Carbon – Plutonium – Zirconium

Kostyantyn Korniyenko

Introduction

From the 1960s, the development of new plutonium compounds for high specific power, high burn-up applications have been of great interest. And so, mixtures of PuC and refractory carbides, in particular, ZrC became the focus of research. The study of phase relationships in the corresponding multicomponent systems has created a theoretical basis for scientific research in this area. Experimental work relating to the C-Pu-Zr ternary system was carried out by Burnham *et al.* [1964Bur], Haines and Potter [1970Hai] and by Benedict [1978Ben]. The results were reviewed by Holleck [1975Hol, 1984Hol1, 1984Hol2] who presented an isothermal section. The experimental methods used by the above, along with the temperature and composition ranges studied are shown in Table 1. However, the information relating to phase equilibria in the C-Pu-Zr system is at present incomplete being represented only via solid-state phase relationships along the PuC-ZrC section. Thus, future investigations should be concentrated on studies of crystallization paths and the precise determination of compositions of the phases taking part in equilibria with respect to temperature. The new knowledge will provide a basis for the search of new practical applications of carbon-plutonium-zirconium alloys.

Binary Systems

The C-Pu and C-Zr systems are accepted from [Mas2]. The Pu-Zr system is accepted from [1993Oka].

Solid Phases

No ternary phases have been reported. Crystallographic data relating to the known unary and binary phases are presented in Table 2. The μ, PuC and ρ, ZrC phases possess the same type of crystal structure but are distinguished by their paths of crystallization (the ρ phase crystallizes congruently from the melt but the μ phase forms by a peritectic reaction) and do not form a continuous series of solid solutions. The solubility of the μ phase in the ρ phase at 1500°C was studied by [1964Bur]. Later, [1970Hai] reported a solubility of about 4 mol% ZrC in PuC that was derived from the measured lattice parameter for the μ phase in an arc-melted C-Pu-Zr sample, assuming the validity of Vegard's law between PuC and ZrC. The sample contained the μ, ρ and θ phases. The solubility of the ρ phase in the μ phase at 1400°C as well as equilibria between them at 1500°C were investigated by [1978Ben].

Isothermal Sections

A schematic isothermal section for the whole range of compositions at 1250°C was presented by [1970Hai]. The solubility of zirconium in the μ phase was reported to be about 2 at.%. The solubility of Pu in the ρ phase was not shown since it was found to decrease during annealing. The constitution of this section does not seem to be reliable because the investigation was carried out only for two alloys of different composition. The isothermal section presented by [1970Hai] contains a mistake - in the binary Zr-Pu system, the equilibrium L + (βZr,εPu) is missing. The author also carried out the annealing treatments at 1650°C and 1800°C for short periods (30 min and 5 h, respectively) as well as annealing at 1450°C for 288 h. Holleck [1975Hol] has presented an estimated isothermal section of the C-Pu-Zr system for a temperature of 1600°C. The mutual solubilities of the μ and ρ phases are about 1-2 at.% of Pu or Zr. Later, the same author [1984Hol1, 1984Hol2] published an isothermal section compiled using the results of [1978Ben]. However, the declared temperature of 1600°C in [1975Hol, 1984Hol1, 1984Hol2] was erroneous as the data of [1978Ben] actually correspond to 1500°C. Figure 1 shows the isothermal section at 1500°C constructed on the basis of accepted binary systems and the data of [1978Ben]. The character of the phase equilibria involving the αPuC_2 phase, as well as the positions of three-phase regions need to be confirmed.

Temperature – Composition Sections

The partial vertical section ZrC-$Pu_{53.8}C_{46.2}$, which shows the experimentally determined melting points of arc melted and annealed ZrC-$Pu_{53.8}C_{46.2}$ mixtures was presented by [1964Bur]. Investigations were carried out using a tungsten V-ribbon furnace. This section needs further experimental investigation.

