Carbon – Palladium – Thorium

Andy Watson, Lesley Cornish

Introduction

Interest in this ternary system is with respect to equilibria between fission products and constituent elements in cladding and structural materials. However, very little work has been carried out on this system. The only phase equilibrium study is the work of [1971Hol], which produced an isothermal section for 1100°C. Fourteen samples were prepared by arc-melting thorium turnings (0.3% O), palladium (purity >99.9%) and spectroscopic grade graphite. The cast samples were then annealed under high vacuum for 50 h before investigation by XRD and optical microscopy. This work has been quoted in a number of reviews [1975Hol, 1984Hol1, 1984Hol2].

Binary Systems

The binary systems are accepted from [Mas2]. The C-Th system has 4 carbide phases, but the monocarbide (designated here as ThC_{1-x}) and γThC_2 are structurally related to (αTh). At high temperatures, the two phase regions between the (αTh) and ThC_{1-x}, and between ThC_{1-x} and γThC_2 disappear. Three alternative versions of the C-Th phase diagram are available in [S], each focussed on the region from 45 - 70 at.% C, but that produced in [Mas2] is preferred as it is based on more recent work.

Solid Phases

Solid phases associated with the system are given in Table 1. No ternary phases have been reported.

Isothermal Sections

The isothermal section for 1100°C given by [1971Hol] is shown in Fig. 1. Some additions (in the Pd corner) and alterations have been made in order to maintain consistency with the C-Pd and C-Th binary phase diagrams.

Miscellaneous

Adding boron has produced a compound $ThPd_2B_2C$ that shows superconductivity with a critical temperature of 14.5 K [1994Sar, 1994Zan].

References

[1971Hol] Holleck, H., "Phase Equilibria in the Systems U-Pd-C,U-Pt-C, and Th-Pd-C" (in German), *Monatsh. Chem*., **102**, 1699-1708 (1971) (Phase Diagram, Experimental, #, 25)

[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)

[1984Hol1] 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, 92-111 (1984) (Crys. Structure, Phase Diagram, Phase Relations, Review, 91)

[1984Hol2] Holleck, H., "Ternary Carbid Systems of Actinoids with the Transitions Metals of 4. to 8. Groups" (in German), *J. Nucl. Mater*., **124**, 129-146 (1984) (Review, Crys. Structure, Phase Diagram, Phase Relations, 78)

[1994Sar] Sarrao, J.L., de Andrade, M.C., Herrmann, J., Han, S.H., Fisk, Z., Maple, M.B., Cava, R.J., "Superconductivity to 21K in Intermetallic Thorium-Based Boride Carbides", *Physica C*, **229**(1-2), 65-69 (1994) (Experimental, Superconduct., 10)

[1994Zan] Zandbergen, H.W., Gortenmulder, T.J., Sarrac, J.L., Harrison, J.C., de Andrade, M.C., Hermann, J., Han, S.H., Fisk, Z., Maple, M.B., Cava, R.J., "Structure and Composition Analysis of the Phases in the System Th-Pd-B-C Containing Superconductors with T_c = 14.5 K and T_c = 21 K", *Physica C*, **232**, 328-336 (1994) (Crys. Structure, Phase Relations, Experimental, Superconduct., 14)

