , the PuO_2 was reduced to hexagonal Pu_2O_3 with liberation of N_2 . The solid solubility of PuO in PuN is approximately 3 percent.

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1. INTRODUCTION

1.1 Refractory plutonium fuels have an increasing importance as plutonium becomes more available from converter and fast breeder reactors. At the present time the fuel composition and form is uncertain. For fast breeder reactor applications the plutonium will be diluted, probably with a corresponding uranium compound as an internal breeder. Alternatively, undiluted plutonium refractories will also have application to special purpose reactors.

1.2 This paper summarizes work done at Los Alamos Scientific Laboratory on refractory plutonium compounds.

2. CARBIDES

2.1 Plutonium Carbides

2.1.1 Four carbides of plutonium are known Pu_3C_2 (ζ), PuC_{1-x} , Pu_2C_3 , and PuC_2 . The zeta carbide decomposes peritectoidally on heating to 575°C , while the dicarbide decomposes to sesquicarbide and carbon on cooling below $\sim 1700^\circ\text{C}$.⁽¹⁾ Thus the compounds of principal interest as fuel materials are the monocarbide and sesquicarbide.

2.1.2 The homogeneity range of hypostoichiometric PuC extends from $\text{PuC}_{0.77}$ to $\text{PuC}_{0.92}$ at $\sim 570^\circ$, and becomes more narrow at lower temperatures. A dilatometric study indicated that the low temperature $\zeta + \text{PuC}_{1-x}/\text{PuC}_{1-x}$ phase boundary is at $\text{PuC}_{0.84}$.⁽²⁾ The composition Pu_2C_3 is nearly single phase, although there is evidence for a homogeneity range that extends down to $\text{PuC}_{1.41-1.46}$ between 610° and 555°C .⁽³⁾

2.1.3 Single phase $\text{PuC}_{0.85}$ was prepared by arc melting electrorefined Pu with spectrographic grade graphite in a helium-argon atmosphere, followed by homogenization at 1300° by heating in vacuum. The material prepared in this manner was free of extraneous carbide phases by x-ray diffraction analysis and by metallographic examination. Attempts to prepare single phase PuC_{1-x} by reduction of PuO_2 and C in vacuo were unsuccessful.⁽⁴⁾

2.1.4 Powder prepared by crushing and screening arc melted PuC_{1-x} to -325 mesh was pressed without binder at 40 t.s.i. to a density of 9.80 g/cc (72%). Sintering for 5 hr. at 1245°C in vacuum resulted in pellet densities of 12.2 g/cc (90%); sintering for 5 hr. at 1500°C resulted in a density of 12.8 g/cc (94%).

2.1.5 Although reaction of PuO_2 with C was unsuitable for preparing PuC_{1-x} , the preparation of Pu_2C_3 by this method is straightforward.⁽⁴⁾ Single-phase sesquicarbide was prepared by reaction-sintering pressed compacts of PuO_2 and C at 1250-1450°C for 6 hr. in vacuum. Single phase sesquicarbide also has been prepared by arc melting electrorefined Pu and spectroscopic grade C directly in a He-Ar atmosphere. Unlike U_2C_3 , the arc-melted product is single phase sesquicarbide having a lattice dimension $a_0 = 8.1269$.

2.1.6 Properties of plutonium carbides are shown in Table I.

2.2 Uranium-plutonium carbides

2.2.1 The monocarbides of uranium and plutonium form a continuous series of solid solutions. For fast neutron breeder reactors, the composition of approximately $(\text{U}_{0.85}\text{Pu}_{0.15})\text{C}$ is of major interest. Solid solutions of UC and PuC were first prepared by direct reaction sintering of UO_2 , PuO_2 and C powders.⁽⁴⁾ The compositions $(\text{U}_{0.7}\text{Pu}_{0.3})\text{C}_{0.95}$, $(\text{U}_{0.8}\text{Pu}_{0.2})\text{C}_{0.95}$ and $(\text{U}_{0.9}\text{Pu}_{0.1})\text{C}_{0.95}$ were prepared by reacting the appropriate oxide mixture with carbon for 6 hr. at 1450°-1650°C in vacuum. This method results in hypostoichiometric single phase material that undoubtedly contains a small amount of (U, Pu)O in solid solution with the (U, Pu)C phase. The composition $(\text{U, Pu})\text{C}_{1.0}$ prepared by reaction of oxide and carbon contained $(\text{U, Pu})_2\text{C}_3$ as an impurity. Pellets having a density that was 94% of theoretical have been prepared from the single phase (U, Pu) $\text{C}_{0.95}$ powders. More recent work indicates that in this composition range, $(\text{U, Pu})\text{C}_{1.0}$ is single phase^(2, 5) in the absence of oxygen.

