

## Carbon – Palladium – Plutonium

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### Introduction

For an understanding of the chemical constitution of an irradiation carbide nuclear fuel, a knowledge of the phase relationships of the individual fission product elements with the C-Pu system is required. The list of elements in the fission products includes palladium, and thus there is the interest in studying the C-Pd-Pu system. Experimental studies of this system are restricted to two works only. [1970Hai] performed constitutional studies in U and Pu carbide fission product systems including C-Pd-Pu. [1975Hol] presented an isothermal section for 1200°C based on the experimental results of [1970Hai] and common similarities in the phase equilibria observed in the actinide-platinum group metal-carbon systems. The  $\text{PuC}_2$  carbide in the accepted C-Pu phase diagram decomposes eutectoidally at 1700°C, and therefore, does not take part in phase equilibria at 1200°C [1975Hol]. The absence of a two-phase region between  $\text{PuC}_2$  and  $\text{PuPd}_3$  was experimentally confirmed by [1982Hol]. The isothermal section at 1200°C published in [1977Hol, 1984Hol1, 1984Hol2] is the same as that published in [1975Hol, 1982Hol]. The compositions of alloys, as well as the experimental techniques used to study the C-Pd-Pu system are presented in Table 1.

### Binary Systems

The C-Pd binary system is accepted from [Mas2]. The C-Pu system is accepted from [1969Lea] because the C-Pu phase diagram presented by [Mas2], with reference to [1970Gre], shows a polymorphic transformation of  $\text{PuC}_2$  at 1660°C and the presence of  $\text{PuC}_2$  at room temperature as an equilibrium low-temperature modification. Actually, [1970Gre] showed that low-temperature  $\text{PuC}_2$  is a metastable phase. In the accepted C-Pu phase diagram,  $\text{PuC}_2$  decomposes eutectoidally to  $\text{Pu}_2\text{C}_3$  and carbon at 1660°C. The main discrepancies are concerned with the Pd-Pu system. The Pd-Pu system presented by [Mas2] was redrawn from [1967Kut]. [1967Kut] reported the presence of four compounds in this system:  $\text{Pu}_5\text{Pd}_4$ ,  $\text{PuPd}$ ,  $\text{Pu}_4\text{Pd}_5$  and  $\text{PuPd}_3$ . Their crystal structures were not identified. Later, [1975Cro, 1973Cro, 1976Cro] reported the crystal structures of  $\text{PuPd}$ ,  $\text{Pu}_3\text{Pd}_4$  and  $\text{Pu}_3\text{Pd}_5$ . The stoichiometry of the  $\text{Pu}_3\text{Pd}_4$  and  $\text{Pu}_3\text{Pd}_5$  compounds is different from that reported by [1967Kut]. Hence, the experimental information available is not enough to provide a well defined Pd-Pu system. This uncertainty is not critical in this case because the isothermal section presented by [1982Hol] was constructed for 1200°C, which is higher than the temperature of formation of the intermetallic compounds in the Pd-Pu system apart from  $\text{PuPd}_3$ .

### Solid Phases

No ternary compounds have been found in the C-Pd-Pu system. Some discrepancies in the literature are concerned with the temperature interval over which the  $\text{PuC}_2$  carbide is stable. Room temperature X-ray powder diffraction analysis of  $\text{PuC}_2$  samples quenched from above the transition temperature indicated that this compound is isostructural with tetragonal  $\text{UC}_2$  [1965Cha]. The high-temperature X-ray diffraction studies have indicated that the equilibrium high-temperature structure is cubic [1970Gre]. As it was shown by [1970Gre], substantial amounts of bct  $\text{PuC}_2$  were obtained by quenching from the fcc  $\text{PuC}_2$  + graphite field at approximately  $500 \text{ K}\cdot\text{s}^{-1}$ . It was assumed, that this species was metastable in the C-Pu system and was formed by a diffusionless transformation where the cubic dicarbide is quenched fast enough to kinetically inhibit decomposition. When cooling rates were reduced to approximately  $10 \text{ K}\cdot\text{s}^{-1}$ , no bct  $\text{PuC}_2$  was observed in the quenched samples; however substantial amounts of a material of unknown structure were present. [1970Gre] proposed that this phase was also a kinetically trapped metastable phase, possibly resulting from a massive transformation. The structural data of the unary and binary phases are given in Table 2.

### Isothermal Sections

The isothermal section at 1200°C constructed by [1982Hol] is presented in Fig. 1. As was mentioned earlier, [1975Hol, 1982Hol] accepted the C–Pu phase diagram in which  $\text{PuC}_2$  decomposes eutectoidally at ~1700°C.

