

Carbon – Ruthenium – Uranium

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Introduction

Much attention has been paid to the C–Ru–U system because Ru is a product of nuclear fission and a knowledge of the phase relationships of U and C with Ru is of fundamental importance in the interpretation of irradiation experiments involving carbide fuel materials. Table 1 summarizes investigations of the phase relations and thermodynamics of the C–Ru–U system with the experimental techniques and the observed temperature and composition ranges are indicated.

Experimental phase equilibrium data for the C–Ru–U system were presented as isothermal sections at 1300°C [1970Hol, 1975Hol, 1984Hol1, 1984Hol2] and 1000°C [1970Hai, 1991Ale] along with a liquidus surface projection [1970Hai, 1991Ale]. The C–Ru–U isothermal section at 1300°C was established by [1970Hol]. [1970Hol] arc-melted and sintered samples of different compositions that were then characterized by X-ray powder photography, metallography and microanalysis. The system contains one ternary solid phase, U_2RuC_2 that is formed peritectically. The C–Ru–U isothermal section at 1300°C was later refined by the same group of authors [1975Hol, 1984Hol1, 1984Hol2]. [1970Hai] investigated the phase equilibria in the C–Ru–U system using as-cast and equilibrated alloys. The peritectic temperature for the decomposition of U_2RuC_2 was determined to be close to 1500°C by heating a sample of this compound at various temperatures, and then rapidly quenching and examining ceramographically to determine whether liquid had been formed. A schematic diagram of the primary crystallizing phases in the C–Ru–U system, which was indicated with different symbols for different alloys, was also presented by [1970Hai]. It should be noted that the binary phase U_2Ru , which is unstable at 1000°C according to the accepted Ru–U phase diagram, is indicated on the isothermal section at 1000°C by [1970Hai].

From an analysis of the literature data on the binary boundary systems and the C–Ru–U ternary alloys, about 30 topologically nonequivalent isothermal sections in the temperature range from 850 to 2430°C were presented by [1991Ale]. They used a systematic approach that provided a means of establishing the topology of the C–Ru–U phase diagram. Fifteen four-phase equilibria were proposed and the reaction temperatures for these invariant equilibria were estimated. [1991Ale] presented the isothermal section at 1000°C and the liquidus surface projection of the C–Ru–U system in terms of the experimental data obtained by [1970Hai].

A ternary compound U_2RuC_2 was first reported by [1968Hol, 1969Hai]. The crystal structure of the U_2RuC_2 ternary phase and its stability range were investigated by [1968Hol, 1969Hai, 1970Hai, 1970Hol]. [1969Hai] prepared U_2RuC_2 by arc-melting the elements side by side using a carbon electrode under an argon atmosphere (pressure 30 kNm^{−3}) previously gettered with molten zirconium. The as-cast alloy with a nominal composition of U_2RuC_2 showed a complex structure consisting of a U carbide, a U-metal binary alloy phase and the ternary compound. The alloy became single-phase if annealed at temperatures of up to 1500°C in vacuum for longer than 100 h. In view of the experimental observation that U_2RuC_2 decomposed to a U carbide and liquid on heating to ~1700°C, it is suggested that this ternary compound is formed peritectically. The crystal structure and lattice parameters of U_2RuC_2 [1969Hai] were determined via X-ray powder photography using an 11 cm Debye-Scherrer camera.

Thermodynamic properties of the U_2RuC_2 and URu_3C_x phases was reported by [1970Hol, 1991Kle1] following electromotive force studies and were reviewed by [1991Kle2].

Information about phase equilibria in the C–Ru–U system is still incomplete. In particular, the existence of the proposed invariant four-phase equilibria [1991Ale] needs experimental verification. Available data regarding the solidus and solvus surfaces are also very limited. More work is required to establish the phase equilibrium relationships at different temperatures and a complete reaction scheme.

Binary Systems

The binary systems C–Ru, C–U and Ru–U are accepted from [Mas2].

Solid Phases

Solid phase data are listed in Table 2. The η phase (URu_3) exhibits a considerable solubility for carbon (up to about 15 at.% C at 1300°C). The ternary phase τ does not possess a visible homogeneity range and is formed peritectically at a temperature of about 1727°C [1984Hol1, 1984Hol2].

Invariant Equilibria

The invariant reactions are listed in Table 3 according to [1991Ale] who used the experimental data of [1970Hai]. Corrections have been made according to the constitution of the accepted binary systems. A partial reaction scheme is presented in Fig. 1.

Liquidus, Solidus and Solvus Surfaces

The partial liquidus surface projection is shown in Fig. 2, which is based mainly on the work of [1991Ale]. Some corrections have been made according to the constitution of the accepted binaries. It should be noted that, unlike the data of [1991Ale], the μ phase does not exist in the liquid state according to [Mas2].

Isothermal Sections

The isothermal section at 1300°C presented in Fig. 3 is based on [1970Hol, 1975Hol, 1984Hol1, 1984Hol2] with the amendment of up to 6 at.% C in the liquid phase in U rich corner in order to be consistent with the accepted C–U phase diagram. According to the accepted Ru–U phase diagram, the η phase does not possess a visible homogeneity range, whereas in [1970Hol], it is shown with a homogeneity range of about 74 to 75 at.% Ru falling with the addition of the third element C.