Table 1: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(C) (graphite) < 3827	*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	at 25°C [Mas2] dissolves ~8 at.% C at 1504°C, ~15 at.% Th at 1145°C [Mas2].
(βTh) 1755 - 1360	*cI*2 $Im\bar{3}m$ W	*a* = 411	[Mas2] dissolves ~9 at.% C at 1707°C, < 1 at.% Pd
(αTh) < 1360	*cF*4 $Fm\bar{3}m$ Cu	*a* = 508.42	at 25°C [Mas2] dissolves < 1 at.% Pd
Th_3Pd_{13} < 1215	*tI**	-	18 - 19 at.% Th [Mas2]
$ThPd_4$ < 1340	*cP*4 $Pm\bar{3}m$ $AuCu_3$	*a* = 411.3 ± 0.3	[V-C2] 19 (at 1215°C) - 21.5 at.% Th [Mas2]
$ThPd_3$ ≲ 1575	*hP*16 $P6_3/mmc$ Ni_3Ti	*a* = 585.8 ± 0.3 *c* = 981.4 ± 0.4	[V-C2] 22.5 (at 1340°C) - 25 at.% Th [Mas2]
Th_3Pd_5 < 1387	*hP*8 $P\bar{6}2m$	*a* = 714.9 ± 0.3 *c* = 389.9 ± 0.2	[V-C2] 37.5 at.% Th [Mas2]
Th_3Pd_4 < 1325	*hR*42 $R\bar{3}$	*a* = 1364.6 *c* = 584.7	[V-C2] 42.9 at.% Th [Mas2]
ThPd < 1412	*oP*8 *Pnma* FeB	*a* = 724.9 ± 0.5 *b* = 457.1 ± 0.3 *c* = 585.6 ± 0.4	[V-C2] 50 at.% Th [Mas2]
Th_2Pd < 1162	*tI*12 *I*4/*mcm* $CuAl_2$	*a* = 731.3 ± 0.4 *c* = 594.2 ± 0.4	[V-C2] 66.7 at.% Th [Mas2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
ThC_{1-x} < 2500	*cF*8 *Fm*$\bar{3}$*m* NaCl	a = 532.21 ± 0.05	[V-C2] 50 < x < 56 at.% Th at 25°C [Mas2]
γThC_2 2610 - 1470	*cF*8 *Fm*$\bar{3}$*m* NaCl	a = 580.6	[V-C2]
βThC_2 1495 - 1255	*tI*4 *I*4/*mmm* CoO	a = 422.1 ± 0.3 c = 539.4 ± 0.3	[V-C2]
αThC_2 < 1440	*mC*12 *C*2/*c* ThC_2	a = 668.4 ± 0.2 b = 422.0 ± 0.1 c = 673.5 ± 0.2 α = 103.91 ± 0.01°	[V-C2]

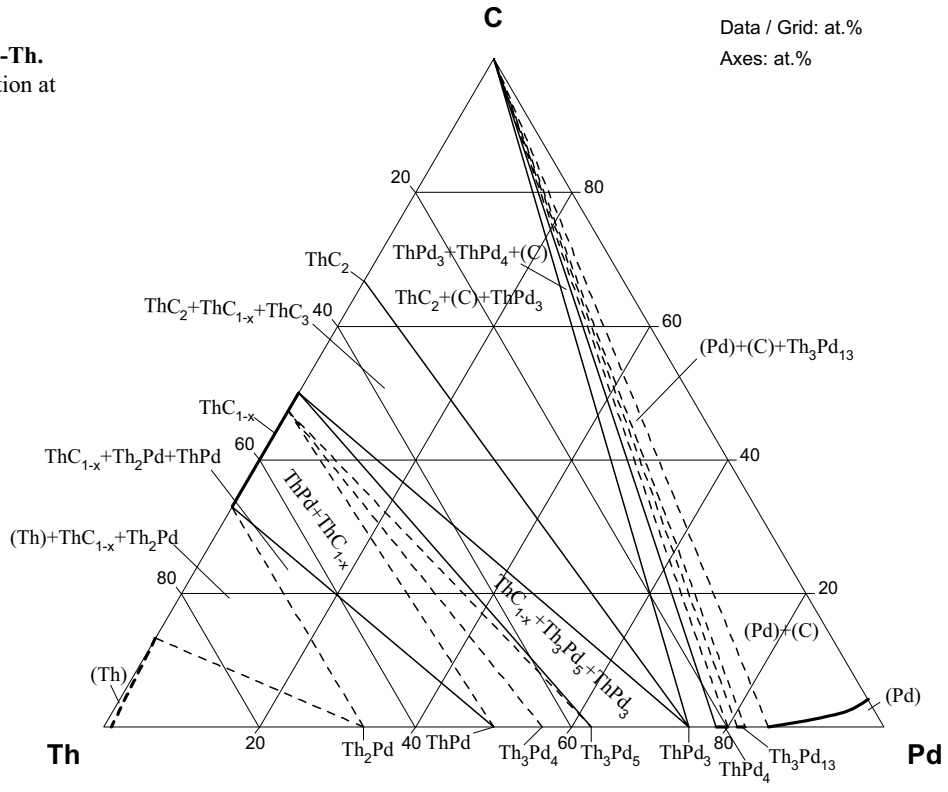

Fig. 1: C-Pd-Th. Isothermal section at 1100°C