Carbon – Plutonium – Ruthenium

Lesley Cornish, Andy Watson

Introduction

The C-Pu-Ru system is of interest because some of the phases are related to fission products of irradiated plutonium carbides fuels in nuclear reactors [1970Hai]. Studies were made of the ternary systems comprising the most important actinides (Th, U and Pu), and many of the U- and Pu- systems were found to contain petrovskite phases of the filled Cu_3Au structure. These phases are important because they are found in both irradiated oxide [1968Bra] and carbide [1970Bra] fast reactor fuels. Experimental investigations of the system are given in Table 1.

Binary Systems

The C-Ru and Pu-Ru binary systems are taken from [Mas2]. However, the C-Pu phase diagram from [Mas2] is in error. The αPuC_2 compound shown in the phase diagram given in [Mas2] is, according to [1970Gre], metastable. This compound does not appear in any of the earlier versions of the phase diagram. An amended version of this phase diagram is given in the evaluation report for C-Pu-Rh (as Fig. 1) in the present volume. As well as six polymorphs of Pu, there are five intermetallic Pu-Ru compounds, three Pu-C intermetallic compounds, but no miscibility between C and Ru.

Solid Phases

The solid phases are given in Table 2. To date, only one true ternary compound has been reported: $PuRu_3C$, although (Pu) extends into the ternary system [1975Hai, 1977Hol, 1980Hol, 1984Hol1, 1984Hol2].

Isothermal Sections

In an assessment and review, [1984Hol1, 1984Hol2] gave an isothermal section at 1200°C showing the $PuRu_3C$ ternary phase as a line compound, and (Pu) with an extension into the ternary, using information from [1975Hol] and [1980Hol] (Fig. 1). However, [1984Hol1, 1984Hol2] eroneously showed solid (Pu) in the isothermal section, which is impossible because it melts at 640°C [Mas2]. Figure 1 is similar to, but not in total agreement with, the partial section of [1977Hol] at 1300°C. The diagram of [1980Hol] is taken to be correct since it is later and complete. An isothermal section was also produced at 800°C by [1975Hai], and is shown in Fig. 2. Both the section at 800°C and that at 1200°C disagree with earlier work of [1970Hai] which suggested that Pu_2C_3 and $PuRu_2$ were in equilibrium with each other at these temperatures. Their later work contradicts this giving equilibrium between Pu_2C_3 and PuRu, presumably benefitting from longer annealing times. Figures 1 and 2 have been amended to ensure consistency with the accepted binary systems, particlualry with respect to the homogeneity ranges for Pu_2C_3 and $PuRu_2$ which appear as having a range of homogeneity in the binary diagrams.

Thermodynamics

The Gibbs energy of formation of PuRu and $PuRu_3C$ were estimated using data for the Pu carbides and $PuRu_2$ [1968Cam]. For PuRu;

$\Delta_f G°$ (PuRu) < –78538+ 12.72T J·mol^{-1} (800 < T < 1000°C)

For $PuRu_3C$;

–89789 + 8.79 T > $\Delta_f G°$ ($PuRu_3C$) >–218501 + 64.27T J·mol^{-1} (662 < T < 796°C)

References

[1968Bra] Bramman, J.I., Sharpe, R.M., Thorn, D., Yates, G, *J. Nucl. Mater*., **25**(2), 201-205 (1968) as quoted in [1975Hai]

[1968Cam] Campbell, G.N., Mullins, L.J., Leary, J.A., *Thermodynamics of Nuclear Materials*, Proc. Symp. on Thermodynamics of Nuclear Materials with Emphasis on Solution Systems, International Atomic Energy Agency, Vienna, Austria, 1967, 75, (1968) as quoted in [1975Hai]

[1970Bra] Bramman, J.I, Proc. 9th Commonwealth Mining and Met. Cong., (London 1989), 4 (1970) as quoted in [1975Hai]

[1970Gre] Green, J.L., Leary, J.A., "Thermal Expansion and Phase Equilibria of the Carbon-Saturated Plutonium Carbides", *J. Appl. Phys.*, **41**(13), 5121-5124, (1970) (Crys. Structure, Experimental, 15)

[1970Hai] Haines, H.R., Potter, P.E., "Constitutional Studies in U and Pu Carbide-Fission Product Systems. 2.", *U. S. Atomic Energy Authority*, Report AERE-R6512, (1970)

[1975Hai] Haines, H.R., Potter, P.E., "Constitutional Studies on U-Pu-C-Fission Product Systems", *Thermodynamics of Nuclear Materials*, Proc. Symp., 4th, Vienna, October 21-25,1974 International Atomic Energy Agency, Vienna, Austria, **2**, 145-173 (1975) (Crys. Structure, Experimental, Phase Diagram, Phase Relations, 54)

[1975Hol] Holleck, H., "Ternary Phase Equilibria in the Systems Actinide-Transition Metal-Carbon and Actinide-Transition Metal Nitrogen", *Thermodynamics of Nuclear Materials*, Proc. Symp., 4th, Vienna, October 21-25,1974 International Atomic Energy Agency, Vienna, Austria, **2**, 213-264 (1975) (Crys. Structure, Phase Diagram, Phase Relations, Review, Thermodyn., 47)