The isothermal section for 1000°C according to [1970Hai, 1991Ale] is shown in Fig. 4 with the phase boundaries of the binary phases altered or corrected, especially for U_2Ru , which is unstable at 1000°C according to the accepted Ru–U binary phase diagram.

Thermodynamics

The Gibbs energies of formation of URu_3 and URu_3C_x were determined by [1970Hol] using the emf method employing a solid CaF_2 electrolyte. The standard entropy of URu_3 and the Gibbs free energy of formation of U_2RuC_2 were estimated. [1991Kle1] performed thermodynamic measurements for the binary phases (URu_3 and U_3Ru_5) and the ternary carbides ($\text{URu}_3\text{C}_{0.7}$ and U_2RuC_2) between 950 and 1200 K (677 to 927°C) using galvanic cells employing CaF_2 single crystal electrolytes: U, $\text{UF}_3|\text{CaF}_2|\text{UF}_3$, URu_3 , Ru; U, $\text{UF}_3|\text{CaF}_2|\text{UF}_3$, U_3Ru_5 , URu_3 ; Ru, URu_3 , $\text{UF}_3|\text{CaF}_2|\text{UF}_3$, $\text{URu}_3\text{C}_{0.7}$, Ru, C; U, $\text{UF}_3|\text{CaF}_2|\text{UF}_3$, $\text{URu}_3\text{C}_{0.7}$, U_2RuC_2 , C. The Gibbs energies of formation of URu_3 , U_3Ru_5 , $\text{URu}_3\text{C}_{0.7}$ and U_2RuC_2 were evaluated from the measured emf. According to the work of [1991Kle1], the reaction of UC_{1+x} with the fission product ruthenium is possible according to the reaction $2\text{UC} + \text{Ru} \rightleftharpoons \text{U}_2\text{RuC}_2$, where relative partial molar Gibbs energy of ruthenium is $\Delta G_{\text{Ru}} = -108000 \text{ J}\cdot\text{mol}^{-1}$ at 827°C. Further reaction of Ru follows the equation $\text{U}_2\text{RuC}_2 + \text{Ru} \rightleftharpoons 2\text{URu}_3\text{C}_{0.7} + 0.6\text{C}$, where $\Delta G_{\text{Ru}} = -11450 \text{ J}\cdot\text{mol}^{-1}$. Both types of phases were observed in irradiated nuclear carbide fuels.

Experimentally measured thermodynamic data for several reactions and those for the η and τ phases are listed in Tables 4 and 5, respectively.

Notes on Materials Properties and Applications

The C–Ru–U alloys are the prospective materials for nuclear technology applications as alloys consisting of uranium carbide containing the transition metal ruthenium.

The thermal diffusivity of the U_2RuC_2 phase was measured by [1985Ara] over the temperature range 750 to 1500 K (477 to 1227°C). The temperature dependence obtained is shown in Fig. 5. These values are not corrected for porosity. The thermal conductivity of U_2RuC_2 was calculated using the thermal diffusivity data, the heat capacity and the density of the samples. Because thermal expansion and heat capacity data for U_2RuC_2 were not available, the thermal expansion data of UC were used and heat capacity values were estimated from the sum of those for the individual components as a first approximation. Fig. 6 presents the thermal conductivity of U_2RuC_2 over the temperature range 750 to 1500 K (477 to 1227°C) corrected to 100% theoretical density. The solid line in Fig. 6 was obtained by fitting the experimental data to second order equations using the least squares method.

The magnetic susceptibility of the U_2RuC_2 phase was investigated by [1996Ebe] using a SQUID magnetometer with magnetic flux densities of up to 5.5 T over the temperature range 2 and 300 K (–271°C to 27°C). This phase shows temperature-dependent paramagnetism (Fig. 7) with a room temperature susceptibility of $\chi_{\text{mol}} = (27 \pm 1) \cdot 10^{-9} \text{ m}^3 (\text{f.u})^{-1}$. The magnitude of this susceptibility is considerably higher (at least by a factor of 10) than the Pauli paramagnetism of ordinary metals.

Miscellaneous

[1970Hol] measured the lattice parameter of the URu_3C_x phase with respect to C content, which is shown in Fig. 8.