Notes on Materials Properties and Applications

Uranium-plutonium mixed carbide is a possible fuel for future use in fast breeder reactors. However, the properties of the fuel will be strongly affected by the dissolution of Zr which is produced in large amounts among the solid fission products during irradiation [1978Ben]. Hence, it is desirable to know the effect of Zr that is dissolved in the mixed carbide on the thermal conductivity in order to evaluate heat conduction within the fuel. Experimental studies have demonstrated that thermal conductivity decreases with ZrC content in the solid solutions. It was found from electrical resistivity measurements that the decrease was caused mainly by a decrease in the electronic heat conduction.
Arai *et al.* [1989Ara] studied the thermal conductivity of near-stoichiometric (U,Pu,Zr)C solid solutions containing ZrC up to 10 mol% in the temperature range 407-1327°C by a laser flash method.

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

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1964Bur]	Arc melting, annealing, X-ray studies, melting points measurements	1500°C, the $Pu_{53.8}C_{46.2}$-ZrC section
[1970Hai]	Arc melting, X-ray studies	The PuC_{1-x}-ZrC section
[1978Ben]	Arc melting, sintering of pressed pellets, X-ray diffraction, EMPA, chemical analysis	1400°C, 1500°C, the PuC_{1-x}-ZrC section

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(C) (I) < 3827 ± 50 (sublimation point), 1.013 bar	*hP*4 $P6_3/mmc$ C (graphite)	a = 246.12 c = 670.9	at 25°C [Mas2]
(C) (II) > 60.78 bar	*cF*8 $Fd\bar{3}m$ C (diamond)	a = 356.69	at 25°C [Mas2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(ηPu) (h_5) 640 - 483	*cI*2 *Im*$\bar{3}$*m* W	*a* = 363.43	[Mas2]
(εPu) (h_4) 483 - 463	*tI*2 *I*4/*mmm* In	*a* = 332.61 *c* = 446.30	labelled as "(δ'Pu)" [Mas2]
$Pu_{1-x-y}Zr_xC_y$			*y* = 0, *x* = 0 to 1 [1993Oka]
(δPu) (h_3) 463 - 320	*cF*4 *Fm*$\bar{3}$*m* Cu	*a* = 463.71	[Mas2]
(γPu) (h_2) 320 - 215	*oF*8 *Fddd* γPu	*a* = 315.87 *b* = 576.82 *c* = 1016.2	[Mas2]
(βPu) (h_1) 215 - 125	*mC*34 *C*2/*m* βPu	*a* = 928.4 *b* = 1046.3 *c* = 785.9 β = 92.13°	[Mas2]
(αPu) (r) < 125	*mP*16 $P2_1/m$ αPu	*a* = 618.3 *b* = 482.2 *c* = 1096.3 β = 101.97°	at 25°C [Mas2]
(βZr) (h) 1855 - 863	*cI*2 *Im*$\bar{3}$*m* W	*a* = 360.90	pure Zr, *T* > 882°C [Mas2]
$Pu_xZr_{1-x-y}C_y$			*y* = 0, *x* = 0 to 1 [1993Oka]
(αZr) (r) < 863	*hP*2 $P6_3/mmc$ Mg	*a* = 323.16 *c* = 514.75	pure Zr, *T* = 25°C [Mas2]
(ωZr) (hp)	*hP*3 *P*6/*mmm* ωTi	*a* = 503.6 *c* = 310.9	metastable pure Zr, *T* = 25°C [Mas2] high pressure
