Carbon – Palladium – Uranium

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Introduction

The reaction behavior of multicomponent systems containing actinide carbides is of great interest for many problems in nuclear technology. Of particular importance in this respect are ternary systems involving the transition metals, which are the most frequently occurring fission products. The clearest way of surveying the reaction behavior for specific combination of elements at high temperatures is to extract information from the appropriate phase diagrams. The list of elements in fission products includes palladium. This fact triggered the interest to study the C-Pd-U system. Experimental studies of this system are limited to two works only. [1970Hai] performed constitutional studies in U carbide fission product system including the C-Pd-U. A preliminary ternary phase diagram at 1300°C has been given by [1971Hol]. Compositions of alloys, as well as experimental technique used to study the C-Pd-U system are presented in Table 1.

Binary Systems

The C-Pd binary system is accepted from [Mas2]. The Pd-U is accepted from [1992Oka], who took into account results of [1991Kle]. Despite the fact that the C-U system presented in [Mas2] is based on [1967Sto] there is a substantial difference between them. [Mas2] shows a single-phase region between UC and βUC_2 as one phase (δ), that leads to the appearance of the two-phase regions: l+δ and δ+C on both sides from the borders of the δ phase. Actually, the phase designated by [Mas2] as δ represents a solid solution between UC and βUC_2 with the graded junction from the NaCl type to the CaF_2? type structure realized by a gradual change of the carbon atom fraction located in the tetrahedral interstices for the octahedral ones. In accordance with [1967Sto] such designation is consistent with the existance of a miscibility gap at lower temperatures. This is accepted by in the present evaluation.

Solid Phases

No ternary compounds have been found in the C-Pd-U system [1970Hai, 1971Hol]. Some discrepancies in literature data are concerned with the stoichiometry of compounds existing in the Pd rich region of the Pd-U system. [1968Ter] found, that UPd_3, UPd_4 and UPd_8 exist in the range of 75 to 100 at.% Pd rather than UPd_3, UPd_4, UPd_5, U_2Pd_{11} and U_2Pd_{17} reported by [1964Pel]. [1991Kle] confirmed the results of [1968Ter]. The "UPd_5" compound with the fcc structure reported by [1987Zol] may be regarded as supersaturated nonequilibrium Pd based solid solution. The transformation of "UPd_5" into the hexagonal UPd_5 compound under high temperature treatment, reported by [1987Zol], may be regarded as a result of nonequilibrium solid state reaction and this phase most likely is metastable. [2003Hea] examined the behavior of the UPd_3 crystal lattice under the pressure up to 53 GPa. The study does not reveal any volume anomaly, which could be associated with a delocalization of the 5*f* electronic states, in the entire pressure range. Crystal structure of unary and binary phases is presented in Table 2.

Isothermal Sections

The isothermal section at 1300°C published by [1971Hol] was constructed basing on his own results of the study of two alloys 25U-25Pd-50C (at.%) and 40U-20Pd-40C (at.%). These results well coincide with those presented by [1970Hai], who studied alloys of the nominal composition U_2PdC_2 and $UPdC_2$. This section was reproduced by [1975Hol, 1977Hol, 1982Hol, 1984Hol1, 1984Hol2]. It is presented in Fig. 1 with minor modifications, that take into account the latest results concerning the location of the liquid region and the homogeneity regions of UPd_3 and (Pd) in the binary systems and the absence of the UPd_5 compound in the assessed Pd-U system.

References

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

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1970Hai]	X-ray diffraction, electron probe micro analysis, ceramographic analysis	annealed at 800°C for 200 h and at 1250°C for 60 h, U_2PdC_2, $UPdC_2$
[1971Hol]	X-ray diffraction, optical light microscopy	annealed at 1300°C for 63 h, 25 at.% U+25 at.% Pd+50 at.% C; 40 at.% U+20 at.% Pd+40 at.% C, UC_2+UPd_3, U_2C_3+UPd_3, UC+U_2C_3+UPd_3

