

Carbon – Iron – Plutonium

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Introduction

Phase equilibria in the system were studied in the only work [1963Nic] to provide background to studies of compatibility between carbides and steel canning materials as well as metal bonded cermets. Pu used was of 99.7 mass% purity, and C and Fe were spectrally pure. The system was studied only in the region $\text{PuC-Pu}_2\text{C}_3\text{-Fe}_3\text{C-FePu}_2$. Two ternary phases were found: PuFeC_2 (τ_1) and a phase with an approximate stoichiometry $\text{Pu}_3\text{Fe}_4\text{C}_5$ (τ_2). Authors also acknowledged earlier unpublished investigation, results of which were incorporated basing on private communication from the authors of this work.

The crystal structures of both ternary phases are known. For the τ_1 phase [1986Ger] showed it to be isotypic with UCoC_2 whose structure was established in this work using single-crystal X-ray study. For the τ_2 phase [1995Wac] found perfect agreement between X-ray pictures, calculated by the latter author basing on $\text{Th}_{11}\text{Ru}_{12}\text{C}_{18}$ structure type and presented in [1963Nic]. Based on that, he ascribed to the τ_2 phase this structural type and the composition $\text{Pu}_{11}\text{Fe}_{12}\text{C}_{18}$.

Thermodynamic data were obtained for τ_1 phase by [1983Suz] using Knudsen mass spectrometry. They determined the Gibbs energy of formation of this phase at 1147 to 1377°C. In addition, the temperature of the peritectic formation of PuFeC_2 was refined.

The results of [1963Nic] were slightly modified in the review article [1984Hol1] and in the reference book [1984Hol2].

An overview of experimental investigation of the system is given in Table 1.

Binary Systems

All the three binary systems are taken from [Mas2].

Solid Phases

The structure of the PuFeC_2 (τ_1) phase was determined by [1986Ger] to be of UCoC_2 type. It is isotypic with UFeC_2 and a number of other ternary carbides of actinoids and transition metals.

The temperature of peritectic formation of PuFeC_2 is accepted to be 1377°C after [1983Suz], as thermodynamic measurements are usually considered to be closer to equilibrium state.

The composition $\text{Pu}_{11}\text{Fe}_{12}\text{C}_{18}$, suggested by [1995Wac] based on the stoichiometry of the prototype, is accepted in the present evaluation, because real composition of this phase seems not to be determined by [1963Nic] with high precision. However it might be mentioned that a sample C-33Fe-25Pu (at.%), as claimed in the “Discussion” part of [1963Nic], was “almost single-phase” after annealing at 1160°C for 90 h.

The lattice spacing of (Fe) in three-phase sample was found to be essentially identical to that of pure iron, indicating absence of Pu solubility [1963Nic]. The authors also claimed that no marked line shifts were observed on X-ray patterns indicating absence of significant solubilities in solid phases.

Crystallographic data of all phases stable in the studied region of the C-Fe-Pu system are given in Table 2.

Invariant Equilibria

The temperatures of invariant reactions were determined by [1963Nic], based on thermal analysis of about 20 samples (including those studied in previous unpublished work). Data exist only for the region with the Fe content >50 at.%. As noted by the authors, the compositions of liquid in invariant reactions are “rather uncertain”. This seems to be especially true for the reactions of peritectic formation of both ternary carbides, where compositions of liquid, given only in figures, seem to be estimated by extrapolation of liquidus isotherms.

The data for invariant equilibria occurring in the studied region are given in Table 3. The compositions of liquid are taken by the present author from figures.

The temperature of the U_2 reaction is accepted from the “Discussion” part in [1963Nic] (written contribution of one of the authors).

In addition to equilibria listed in Table 3, [1963Nic] mentioned quasibinary eutectic $1 \rightleftharpoons PuFeC_2 + Fe_3C$ which occurs at 1096°C. As Fe_3C is not stable in the C-Fe system, this reaction can not occur in the stable system C-Fe-Pu, though it may belong to a metastable system Fe_3C -Fe-Pu.

Liquidus, Solidus and Solvus Surfaces

Figure 1 presents a tentative partial liquidus contours after [1963Nic]. The equilibria with the participation of the Fe_3C phase are rejected because this phase is not stable in the C-Fe binary system and no Pu solubility, which in principle could stabilize it, was observed. Also rejected are very uncertain connections of the studied part of the system with the C-Pu edge.

Liquidus lines in Fig. 1 were somewhat corrected to bring them into agreement with the accepted binaries.