ν, Pu_4Zr < 345	*tP*80 *P*4/*ncc*	 *a* = 1039 *b* = 1044 *c* = 1118	~ 10 to ~ 30 at.% Zr [V-C2] labelled as "Pu_6Zr" [1959Boc]
κ, $PuZr_3$ < 380(?)	*hP*3 *P*6/*mmm* AlB_2	*a* = 505.5 *c* = 312.3 *a* = 506.0 *c* = 311.9	74 at.% Zr [V-C2] [E] labelled as "$PuZr_2$" [1959Boc]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
λ, Pu_3C_2 ≲ 575			40 at.% C [Mas2]
μ, PuC ≲ 1654	*cF*8 $Fm\bar{3}m$ NaCl		~ 45 to ~ 48 at.% C [V-C2] sometimes labelled as "PuC_{1-x}"
		a = 495.82 to 497.37	[E]
		a = 495.57	in the alloy $Pu_{62.5}C_{37.5}$ annealed and quenched from T = 570°C [S]
		a = 497.21	in the alloy $Pu_{52.5}C_{47.5}$ annealed and quenched from T = 1500°C [S]
		a = 496.6	[1959Boc]
		a = 495.0 to 497.38	in alloys with 38 to 49 at.% C annealed at T = 1500°C [1964Bur]
		a = 496.96	[1978Ben]
$(Pu_{1-x}Zr_x)C$			x = 0 to 0.04, arc melted sample [1970Hai]
			x = 0 to 0.23, T = 1500°C [1978Ben]
			x = 0 to 0.2, T = 1400°C [1978Ben]
		a = 496.19	x = 0, arc melted [1978Ben]
		a = 496.3	x = 0.25, arc melted [1970Hai]
		a = 496.7	in the alloy $Pu_{0.75}Zr_{0.25}C$ annealed for 288 h at T = 1250°C in vacuum, together with the θ and ρ phases [1970Hai]
		a = 491.33 to 494.37	in the alloys $Pu_{0.4}Zr_{0.6}C$ to $Pu_{0.8}Zr_{0.2}C$ sintered for 4 h at T = 1400°C in vacuum, together with the ρ phase [1978Ben]
		a = 491.05	x = 0.23, in the $Pu_{0.4}Zr_{0.6}C$ alloy sintered for 4 h at T = 1500°C in argon, together with the ρ and θ phases [1978Ben]
		a = 491.23	x = 0.165, in the alloy $Pu_{0.8}Zr_{0.2}C$ annealed for 70 h at T = 1500°C in argon, together with the ρ and θ phases [1978Ben]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
θ, Pu_2C_3	*cI*40		~ 59 to ~ 60 at.% C
≲ 2050	$I\bar{4}3d$		[V-C2]
	Pu_2C_3	a = 812.58 to 813.17	[E]
		a = 814.5	[H]
		a = 812.10	in the alloy $Pu_{44.3}C_{55.7}$ [1963Kru]
		a = 812.56	in the alloy $Pu_{40.4}C_{59.6}$ [1963Kru]
		a = 812.56 to 813.30	[1978Kot]
		a = 812.8	in the alloys $Pu_{0.75}Zr_{0.25}C$ and $Pu_{0.25}Zr_{0.75}C$ annealed for 288 h at T = 1250°C in vacuum, together with the μ and ρ phases or with (C) and the ρ phase, respectively [1970Hai]
		a = 813.0	in the alloy $Pu_{0.75}Zr_{0.25}C$ annealed for 30 min at T = 1650°C in vacuum, together with liquid and the ρ phase [1970Hai]
		a = 813.0	in the alloy $Pu_{0.25}Zr_{0.75}C$ annealed for 5 h at T = 1800°C in vacuum, together with (C) and the ρ phase [1970Hai]
βPuC$_2$ (h)	*c***		66.7 at.% C [V-C2]
> 1660			
αPuC$_2$ (r)	*tI*6		66.7 at.% C [V-C2]
< 1660	*I*4/*mmm*	a = 363 to 362	[1978Kot]
	CaC_2	c = 604 to 610.5	
		a = 363	[1987Ben]
		c = 609.4	

