Carbon – Ruthenium – Thorium

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Introduction

For many problems in nuclear technology, information about phase relations in multicomponent systems containing actinide (in particular, thorium) carbides is of a great interest. Of particular importance in this context 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 concerning the ternary C-Ru-Th system are represented by isothermal sections at 1200°C [1975Hol, 1977Hol, 1984Hol1, 1984Hol2] and 900°C [1995Wac] and the crystal structures of the ternary phases [1971Hol, 1977Hol, 1990Aks1, 1990Aks2, 1995Wac]. The experimental methods used together with the temperature and composition ranges studied are presented in Table 1. Information relating to the phase equilibria of the C-Ru-Th system is incomplete. In particular, experimental data for the Th corner are in need of further refinement. Future investigations of phase relations in the C-Ru-Th system need to be concentrated on obtaining information relating to the conditions of alloy crystallization as well as continuing the study of alloy behavior in the equilibrium state at different temperatures.

Binary Systems

Data relating to the forming C-Ru, C-Th and Ru-Th systems are accepted from [Mas2].

Solid Phases

Crystallographic data relating to the known unary, binary and ternary phases are listed in Table 2. In the C-Th system at high temperatures, a continuous series of solid solutions between (αTh), the μ phase and the γThC_2 phase are present (labelled as π). All of these phases possess a cubic structure but of differing space groups and prototypes. It was established that at temperatures of 1200 and 900°C, three ternary phases, τ_1, τ_2 and τ_3, exist [1971Hol, 1975Hol, 1977Hol, 1984Hol1, 1984Hol2, 1995Wac], but the temperature ranges of their stability were not determined. These phases do not possess visible homogeneity ranges.

Isothermal Sections

Figure 1 presents an isothermal section for 1200°C covering the whole range of compositions, taken from the data of [1975Hol, 1977Hol, 1984Hol1, 1984Hol2] with amendments in accordance with the refinement of the compositions of the τ_1 and τ_2 phases ([1990Aks1, 1990Aks2, 1995Wac] data compared with the data from earlier publications). In the boundary binary C-Th system, homogeneity region of the π phase stretches from 50 to 100 at.% Th, but in the ternary system, this phase probably does not possess a visible homogeneity with respect to ruthenium content; as in the boundary binary Ru-Th system. The positions of the three-phase regions π + γ + δ and π + δ + ε need to be refined.

The isothermal section for a temperature of 900°C covering the whole composition range taken from [1995Wac] is shown in Fig. 2. The constitution of the boundary Ru-Th binary system, according to the accepted [Mas2] data, is well established for temperatures above 1000°C. For this reason, it is accepted that the stoichiometries and homogeneity regions of the Ru-Th binary phases at 900°C are the same as those at 1000°C. In the C-Th system, a two-phase field between (αTh) and μ phases is present, but its position was corrected after comparing with [1995Wac] data. Therefore, the positions of the (αTh) + μ + γ, μ + γ + δ and μ + δ + ε three-phase fields were also corrected (marked by dashed lines).

Thermodynamics

The free enthalpies of formation of the τ_1 and τ_3 phases in the ternary system at 1473 K (1200°C) were estimated by [1977Hol] using binary Ru-Th data for 1020 to 1170 K (747 to 897°C) [1974Kle], binary C-Th data [1975Kub, 1977Hol] and by taking into account the observed phase equilibria. From the reactions $4\varepsilon + 6(\alpha ThC_2) = 7\mu + \tau_1$ and $\tau_1 + 6Th = 5\mu + 4\varepsilon$, the free enthalpy of formation of the τ_1 phase at 1200°C was estimated to be –824.80 to –464.73 kJ·mol^{-1}. From the reactions $\mu + 3\eta = 3\varepsilon + \tau_3$ and $\tau_3 + 3\delta = 9\varepsilon + \mu$, the free enthalpy of formation of the τ_3 phase at 1200°C was estimated to be –226.09 to –117.23 kJ·mol^{-1}.

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

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1971Hol]	Arc melting, annealing, X-ray studies, metallography, microanalysis	1200°C, the $Th_{20}Ru_{40}C_{40}$ alloy
[1975Hol]	Experimental techniques	1200°C, whole range of compositions
[1977Hol]	Arc melting, annealing, X-ray studies, metallography, microanalysis	1200°C, 1300°C, whole range of compositions
[1984Hol1]	Experimental techniques	1200°C, whole range of compositions
[1984Hol2]	Experimental techniques	1200°C, whole range of compositions
[1990Aks1]	Laue, rotation and lines layers scanning techniques	$Th_2Ru_6C_5$
[1990Aks2]	Annealing; Laue, rotation and lines layers scanning techniques, powder X-ray diffraction	$Th_{11}Ru_{12}C_{18}$
[1995Wac]	Arc melting, annealing, EDX, Guinier X-ray diffraction	900°C, whole range of compositions