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**Table 1:** Investigations of the C-Pd-Pu Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1970Hai]	X-ray diffraction, electron micro-probe analysis, ceramographic analysis	annealed at 800°C for 260 h and at 1000°C for 72 h, Pu <sub>2</sub> PdC <sub>2</sub> , PuC+Pu <sub>2</sub> C <sub>3</sub> +PuPd <sub>3</sub>
[1982Hol]	Optical light microscopy, X-ray diffraction, electron micro-probe analysis	annealed at 1200°C for 40 h, 20 at.% Pu-60 at.% Pd-20 at.% C, PuC <sub>1-x</sub> +Pu <sub>2</sub> C <sub>3</sub> +PuPd <sub>3</sub>

**Table 2:** Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(C) ≤ 3827 (S.P.)	<i>hP4</i> <i>P6<sub>3</sub>/mmc</i> C (graphite)	<i>a</i> = 246.12 <i>c</i> = 670.90	at 25°C [Mas2]
(Pd) < 1555	<i>cF4</i> <i>Fm<math>\bar{3}</math>m</i> Cu	<i>a</i> = 389.03	at 25°C [Mas2]
(εPu) 640 - 483	<i>cI2</i> <i>Im<math>\bar{3}</math>m</i> W	<i>a</i> = 363.43	[Mas2]
(δ'Pu) 483 - 463	<i>tI2</i> <i>I4/mmm</i> In	<i>a</i> = 332.61 <i>c</i> = 446.30	[Mas2]
(δPu) 463 - 320	<i>cF4</i> <i>Fm<math>\bar{3}</math>m</i> Cu	<i>a</i> = 463.71	[Mas2]
(γPu) 320 - 215	<i>oF8</i> <i>Fddd</i> γPu	<i>a</i> = 315.87 <i>b</i> = 576.82 <i>c</i> = 1016.2	[Mas2]
(βPu) 215 - 125	<i>mC34</i> <i>C2/m</i> βPu	<i>a</i> = 1183 <i>b</i> = 1045 <i>c</i> = 923 β = 138.7°	[V-C2]
		<i>a</i> = 928.4 <i>c</i> = 1046.3 <i>b</i> = 785.9 β = 92.13°	[Mas2]
(αPu) < 125	<i>mP16</i> <i>P2<sub>1</sub>/m</i> αPu	<i>a</i> = 618.3 <i>b</i> = 482.2 <i>c</i> = 1096.3 β = 101.97°	[Mas2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
Pu <sub>3</sub> C <sub>2</sub> < 575	-	-	[Mas2]
PuC < 1654	<i>cF8</i> <i>Fm<math>\bar{3}m</math></i> NaCl	<i>a</i> = 497.2	[1975Hai]
Pu <sub>2</sub> C <sub>3</sub> < 2050	<i>cI40</i> <i>I<math>\bar{4}3d</math></i> Pu <sub>2</sub> C <sub>3</sub>	<i>a</i> = 813.13	[1969Lea]
βPuC <sub>2</sub> ~2230 - 1660	<i>c**</i>	<i>a</i> = 569.0	[1970Gre]
αPuC <sub>2</sub> < 1660	<i>tI6</i> <i>I4/mmm</i> CaC <sub>2</sub>	<i>a</i> = 363 <i>c</i> = 609.4	[1965Cha] metastable [1970Gre]
Pu <sub>5</sub> Pd <sub>4</sub>	-	-	[Mas2]
PuPd 1150 - 950	<i>oP8</i> <i>Pnma</i> FeB	<i>a</i> = 703.6 <i>b</i> = 455.0 <i>c</i> = 566.3	[1975Cro]
Pu <sub>3</sub> Pd <sub>4</sub>	<i>hR42</i> <i>R<math>\bar{3}</math></i> Pu <sub>3</sub> Pd <sub>4</sub>	<i>a</i> = 1334.4 <i>c</i> = 574.4	[1973Cro]
Pu <sub>3</sub> Pd <sub>5</sub>	<i>oC32</i> <i>Cmcm</i> Pu <sub>3</sub> Pd <sub>5</sub>	<i>a</i> = 920.1 <i>b</i> = 715.9 <i>c</i> = 977.1	[1976Cro]
PuPd <sub>3</sub>	<i>cP4</i> <i>Pm<math>\bar{3}m</math></i> AuCu <sub>3</sub>	<i>a</i> = 410.2	[1970Hai]

**Fig. 1: C-Pd-Pu.**  
Isothermal section at  
1200°C

