

Carbon – Rhodium – Thorium

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Introduction

Phase relations in the multicomponent systems containing actinide carbides are of great interest in nuclear technology. Of particular importance are ternary systems involving the transition metals, which are the most frequently occurring fission products, the main constituents of the cladding and structural materials and potential alloying elements [1975Hol]. Experimental results relating to the C–Rh–Th system are presented in [1975Hol, 1977Hol, 1984Hol1, 1984Hol2]. To study the phase configurations alloy specimens at 30 different compositions were prepared by arc melting and homogenizing at 1200°C. The alloys were studied by X-ray diffraction, metallography and EMPA in the annealed state. On the basis of the results obtained, an isothermal section covering the whole range of compositions at 1200°C was constructed. [1978Gup] evaluated the free energy and heat content values at different temperatures and obtained the standard value of the atomization energy for the ThRhC₂ molecule. Future investigations of phase relations in the C–Rh–Th system should be concentrated on the study of alloy properties in the equilibrium state at different temperatures. Changes in the character phase equilibria at temperatures higher and lower than 1200°C are needed in particular because of the changes in the compositions and the crystal structures of intermediate phases in the boundary C–Th binary system.

Binary Systems

The C–Rh, C–Th and Rh–Th binary systems are accepted from [Mas2].

Solid Phases

Crystallographic data relating to the known unary and binary phases are listed in Table 1. No ternary phases have been reported. At high temperatures, the C–Th system presents a continuous series of solid solutions between (α Th), the μ phase and the γ ThC₂ phase (labelled as π). All of these phases crystallize into a cubic structure with differing space groups and prototypes.

Isothermal Sections

An isothermal section for the whole range of compositions at 1200°C is shown in Fig. 1. It is presented according to the results of [1975Hol, 1977Hol, 1984Hol1, 1984Hol2] with some corrections for compatibility with the accepted binary systems. Owing to the existence of a continuous series of solid solutions π between (α Th) and the ThC phase at 1200°C, the three-phase region ThC + Th₇Rh₃ + (α Th) is replaced by a two-phase region π + Th₇Rh₃. In the composition range 50 to 100 at.% Th, the two- and three-phase regions are respectively named as ThRh + π and Th₇Rh₃ + ThRh + π . The ThRh₃ phase was shown in [1975Hol, 1977Hol, 1984Hol1, 1984Hol2] as possessing some homogeneity but without any experimental evidence.

Thermodynamics

[1977Hol] noted that dissolving about 5 to 7 at.% C in the κ , ThRh₃ phase stabilizes this phase relative to the neighboring Rh–Th phases and suppresses the α ThRh₂ and λ phases in the ternary region. The free enthalpy of formation of the κ phase in the ternary system at 1200°C was estimated in [1977Hol] from binary data [1975Mur], taking into account the observed phase equilibria. The free enthalpy of formation of the κ phase containing about 5 to 7 at.% C was estimated to be about -305.9 to -268.2 kJ·mol⁻¹. This value is higher than the value measured in the C–Th binary system (-263.6 kJ·mol⁻¹ according to the formula of [1975Mur]). This result confirms the stabilization of the κ phase by carbon.

[1978Gup] observed the gaseous molecule ThRhC₂ in the Knudsen-cell effusate from the C–Rh–Th–U alloys at high temperatures. The thermodynamic properties of ThRhC₂ were evaluated from the various reaction enthalpies determined by the third law method, $\Delta H_{298}^{\circ} = T \cdot \{-R \cdot \ln K_p - \Delta((G_T^{\circ} - H_{298}^{\circ})/T)\}$. The free energy functions $(G_T^{\circ} - H_{298}^{\circ})/T$ were taken from the literature when available or calculated from known or estimated molecular parameters through standard statistical thermodynamic expressions. The calculated values of $-(G_T^{\circ} - H_{298}^{\circ})/T$ and the heat content functions, $H_T^{\circ} - H_{298}^{\circ}$, for ThRhC₂ at various temperatures are listed in Table 2. The values of the $H_{298}^{\circ} - H_0^{\circ}$ heat content functions were obtained as 15.443 kJ·mol⁻¹ for the Rh–Th–C–C structure and 13.748 kJ·mol⁻¹ for the Rh–C–C–Th structure. The atomization energies of gaseous ThRhC₂ were calculated to be 1774 ± 60 kJ·mol⁻¹ and 1763 ± 60 kJ·mol⁻¹ for the temperatures of 25°C and –273.15°C, respectively. After comparison of these data with the estimated value of the heat of formation obtained using the enthalpies of sublimation of C, Rh and Th, the structure Rh–Th–C–C for the ThRhC₂ molecule was proposed. The atomization energy estimated for this structure using the bond additivity method is $H_{at,298}^{\circ} = 1732$ kJ·mol⁻¹.