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(C) (I) < 3827 ± 50 (sublimation point), 1.013 bar	*hP*4 $P6_3/mmc$ C (graphite)	a = 246.12 c = 670.9	at 25°C [Mas2]
(C) (II) > 60.78 bar	*cF*8 $Fd\bar{3}m$ C (diamond)	a = 356.69	at 25°C [Mas2]
(Ru) < 2334 $Th_xRu_{1-x-y}C_y$	*hP*2 $P6_3/mmc$ Mg	a = 270.58 c = 428.16	at 25°C [Mas2] x = 0, 0 ≤ y ≤ 0.03, 1940°C [Mas2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(βTh) (h) 1755 - 1360	*cI*2 $Im\bar{3}m$ W	a = 411	[Mas2]
$Th_{1-x-y}Ru_xC_y$			x = 0, 0 ≤ y ≤ 0.09, 1707°C [Mas2]
γ, Th_7Ru_3 1412 - at least < 1000	*hP*20 $P6_3mc$ Th_7Fe_3		30 at.% Ru [V-C2]
		a = 996.9 c = 630.2	[1963Tho]
		a = 997.1 c = 628.8	Ru rich side [1974Kle]
δ, Th_3Ru_2 1425 - at least < 1000	-	-	40 at.% Ru [V-C2]
ε, ThRu 1462 - at least < 1000	*oC*8 *Cmcm* CrB		50 at.% Ru [V-C2]
		a = 387.8 b = 1129 c = 407.1	[1963Tho]
		a = 390.3 b = 1127 c = 404.6	Th rich side [1974Kle]
		a = 387.8 b = 1126 c = 406.9	Ru rich side [1974Kle]
η, $ThRu_2$ 1500 - at least < 1000	*cF*24 $Fd\bar{3}m$ $MgCu_2$		66.7 at.% Ru [V-C2]
		a = 764.9	[E]
		a = 765.7	[1963Tho]
		a = 765.4	[1974Kle]
βThC_2 (h_1) 1495 - 1255	*tP*6 $P4_2/mmc$		63 to 66 at.% C [V-C2]
		a = 423.5 c = 540.8	[S]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
αThC$_2$ (r) < 1440	*mC*12 *C*2/*c* αThC$_2$		66 at.% C [V-C2]
		a = 653 *b* = 424 *c* = 656 β = 104°	[H]
		a = 669.2 *b* = 422.3 *c* = 674.4 β = 103.12°	[1987Ben]
		a = 669.1 *b* = 423.1 *c* = 674.4 β = 103.83°	[1964Gan]
ω, Th$_2$C$_3$ 1325, $3.5\cdot10^{-4}$ bar	-	*a* = 856.09 to 865.13	Metastable [1996Vel]
π, Th$_{1-x-y}$Ru$_x$C$_y$			*x* = 0, 0.22 ≲ *y* ≲ 0.66, 2000°C [Mas2] *x* = 0, 0.04 ≲ *y* ≲ 0.50, 0.62 ≲ *y* ≲ 0.66, 1500°C [Mas2] *x* = 0, 0.33 ≲ *y* ≲ 0.50, 1100°C [Mas2] *x* = 0, 0.41 ≲ *y* ≲ 0.50, 800°C [Mas2] *x* = 0, *y* = 0.355 [S]
(αTh) (r) < 1360	*cF*4 *Fm*$\bar{3}$*m* Cu	*a* = 508.42	at 25°C [Mas2]
μ, ThC < 2500	*cF*8 *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]
γThC$_2$ (h$_2$) 2610 - 1470	*cP*12 *Pa*$\bar{3}$ FeS$_2$	*a* = 580.8	at 1500°C [1964Hil]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
* τ_1, $Th_{11}Ru_{12}C_{18}$	*cI** $I\bar{4}3m$ $Th_{11}Ru_{12}C_{18}$	a = 1078	at 1200°C, labelled as "$Th_{\sim 0.27}Ru_{\sim 0.30}C_{\sim 0.43}$" and "$Th_{3+x}Ru_{4-x}C_5$" ($x \approx 0.3$) [1971Hol], "$Th_{\sim 3}Ru_{\sim 4}C_{\sim 5}$" [1977Hol]
		a = 1076.4	X-ray powder diffraction [1990Aks2]
		a = 1075.4	single crystal [1995Wac]
* τ_2, $Th_2Ru_6C_5$	*tP** *P*4/*mbm* $Th_2Ru_6C_5$		labelled as "$ThRu_3C_{1.5}$" [1971Hol, 1977Hol]
		a = 911.3 c = 418.6	single crystal [1990Aks1]
		a = 909.6 c = 417.74	single crystal [1995Wac]
* τ_3, $ThRu_3C$	*cP*5 $Pm\bar{3}m$ $CaTiO_3$	a = 421.0	labelled as "$ThRu_3C_{1-x}$" ($0 < x < 0.1$) [1971Hol, 1977Hol]
		a = 422.7	single crystal [1995Wac]