2.2.2 The U_2C_3 - Pu_2C_3 system also forms a series of solid solutions (Table II). The transformation temperature of U_2C_3 is ~1800°C and arc melted $\text{UC}_{1.5}$ results in a mixture of UC + UC_2 (t). Annealing for prolonged times at 1500°C is required to form U_2C_3 .⁽⁶⁾ In contrast, $(\text{U, Pu})_2\text{C}_3$ compositions that contain 30 percent

Pu_2C_3 or greater are b. c. c. (U, Pu) $_2\text{C}_3$ solid solutions in the arc-melted condition. The compositions shown in Table II were prepared by comelting U_2C_3 and Pu_2C_3 .

2.2.3 Properties of uranium-plutonium carbides are shown in Table I.

3. PLUTONIUM OXIDE

3.1 The known oxides of plutonium are PuO (NaCl-type, $a_0 = 4.948$), hexagonal ("β") Pu_2O_3 ($a = 3.841$, $C = 5.958$), cubic ("α") Pu_2O_3 (b. c. c., $a = 11.04$), and PuO_2 (fluorite-type, $a_0 = 5.3952$). At this time the only oxide of importance is PuO_2 .

3.2 All of the PuO_2 used in this study was prepared by calcining either plutonium(IV) peroxide or plutonium(III) oxalate to constant weight at 950° in air. The high calcination temperature was used to avoid ambiguity in regard to the chemical composition of the PuO_2 . In all cases, the PuO_2 was of very high purity. The oxalate-source PuO_2 was then ball-milled overnight before pressing into pellets. The effect of ball milling on the particle size distribution is shown in Figure 1. Powder prepared from plutonium peroxide was used without milling because the powder was too fine to mill effectively. The mass-median particle size of the peroxide source PuO_2 was 4.6μ ; compared to 18.2μ for the ignited oxalate source powder.

3.3 Pellets were pressed at 20 t. s. i. to 0.407 in. dia by ~ 0.3 in. tall in a unidirectional floating die. This pressing pressure was selected after preliminary tests indicated that higher pressures caused laminations. Addition of 0.5% by wt. of a hydrocarbon binder to the unpressed PuO_2 generally produced unsintered pellets that had densities that were slightly higher than pellets pressed without binder. However, the densities of sintered pellets that contained binder generally were a few percent lower than those pressed without binder. Therefore, all the pellets that were subsequently used in this study were pressed without binder. The pellets were sintered in purified flowing Ar, and in flowing CO_2 .

3.4 Results of sintering milled PuO_2 in Ar are shown in Table III. It is clear that 94 percent dense pellets can be achieved by sintering in Ar at 1450°C ., if milled powder is used. However, unmilled powder results in low density pellets.

3.5 The effect of sintering temperature on pellets pressed from peroxide-source PuO_2 that were sintered in Ar is shown in Figure 2. Apparently there is no benefit in sintering above 1350°C in Ar, where pellets can be sintered to a density of 11.2 g/cc. The maximum point in the curve of Figure 2 is attributable to the two simultaneous processes (1) densification and void elimination and (2) decomposition of PuO_2 to PuO_{2-x} with subsequent formation of the less dense b. c. c. oxide, " $\alpha\text{-Pu}_2\text{O}_3$ ". As shown in Table IV the formation of " $\alpha\text{-Pu}_2\text{O}_3$ " is clearly evident in pellets that have been sintered at temperatures greater than 1250°C in Ar. On the other hand, the decomposition reaction can be eliminated by sintering in an oxidizing atmosphere such as CO_2 .

3.6 Typical microstructures of sintered PuO_2 are shown in Figure 3. The type I structures are single phase PuO_2 or PuO_{2-x} where x is ~ 0.05 , whereas type II structures typify two phase systems that are comprised of the $\text{PuO}_{2-y} - \alpha\text{-Pu}_2\text{O}_3$ eutectoid in a PuO_{2-x} matrix. Oxide that was sintered in Ar always had type II microstructure unless the sintering temperature was below 1350°C . On the other hand, only type I microstructures were obtained in oxide that had been sintered in CO_2 .

4. PLUTONIUM NITRIDE

4.1 Unlike the U-N system, plutonium mononitride is the only compound known in the Pu-N system. The homogeneity range of PuN is apparently limited to near-stoichiometric composition. Congruent melting of PuN has never been observed, even at N_2 pressures as high as 24.5 atm. ⁽⁷⁾

4.2 Plutonium nitride powders were prepared by reaction of N_2 with electro-refined Pu metal, with and without the use of H_2 . As reported by Anselin, H_2 is beneficial.⁽⁸⁾ In a typical preparation, a 50 g. Pu rod was hydrided and dehydrided twice to form metal powder. The second dehydriding was purposely incomplete, which resulted in a powder having the composition $PuH_{0.04}$. After adding dry N_2 to a pressure of 500 mm. Hg, the system was slowly heated and P vs. T data were used to indicate the progress of the reaction. The reaction started at $300^\circ C$ and was completed at 540° . As a final step, the nitride was heated in vacuum at $700^\circ C$, followed by reheating in N_2 at $700^\circ C$. The resulting powder could be ground in dry air with no evidence of the pyrophoricity that is usually experienced with PuN powders. Analysis of the powder was 94.34% Pu, 5.5% N (theor. value is 94.47% Pu, 5.53% Ni).