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Table 1: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(C) (I) < 3827 ± 50	<i>hP4</i> <i>P6₃/mmc</i> C (graphite)	<i>a</i> = 246.12 <i>c</i> = 670.9	at 25°C [Mas2] sublimation point at 1.013 bar
(C) (II)	<i>cF8</i> <i>Fd$\bar{3}m$</i> C (diamond)	<i>a</i> = 356.69	at 25°C [Mas2] high pressure phase (> 60.78 bar)
(Rh) < 1963	<i>cF4</i> <i>Fm$\bar{3}m$</i> Cu	<i>a</i> = 380.32	at 25°C [Mas2] dissolves ~ 1 at.% Th at 1450 ± 12°C [Mas2] dissolves ~ 1.5 at.% C at 1694 ± 17°C [Mas2] and ~ 1.4 at.% C at 1250°C [Mas2]
(βTh) (h) 1755 - 1360	<i>cI2</i> <i>Im$\bar{3}m$</i> W	<i>a</i> = 411	[Mas2] dissolves ~ 1 at.% Rh at ~1360°C and ~9 at.% C at 1707°C [Mas2]
γ, Th ₇ Rh ₃ < 1362 ± 12	<i>hP20</i> <i>P6₃mc</i> Th ₇ Fe ₃	<i>a</i> = 1003.1 <i>c</i> = 628.4	30 at.% Rh [Mas2]
		<i>a</i> = 1002 <i>c</i> = 629	[V-C2] in the Th _{68.8} Rh _{31.2} alloy [1961Fer]
		<i>a</i> = 1003.1 <i>c</i> = 628.7	[1963Tho]
δ, ThRh < at least ~ 1500	<i>oC8</i> <i>Cmcm</i> CrB	<i>a</i> = 383.4 <i>b</i> = 1120 <i>c</i> = 424.1	50 at.% Rh [Mas2] [V-C2]
		<i>a</i> = 386.6 <i>b</i> = 1124 <i>c</i> = 422	[1962Tho, 1963Tho]
ε, Th ₃ Rh ₄ < 1487	<i>cF*</i>	<i>a</i> = 508.5 ± 2	57 at.% Rh [Mas2] in the annealed alloys Th ₄₄ Rh ₅₆ , Th ₄₃ Rh ₅₇ and Th ₄₂ Rh ₅₈ [1963Tho]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
η , Th ₃ Rh ₅ < 1450	<i>t</i> **	$a = 482$ $c = 1460$	~ 61.5 at.% Rh [Mas2] at 1200°C [1977Hol]
β ThRh ₂ (h) < at least ~ 1500 - 1250	<i>hP</i> 6 <i>P</i> 6 ₃ / <i>mmc</i> InNi ₂	$a = 462.9 \pm 2$ $c = 584.9 \pm 3$	~ 66.5 at.% Rh [Mas2] in the as-cast alloy Th ₃₅ Rh ₆₅ [1963Tho]
α ThRh ₂ (r) < 1250	-	-	~ 66.5 at.% Rh [Mas2]
κ , ThRh ₃ < at least ~ 1500	<i>cP</i> 4 <i>Pm</i> $\bar{3}m$ AuCu ₃	$a = 417.3$ $a = 413.9$	75 at.% Rh [Mas2] at 1200°C [1977Hol]. Up to ~ 5 to 7 at.% C, $T = 1200^\circ\text{C}$ [1977Hol] [1961Dwi]
λ , ThRh ₅ < at least ~ 1500	-	-	~ 83 at.% Rh [Mas2]
β ThC ₂ (h ₁) 1495 - 1255	<i>tP</i> 6 <i>P</i> 4 ₂ / <i>mmc</i>	$a = 423.5$ $c = 540.8$	63 to 66 at.% C [Mas2] [S]
α ThC ₂ (r) < 1440	<i>mC</i> 12 <i>C</i> 2/ <i>c</i> α ThC ₂	$a = 669.2$ $b = 422.3$ $c = 674.4$ $\beta = 103.0^\circ$ $a = 653$ $b = 424$ $c = 656$ $\beta = 104^\circ$	66 at.% C [Mas2] [H]
ω , Th ₂ C ₃		$a = 856.09$ to 865.13	metastable [1996Vel] high pressure phase (at 1325°C, $3.5 \cdot 10^{-4}$ bar)

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
π , Th _{1-x-y} Ru _x C _y			$x = 0, 0.22 \leq y \leq 0.66$, 2000°C [Mas2] $x = 0, 0.04 \leq y \leq 0.50, 0.62 \leq y \leq 0.66$, 1500°C [Mas2] $x = 0, 0.33 \leq y \leq 0.50$, 1100°C [Mas2] $x = 0, 0.41 \leq y \leq 0.50$, 800°C [Mas2] $x = 0, y = 0.355$ [S]
(α Th) (r) < 1360	$cF4$ $Fm\bar{3}m$ Cu	$a = 508.42$	at 25°C [Mas2]
μ , ThC < 2500	$cF8$ $Fm\bar{3}m$ NaCl	$a = 530.1$ $a = 530.3$ $a = 534.6$ $a = 534.6$ $a = 533.8$ $a = 534$	$x = 0, y = 0.382$ [1996Vel] $x = 0, y = 0.495$ [1996Vel] $x = 0, y = 0.5$ [1962Kem] $x = 0$ [E] $x = 0$ [H]
γ ThC ₂ (h ₂) 2610 - 1470	$cP12$ $Pa\bar{3}$ FeS ₂	$a = 580.8$	at 1500°C [1964Hil]

Table 2: Thermodynamic Properties of the ThRhC₂ Molecule in a Gaseous State

Structure of the Molecule	Temperature [°C]	Free Energy Function $-(G_T^\circ - H_{298}^\circ)/T$ [J·mol ⁻¹ ·K ⁻¹]	Heat Content Function $H_T^\circ - H_{298}^\circ$ [kJ·mol ⁻¹]
Rh-Th-C-C	25	311.76	0.00
	1827	395.87	147.41
	1927	399.15	156.01
	2027	402.32	164.63
	2127	405.38	173.25
	2227	408.34	181.89
	2327	411.20	190.53
	2427	413.98	199.17
Rh-C-C-Th	25	303.16	0.00
	1827	383.52	144.13
	1927	386.74	152.70
	2027	389.84	161.27
	2127	392.83	169.86
	2227	395.74	179.46
	2327	398.55	187.07
	2427	401.27	195.69

Fig. 1: C-Rh-Th.
Isothermal section
at 1200°C