[1977Hol] Holleck, H., "Carbon- and Boron-Stabilized Ordered Phases of Scandium", *J. Less-Common Met.*, **52**, 167-172 (1977) (Crys. Structure, Experimental, Phase Diagram, Phase Relations, 9)

[1982Hol] Holleck, H., Kleykamp, H., Benedict, U., Sari, C., "Constitution of the Pu-Ru-C, Pu-Rh-C and Pu-Pd-C Systems" (in German), *Gov. Rep. Announce. Index (U.S.)*, Report 1980, 13, **82**(5), 964 (1982) (Crys. Structure, Experimental, Morphology, Phase Diagram, Phase Relations, Review, 18)

[1980Hol] Holleck, H., Kleykamp, H., Benedict, U., Sari, C., Bericht KfK 2985 (1980) as quoted in [1984Hol1]

[1984Hol1] Holleck, H., "Ternary Carbide Systems of Actinoids with the Transitions Metals of 4. to 8. Groups", *J. Nucl. Mater.*, **124**, 129-146 (1984) (Assessment, Crys. Structure, Phase Diagram, Phase Relations, 78)

[1984Hol2] Holleck, H., "Ternary Carbide Systems of Actinoids with Transition Metals of other Groups" in "*Binary and Ternary Transition Metal Carbide and Nitride Systems*" (in German), Petzow, G. (Ed.) Gebrueder Borntraeger Berlin, Stuttgart, 92-115 (1984) (Crys. Structure, Phase Diagram, Phase Relations, Review, 91)

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

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1970Hai]	XRD, ceramography and EMPA of arc-melted samples, homogenised at 800 and 1000°C for up to 43 h	Isothermal section at 1000°C
[1975Hai]	XRD, ceramography and EMPA of arc-melted samples, homogenised between 800 and 1250°C for up to 750 h	Isothermal section at 800°C

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1977Hol]	XRD of arc melted samples, homgenized at 1300°C	Ru rich alloys. Partial isothermal section at 1300°C
[1982Hol]	Arc-melted sample, annealed for 40 h at 1200°C. Metallography, atom probe and XRD	20Pu- 60Ru-20C (at.%)

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(C)	*hP*4 $P6_3/mmc$ C (graphite)	*a* = 246.12 *c* = 670.9	at 25°C [Mas2]
(εPu) 640 - 483	*cI*2 $Im\bar{3}m$ W	*a* = 363.43	[Mas2]
(δ'Pu) 483 - 463	tI2 *I*4/*mmm* In	*a* = 332.61 *c* = 446.30	[Mas2]
(δPu) 463 - 320	*cF*4 $Fm\bar{3}m$ Cu	*a* = 463.71	[Mas2]
(γPu) 320 - 215	*oF*8 *Fddd* γPu	*a* = 315.87 *b* = 576.82 *c* = 1016.2	[Mas2]
(βPu) 215 - 125	*mC*34 *C*2/*m* βPu	*a* = 928.4 *b* = 1046.3 *c* = 785.9	[Mas2]
(αPu) < 125	*mP*16 $P2_1/m$ αPu	*a* = 618.3 *b* = 482.2 *c* = 1096.3	at 25°C [Mas2]
(Ru)	*hP*2 $P6_3/mmc$ Mg	*a* = 270.58 *c* = 428.16	at 25°C [Mas2]
Pu_3C_2 < 575	-	-	-
PuC ≲ 1654	*cF*8 $Fm\bar{3}m$ NaCl	*a* = 497.25	[Mas2], [V-C2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
Pu_2C_3 ≲ 2050	*cI*40 $I\bar{4}3d$ Pu_2C_3	*a* = 813.2 *a* = 813.5	isotope ^{239}Pu [V-C2] isotope ^{240}Pu [V-C2]
βPuC_2 2350 - 1660	*cF**	*a* = 569.6	[Mas2], [V-C2]
αPuC_2 < 1660	*tI*6 *I*4/*mmm* CaC_2	*a* = 363.0 *c* = 609.4	metastable [1970Gre], [V-C2]
$Pu_{19}Ru$ < 325	-	-	[Mas2]
Pu_3Ru < 600	*oP*16 *Pmmm* -	*a* = 621.6 *b* = 692.4 *c* = 809.3	[Mas2], [V-C2]
Pu_5Ru_3 < 1025	*tI*32 *I*4/*mcm* W_5Si_3	*a* = 1074.5 ± 0.3 *c* = 571.9 ± 0.2	[Mas2], [V-C2]
PuRu < 1250	*cP*2 $Pm\bar{3}m$ CsCl	*a* = 336.35 ± 0.6	[Mas2], [V-C2]
$PuRu_2$ < 1600	*cF*24 $Fd\bar{3}m$ Cu_2Mg	*a* = 747.2 ± 0.1	[Mas2], [V-C2]
* $PuRu_3C$	*cP*4 $Pm\bar{3}m$ $CaTiO_3$	*a* = 411.3	[1984Hol1] using [1975Hai, 1980Hol] [V-C2]