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
ρ, ZrC	*cF*8		33 to 50 at.% C [Mas2]
3540 - (< 500)	$Fm\bar{3}m$		sometimes labelled as "ZrC_{1-x}"
	NaCl	a = 458.2 to 468.3	[E]
		a = 469.5	at 50 at.% C [E]
		a = 468.4 to 469.2	[1962Bit]
		a = 469.41	in the alloy $Zr_{61.5}C_{38.5}$ [1965Sar]
		a = 469.83	in the alloy $Zr_{51}C_{49}$ [1965Sar]
		a = 469.34 to 470.14	[1968Nic]
		a = 469.7	[1978Ben]
		a = 471.5	in the $Pu_{0.75}Zr_{0.25}C$ arc melted alloy together with the μ and θ phases [1970Hai]
		a = 471.0	in the alloy $Pu_{0.75}Zr_{0.25}C$ annealed for 288 h at T = 1250°C in vacuum, together with the μ and θ phases [1970Hai]
		a = 471.3	in the alloy $Pu_{0.75}Zr_{0.25}C$ annealed for 30 min at T = 1650°C in vacuum, together with liquid and the θ phase [1970Hai]
		a = 470.0	in the $Pu_{0.25}Zr_{0.75}C$ arc melted alloy together with (C) and the θ phase [1970Hai]
		a = 470.1	in the alloy $Pu_{0.25}Zr_{0.75}C$ annealed for 288 h at T = 1450°C or during 5 h at T = 1800°C in vacuum, together with (C) and the θ phase [1970Hai]
$(Pu_xZr_{1-x})C$			x = 0 to 0.24, T = 1500°C [1978Ben]
		a = 474.45	x = 0.21, in the $Pu_{0.6}Zr_{0.4}C$ alloy annealed for 40 h at T = 1500°C and cooled under vacuum [1978Ben]
		a = 470.34	x = 0.03, in the $Pu_{0.4}Zr_{0.6}C$ arc-melted alloy annealed for 4 h at T = 1400°C [1978Ben]
ρ' (Zr-C)	*t***		metastable
≲ 1100		a = 663	39 to 43 at.% C [1979Kha]
		c = 1626	
		a = 663.8	in the crystalline fragment isolated from
		c = 1626.1	the alloy $Zr_{59.3}C_{40.7}$ consequently annealed from 1600°C to 300°C for 1000 h [1983Arb]

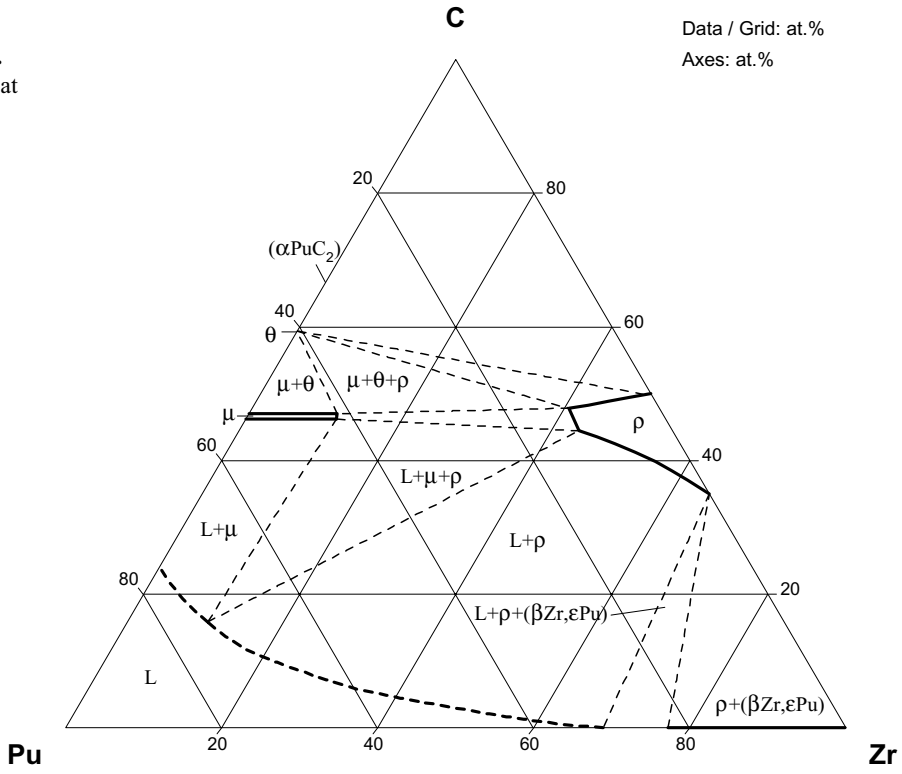

Fig. 1: C-Pu-Zr. Isothermal section at 1500°C