Isothermal Sections

Figure 2 presents isothermal section for room temperature, accepted from [1963Nic] after removing a metastable phase Fe_3C and tentative addition of a tie line $PuFeC_2$ - PuT_2 . These changes made it essentially identical with a version, suggested in [1984Hol1, 1984Hol2], though the latter author arbitrarily ascribed it to 1000°C. For simplicity a small homogeneity range of the $PuC_{0.92}$ phase is not shown.

A number of “isothermal sections” at temperatures of invariant reactions, suggested by [1963Nic], are not presented here, as those seem to be nothing more than separate liquidus contours from a figure, corresponding to our Fig. 1.

Thermodynamics

$PuFeC_2$ phase was studied [1983Suz] by Knudsen mass spectrometry of vaporization which was accepted to occur by reaction $PuFeC_2(s) \rightleftharpoons 1/2Pu_2C_3(s) + C(gr) + Fe(g)$. The Gibbs energy of formation of $PuFeC_2$, obtained by these authors, is presented in Table 4.

References

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

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1963Nic]	Metallography, thermal analysis and XRD	“room temperature” to app. 1350°C; composition region PuC-Pu ₂ C ₃ -Fe ₃ C-FePu ₂
[1983Suz]	Knudsen mass spectrometry	1147 to 1580°C, PuFeC ₂ (τ_1) phase; samples contained excess C, solid to 1397°C
[1986Ger]	Single crystal X-ray crystal structure study	τ_1 phase (PuFeC ₂)
[1995Wac]	Interpretation of X-ray diffraction data of [1963Nic]	τ_2 phase (Pu ₁₁ Fe ₁₂ C ₁₈)

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(C) (graphite) < 3827	<i>hP4</i> <i>P6₃/mmc</i> C (graphite)	<i>a</i> = 246.12 <i>c</i> = 670.90	at 25°C [Mas2] sublimation point
(δ Fe) 1538 - 1394	<i>cI2</i> <i>Im$\bar{3}m$</i> W	<i>a</i> = 293.15	[Mas2]
(γ Fe) < 1394 - 912	<i>cF4</i> <i>Fm$\bar{3}m$</i> Cu	<i>a</i> = 364.67	at 915°C [V-C2, Mas2]
(α Fe) < 912	<i>cI2</i> <i>Im$\bar{3}m$</i> W	<i>a</i> = 286.65	at 25°C [Mas2]
(ϵ Pu) 640 - 483	<i>cI2</i> <i>Im$\bar{3}m$</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]
(δ Pu) 463 - 320	<i>cF4</i> <i>Fm$\bar{3}m$</i> Cu	<i>a</i> = 463.71	[Mas2]
(γ Pu) 320 - 215	<i>oF8</i> <i>Fddd</i> γ Pu	<i>a</i> = 315.87 <i>b</i> = 576.82 <i>c</i> = 1016.2	[Mas2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(βPu) 215 - 125	<i>mC34</i> <i>C2/m</i> βPu	$a = 1183$ $b = 1045$ $c = 923$ $\beta = 138.7^\circ$	[V-C2]
		$a = 928.4$ $b = 1046.3$ $c = 785.9$ $\beta = 92.13^\circ$	[Mas2]
(αPu) < 125	<i>mP16</i> <i>P2₁/m</i> αPu	$a = 618.3$ $b = 482.2$ $c = 1096.3$ $\beta = 101.97^\circ$	[Mas2]
PuC _{0.92} < 1654	<i>cF8</i> <i>Fm$\bar{3}m$</i> NaCl	$a = 496.19$	[Mas2]
Pu ₂ C ₃ < 2050	<i>cI40</i> <i>I$\bar{4}3d$</i> Pu ₂ C ₃	$a = 813.50$	[Mas2]
PuC ₂ (h) 2350 to 1660	<i>cF36</i> <i>Fm$\bar{3}m$</i> CaF ₂	$a = 569.0$	[Mas2]
PuC ₂ (r) < 1660	<i>tI6</i> <i>I4/mmm</i> CaF ₂	$a = 363$ $c = 609.4$	[Mas2]
PuFe ₂ (h) 1240 - 1020	<i>cF24</i> <i>Fd$\bar{3}m$</i> MgCu ₂	$a = 715.0$	[Mas2]
PuFe ₂ (r) < 1050	-	-	[Mas2]
* τ ₁ , PuFeC ₂ < 1377	<i>tP8</i> <i>P4/mmm</i> UCoC ₂	$a = 350.1$ $c = 746.7$	[1983Suz] (temperature of formation) [1986Ger] (crystal structure established based on published data)
* τ ₂ , Pu ₁₁ Fe ₁₂ C ₁₈ < 1197	<i>cI82</i> <i>I$\bar{4}3m$</i> Th ₁₁ Ru ₁₂ C ₁₈	$a = 1010.5$	[1963Nic] (temperature of formation, X-ray pattern) [1995Wac] (interpretation of X-ray data)