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(C) ≤ 3827 ± 50 (S.P.)	*hP*4 $P6_3/mmc$ C (graphite)	*a* = 246.12 *c* = 670.90	at 25°C [Mas2] sublimation point
(Pd) < 1555	*cF*4 $Fm\bar{3}m$ Cu	*a* = 389.03 *a* = 401.1 *a* = 406.1 ± 0.1	pure Pd, at 25°C [Mas2] 15.0 ± 0.2 at.% U [1991Kle] at 1050°C 16.6 at.% U, may be supersaturated metastable solid solution, [1987Zol]
(γU) 1135 - 776	*cI*2 $Im\bar{3}m$ W	*a* = 352.4	pure U, [Mas2] dissolves ~ 5 at.% Pd at 998°C [1991Kle]
(βU) 776 - 668	*tP*30 $P4_2/mnm$ βU	*a* = 1075.9 *c* = 565.6	pure U, [Mas2]
(αU) < 668	*oC*4 *Cmcm* αU	*a* = 285.37 *b* = 586.95 *c* = 495.48	pure U, at 25°C [Mas2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
UC < 2515	*cF*8 $Fm\bar{3}m$ NaCl		from 47 to 66 at.% C miscibility gap (critical point at 2050°C, 43.8 at.% C) [2001Che]
		a = 495.97	stoichiometric [2001Che]
		a = 495.63	48 at.% C [2001Che]
β, UC_2 2434 - 1762	*cF*12 $Fm\bar{3}m$ CaF_2?	*a* = 545.0	[2001Che] actually, "β,UC_2" phase represents the UC phase in equilibrium with graphite [2001Che]
α, UC_2 1762 - 1477	*tI*6 *I*4/*mmm* CaC_2	*a* = 351.90 *c* = 597.87	U rich, [2001Che]
		a = 352.41 *c* = 599.62	C rich, [2001Che]
U_2C_3 < 1833	*cI*40 $I\bar{4}3d$ Pu_2C_3	*a* = 808.89	[1969Lea]
UPd 1047 - 970	-	-	50 at.% Pd [1991Kle]
U_5Pd_6 1110 - 980	-	-	54.54 at.% Pd [1991Kle]
UPd_3 < 1640	*hP*16 $P6_3/mmc$ Ni_3Ti	*a* = 577.0 ± 0.1 *c* = 961.9 ± 0.4	[2003Hea]
UPd_4 < 1585	*cP*4 $Pm\bar{3}m$ $AuCu_3$	*a* = 404.7 to 407.4	from 19.1 ± 0.2 to 21.6 ± 0.2 at.% U at 1050°C, [1991Kle] defect structure
UPd_8 < 800	*t**	*a* = 388.2 *c* = 408.3	[1968Ter]
UPd_5	*h**	*a* = 550.6 ± 0.2 *c* = 703.4 ± 0.5	16.6 at.% U, [1987Zol] most likely is metastable

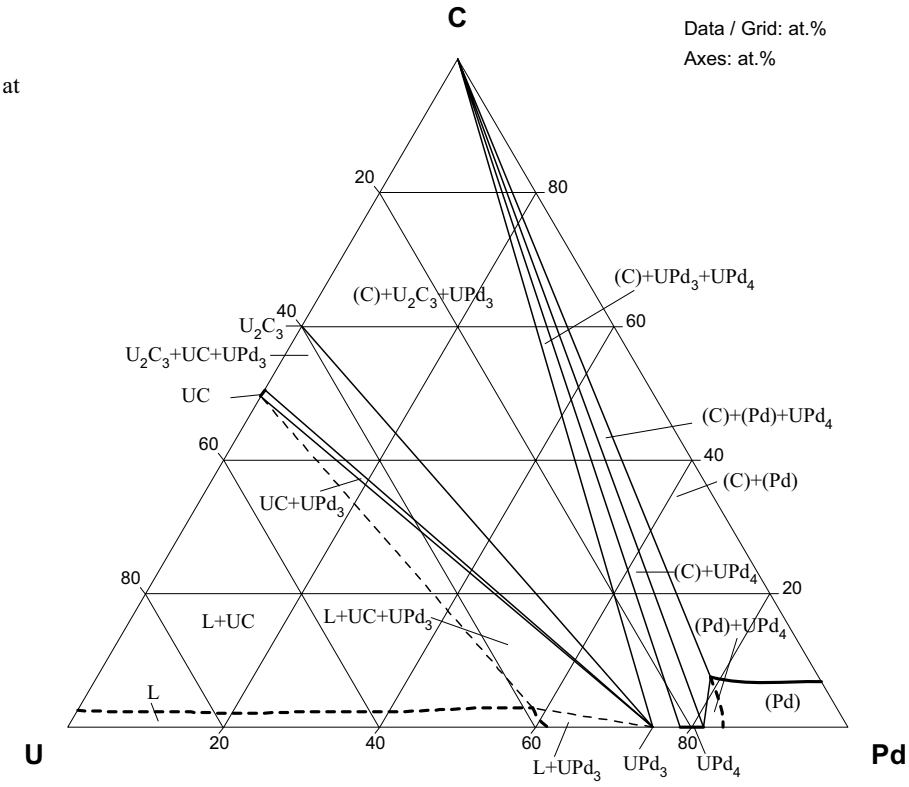

Fig. 1: C-Pd-U. Isothermal section at 1300°C