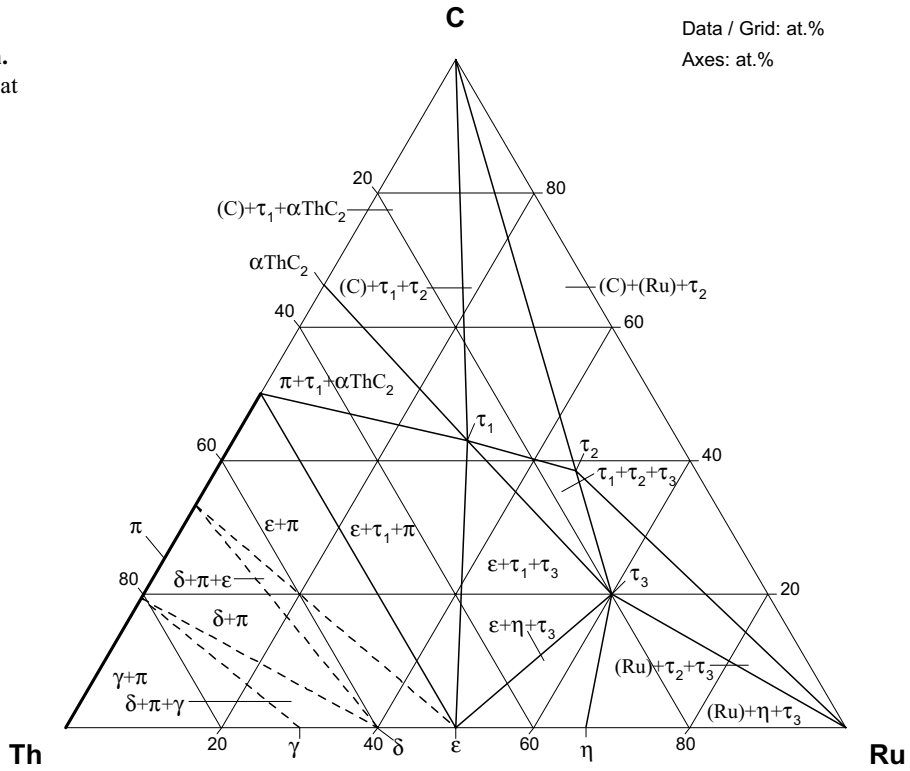

Fig. 1: C-Ru-Th. Isothermal section at 1200°C

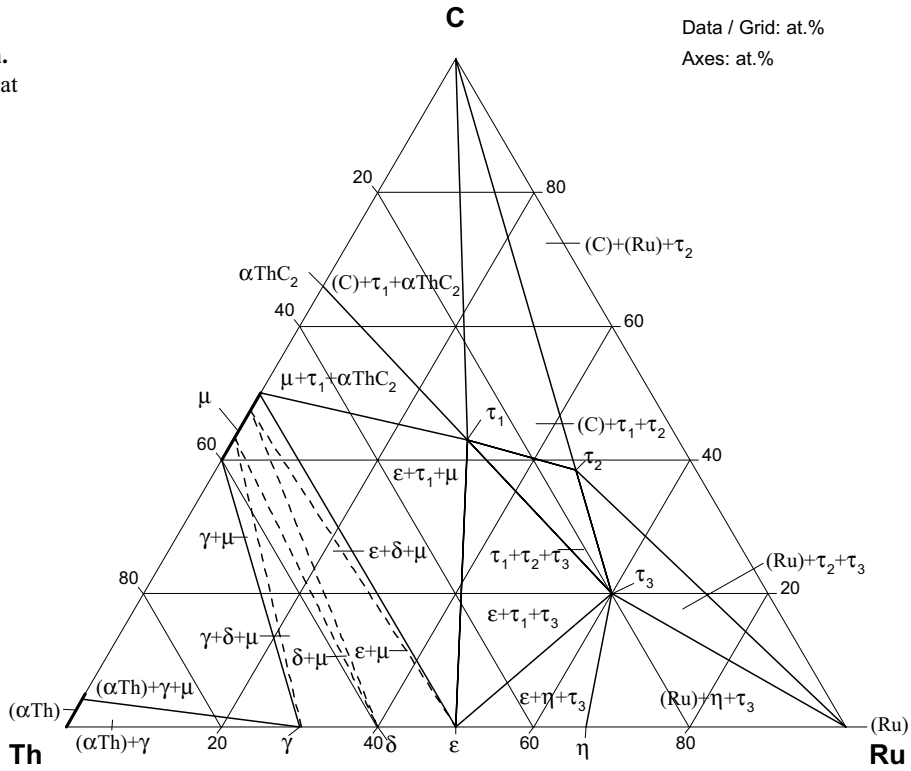

Fig. 2: C-Ru-Th. Isothermal section at 900°C