Table 3: Invariant Equilibria

Reaction	T [°C]	Type	Phase	Composition (at.%)		
				C	Fe	Pu
$L + \text{Pu}_2\text{C}_3 + (\text{C}) \rightleftharpoons \tau_1$	1377	P_1	L	~30	~50	~20
$L + \text{Pu}_2\text{C}_3 + \tau_1 \rightleftharpoons \tau_2$	1197	P_2	L	~35	~43	~22
$L \rightleftharpoons \tau_1 + (\gamma\text{Fe})$	1156	e_1	L	19	69	12
$L + \tau_1 \rightleftharpoons \tau_2 + (\gamma\text{Fe})$	1143	U_1	L	17	68	15
$L \rightleftharpoons \text{Pu}_2\text{C}_3 + \text{PuFe}_2$	1100	e_2	L	19	45	36
$L + \text{Pu}_2\text{C}_3 \rightleftharpoons \text{PuFe}_2 + \text{PuC}_{0.92}$	1090	U_2^a	-	-	-	-
$L + \text{Pu}_2\text{C}_3 \rightleftharpoons \tau_2 + \text{PuFe}_2$	1051	U_3	L	18	55.5	26.5
$L \rightleftharpoons \text{PuFe}_2 + \tau_2 + (\gamma\text{Fe})$	1037	E_1	L	15	63	22

^aNote: no data for composition of liquid provided

Table 4: Thermodynamic Properties of Single Phases

Phase	Temperature Range [°C]	Property, per mole of atoms [J·mol ⁻¹]	Comments
PuFeC_2	1147 to 1377	$\Delta_f G = -(6000 \pm 2000) - (5 \pm 0.75)T$	[1983Suz], Knudsen effusion

Fig. 1: C-Fe-Pu.
Tentative liquidus
surface projection

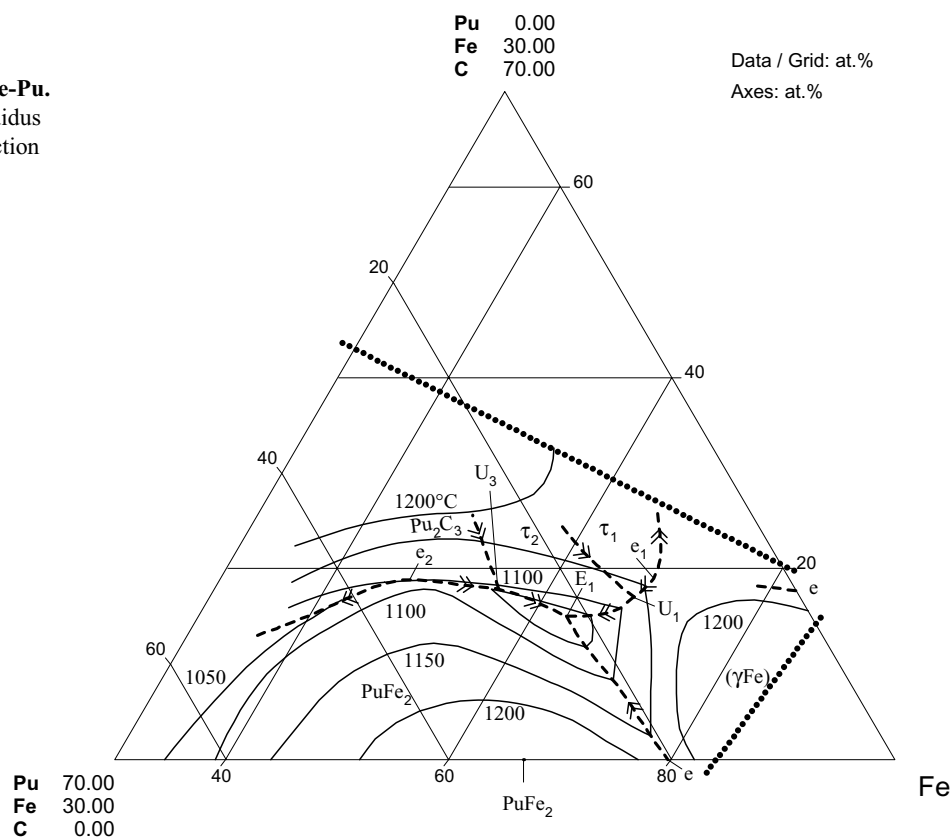


Fig. 2: C-Fe-Pu.
Isothermal section at
room temperature