4.3 The lattice constant for powder samples of PuN prepared in the above manner is 4.9056 ± 0.0002 after grinding in air. This is identical to that previously reported for PuN heated at $1500^\circ C$ under 75 psi N_2 and at $2700^\circ C$ under 250 psi N_2 .⁽⁷⁾

4.4 Although PuN powder prepared in the above manner can be ground in air, the powder readily picks up oxygen. The powder normally contains ~ 300 p.p.m. by wt. oxygen after preparation and sampling in an inert atmosphere. After milling for 16 hr. in an Ar filled jar, the oxygen content was increased to 750 p.p.m. Grinding in air in a mortar and pestle resulted in an oxygen content of ~ 3000 p.p.m. The lattice constant of PuN in the freshly-prepared condition was 4.9048; the lattice constant for PuN ground in air was 4.9054.

4.5 The results of pressing and sintering PuN powders in flowing dry N_2 are shown in Table V. Regardless of powder treatment, densification was poor at temperatures up to $1600^\circ C$. The microstructure shown in Figure 4A also indicates single phase PuN with excessive porosity.

4.6 Porosity in PuN pellets can be reduced markedly by the addition of PuO_2 , as shown in Figure 4B and Table VI. The weight loss measurements and x-ray diffraction analysis of the sintered material indicate that PuN reacts with PuO_2 according to the equation

The difference in nitrogen content found by analysis and that calculated from eq. (1) could result from an accumulated oxygen impurity concentration of ~ 2500 p. p. m.

4.7 Small amounts of PuO_2 have a greater relative effect on density than do larger amounts. Thus the addition of 5% by wt. PuO_2 caused an increase in density of sintered pellets of from 73.7 to 86.8% of theoretical density. A further increase of from 5% to 20% PuO_2 increased the density to 93.5% of theoretical. The microstructure shown in Figure 4B indicates that liquid phase sintering may have occurred.

4.8 The lattice constant of PuN sintered in the presence of oxygen is somewhat greater than that of sintered PuN powder or unsintered PuN. Using a lattice constant of 4.948 Å, for PuO, this would correspond to a solid solubility of PuO in PuN of about 3 percent. This is approximately the same as that reported for the solubility of UO in UN.⁽⁹⁾

4.9 The PuO_2 is reduced to hexagonal Pu_2O_3 with lattice constants $a = 3.841$ and $c = 5.958$. These dimensions correspond to those reported for pure hexagonal Pu_2O_3 .

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Table I

Some Properties of Plutonium Carbides and Uranium-Plutonium Carbides

Composition	Density g/cc	Pu Density g/cc	Melting Pt. °C	Avg. Thermal Exp. ^(a)		Thermal Cond'y, cal/cm-sec	Elect. Resist'y μΩcm	Structure
				$\frac{\Delta L}{L}$	°C ⁻¹ (10 ⁶)			
PuC _{0.87}	13.6	13.0	1650		11.0	0.0155 + 38.5x10 ⁻⁶ (°C)	267	f. c. c. (NaCl-type) a = 4.96
Pu ₂ C ₃	12.7	12.0	2050		...	...	...	b. c. c. (a = 8.126)
(U _{0.8} Pu _{0.2})C	13.3	2.55	~ 2350		11.1 ^(a)	0.0340 + 20.0x10 ⁻⁶ (°C)	82	f. c. c.
(U, Pu) ₂ C ₃	...	(variable)	...		...	...	...	b. c. c.

(a) Composition (U_{0.87}Pu_{0.13})C

Table II

Lattice Parameters in the U_2C_3 - Pu_2C_3 System

Composition	Heat Treatment	Lattice Constant M_2C_3 Phase	Other Phases (traces)
U_2C_3	35 hr. 1500°C.	8.0880	MC(a = 4.960)
$(U_{0.94}Pu_{0.09})C_{1.47}$	arc cast	8.114	MC(a = 4.960
" " "	24 hr. 1700°	8.0902	MC(a = 4.956)
$(U_{0.74}Pu_{0.26})C_{1.50}$	arc cast	8.0943	none
" " "	24 hr. 1700°	8.0940	none
$(U_{0.52}Pu_{0.49})C_{1.45}$	arc cast	8.0962	none
" " "	24 hr. 1700°	8.0995	none
$(U_{0.33}Pu_{0.69})C_{1.40}$	arc cast	8.1061	none
" " "	24 hr. 1700°	8.1083	none
Pu_2C_3	arc cast	8.1258 ^(a)	none

(a) All lattice constants in this paper have been corrected for self-radiation damage, when applicable.