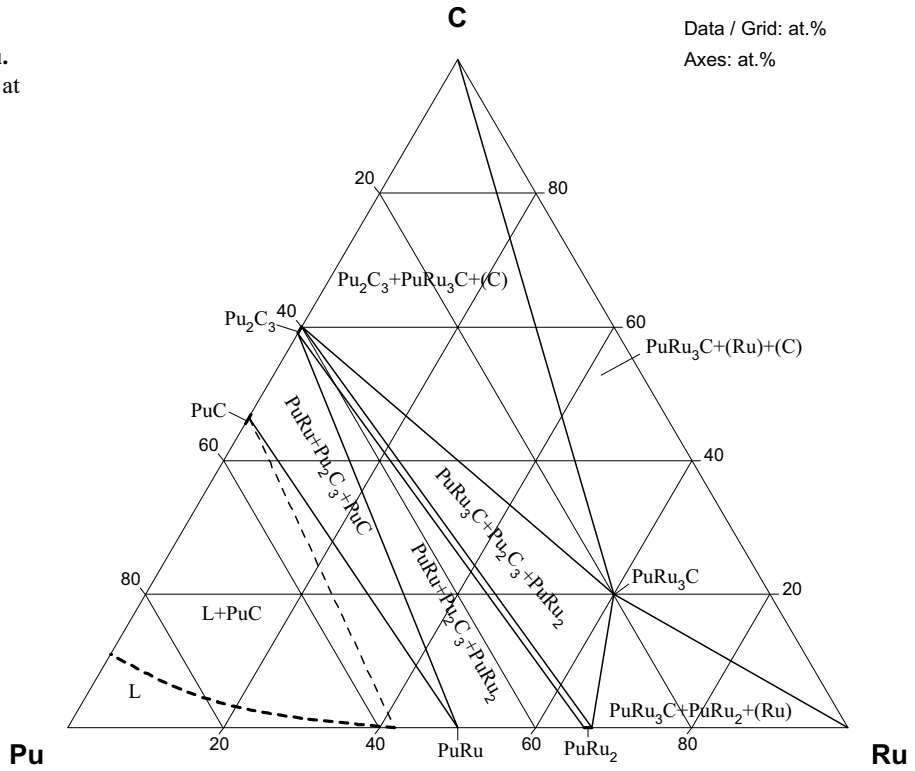

Fig. 1: C-Pu-Ru.
Isothermal section at 1200°C

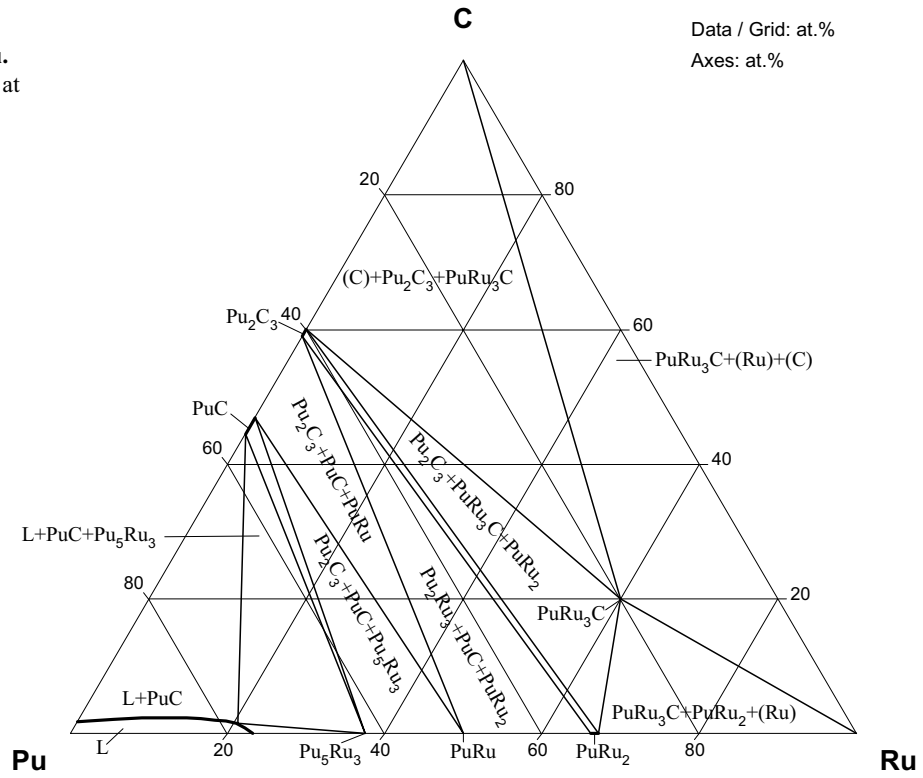

Fig. 2: C-Pu-Ru.
Isothermal section at 800°C