Table III

Densification of Ball Milled PuO_2 Powder
(Pressed at 20 t.s.i, Sintered 6 hr. in Ar)

Sintering Temp., °C	Milling Time, hr.	Pellet Densities, g/cc (%Theor.)	
		Unsintered	Sintered
1450	0	6.94 (61)	9.16 (80)
1450	16	7.58 (66)	10.8 (94)
1650	0	6.94 (61)	10.0 (a)
1650	16	7.58 (66)	10.8 (a)

(a) Pellets not single phase.

Table IV

Effect of Sintering Conditions on Composition of PuO_2 Pellets

(Pressed at 20 t. s. i, Sintered for 6 hr.)

Temp. °C	Atmosphere	Microstructure	X-ray Powder Diffraction (lattice parameter)
1150	Ar	Type I	...
1250	Ar	Type I	PuO_2
1350	Ar	Type II	...
1450	Ar	Type II	$\left\{ \begin{array}{l} \text{PuO}_2 \text{ (5.3969)} \\ \alpha \text{ Pu}_2\text{O}_3 \end{array} \right.$
1650	Ar	Type II	$\left\{ \begin{array}{l} \text{PuO}_2 \text{ (5.3972)} \\ \alpha\text{-Pu}_2\text{O}_3 \text{ (11.04)} \end{array} \right.$
1450	CO_2	Type I	PuO_2
1650	CO_2	Type I	$\text{PuO}_2 \text{ (5.3953)}$

Table V

Pressing and Sintering of PuN in 580 mm. Hg N₂

Milling Time, hr.	Pressing Pressure t. s. i	Pellet Densities, g/cc (% Theor.)		Sintering Conditions
		unsintered	sintered	
0	60	10.34 (72.6)	10.45 (73.4)	3 hr. at 1250°C
0	80	10.68 (75.0)	10.94 (76.8)	3 hr. at 1450°C
0	80	10.65 (74.8)	11.05 (77.6)	3 hr. at 1560°
0	80	10.61 (74.5)	11.14 (78.2)	6 hr. at 1650°
16	20	8.90 (62.5)	9.34 (65.6)	12 hr. at 1600°
16	50	9.84 (69.1)	10.35 (72.7)	12 hr. at 1600°
16	80	10.22 (71.8)	10.58 (74.3)	12 hr. at 1600°

Table VI
Effect of Co-Sintering PuN with PuO₂ in N₂
(3 hr. at 1600°C)

PuO ₂ added w/o	Pellet Density, g/cc (% Theor.)		% Wt. Loss,		% N in Sintered Pellet		Lattice Constant of PuN
	unsintered	sintered	by eq. (1)	actual	by eq. (1)	analysis	
0	10.10(70.9) ^a	10.49 (73.7) ^b	0.00	0.07	5.53	5.34	4.9048 ± 0.0001
5	10.07(71.5)	12.17 (86.8)	0.09	0.24	...	...	...
20	9.90(73.3)	12.53 (93.5)	0.34	0.48	4.09	3.96	4.9061 ± 0.0002
27.5	9.82(73.5)	12.60 (96.2)	0.47	0.60	3.55	3.37	4.9064 ± 0.0002
40	9.52(73.3)	12.27 (97.0)	0.68	0.75	2.65	2.54	4.9060 ± 0.0006
50	9.14(72.8)	11.92 (98.1)	0.86	1.03	...	...	

Notes:

(a) Based on PuN + PuO₂

(b) Based on PuN + hexagonal Pu₂O₃

Figure 1. The Effect of Ball Milling on Particle Size of Oxalate-Source PuO_2

THE EFFECT OF BALLMILLING ON THE PARTICLE SIZE
DISTRIBUTION OF LOT P-13 PuO_2

Figure 2. Density of Sintered PuO_2 as Function of Sintering Temperature.
(Peroxide-source PuO_2 pressed at 20 t.s.i, 6 hr. at temperature.
Theoretical density = 11.46 g/cc)

Type I Microstructure, 500X
Sintered 6 hr. 1650°C. in CO₂

Type II Microstructure, 500X
Sintered 6 hr. 1650°C in Ar

Figure 3. Microstructures of PuO₂.

4A

4A. Sintered PuN, 365X
12 hr. 1600°C in N₂

as polished

4B

4B Sintered PuN-40 w/o PuO₂, 365X
3 hr. 1600°C in N₂

Figure 4. Microstructures of PuN.