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Table 1: Investigation of the C-Ru-U Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1968Hol]	X-ray Debye-Scherrer and Guinier	1300-1600°C, $\sim \text{U}_2\text{RuC}_2$
[1969Hai]	X-ray Debye-Scherrer	< 1500°C, U_2RuC_2
[1970Hai]	Metallography, microanalysis	Primary crystallizing phases Limited data in the temperature range of 1000 to 1500°C. Solid solubility of Ru in UC and U_2C_3 . Solid solubility of C in URu_3
[1970Hol]	Arc melting, sintering, X-ray Debye - Scherrer studies, metallography, Microanalysis, emf measurements	587-797°C, 1300-1500°C, whole composition range
[1985Ara]	Sintering, X-ray diffraction studies, chemical analysis, density and thermal diffusivity measurements	477 to 1227°C, U_2RuC_2
[1991Kle1]	Emf measurements	747 to 927°C, $\text{URu}_3\text{C}_{0.7}$, U_2RuC_2

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1991Kle2]	Emf measurements	747 to 927°C, URu ₃ C _{0.7} , U ₂ RuC ₂
[1996Ebe]	Arc melting, annealing, X-ray Guinier studies, SQUID magnetic susceptibility measurements	–271 to 27°C, 900°C, U ₂ RuC ₂

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	<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)
(Ru) < 2334	<i>hP2</i> <i>P6₃/mmc</i> Mg	<i>a</i> = 270.58 <i>c</i> = 428.16	at 25°C [Mas2] dissolves 3 at.% C at 1940°C; ~1.3 at.% C at 1850°C [Mas2]
(γU) (h ₂) 1135 - 776	<i>cI2</i> <i>Im$\bar{3}m$</i> W	<i>a</i> = 352.4	[Mas2] dissolves 0.22 at.% C at 1119 ± 1°C [Mas2] dissolves ~4.5 at.% Ru at 886°C [Mas2]
(βU) (h ₁) 776 - 668	<i>tP30</i> <i>P4₂/mm</i> βU	<i>a</i> = 1075.9 <i>c</i> = 565.6	[Mas2] dissolves 0.02 at.% C at 772°C [Mas2] dissolves 2 at.% Ru at 681°C [Mas2]
(αU) (r) < 668	<i>oC4</i> <i>Cmcm</i> αU	<i>a</i> = 285.37 <i>b</i> = 586.95 <i>c</i> = 495.48	at 25°C [Mas2] dissolves ~ 6·10 ^{–3} at.% C at 660°C [Mas2] dissolves ~ 1.1 at.% Ru at 625°C [Mas2]
γ, U ₂ Ru 937 - at least <400	<i>mP12</i> <i>P2/m</i> or <i>P2₁/m</i> U ₂ Ru	<i>a</i> = 1310.6 <i>b</i> = 334.3 <i>c</i> = 520.2 β = 96.16°	33.3 at.% Ru [Mas2] [1961Ber]
βURu (h ₂) 1158 - 795	-	-	47.2 at.% Ru [Mas2]
αURu (h ₁) 795 - at least <400	-	-	47.2 at.% Ru [Mas2]
δ, U ₃ Ru ₄ 1163 - at least <400	-	-	57 at.% Ru [Mas2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
ϵ , U_3Ru_5 1182 - at least <400	-	-	62.5 at.% Ru [Mas2]
η , URu_3 1850 - at least <400	$cP4$ $Pm\bar{3}m$ AuCu_3		75 at.% Ru [Mas2]
URu_3C_x		$a = 398.8$ to 406	$x = 0$ to 0.7 (0 to 14.9 at.% C), 1300°C [1970Hol]
κ , UC (I) 2585 - 1119	$cF8$ $Fm\bar{3}m$ NaCl	$a = 495.98$ $a = 495.63$ $a = 495.1$ $a = 496$ to 496.2 $a = 507$ $a = 495.6$ $a = 496.05$	47 to 66 at.% C [Mas2] [E] at 48 at.% C [S] [1957Kie] [1961Ben] at 2100°C [1972Ben] at 1400°C [S] at 25°C [1972Ben]
UC (II) > $2.7 \cdot 10^5$ bar	r^{**}	-	[1987Ben]
λ , U_2C_3 1823 - ~850	$cI40$ $\bar{I}43d$ Pu_2C_3	$a = 808.8$ $a = 808.90$ $a = 808.89$	60 at.% C [Mas2] [H] [S] [1972Ben]
μ , UC_2 1793 - 1516	$tI6$ $I4/mmm$ CaC_2	$a = 351.7$ $c = 598.7$ $a = 352.4$ $c = 599.9$ $a = 351.9$ to 352.41 $c = 597.87$ to 599.62 $a = 352.7$ $c = 598$	62 to 62.5 at.% C [Mas2] [E] [H] [S] [1961Ben]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
UC ₂ 2434 - 1762	<i>cF12</i> <i>Fm$\bar{3}m$</i> CaF ₂ ?	$a = 545.0$	actually, “UC ₂ ” phase represents the κ ,UC phase in equilibrium with graphite [2001Che]
* τ , U ₂ RuC ₂ ≤ 1727	<i>tI*</i> <i>I4/mmm</i> U ₂ IrC ₂	$a = 344.5$ $c = 1252$	[1968Hol]
		$a = 344.89$ $c = 1257.08$	annealing up to 1500°C in vacuum during 100 h [1969Hai]
		$a = 344.5$ to 345.5 $c = 1256.3$ to 1259.2	annealing at 1300°C in vacuum [1970Hol]
		$a = 344$ $c = 1256$	sintering at 1550°C about 7 h in argon [1985Ara]

Table 3: Invariant Equilibria

Reaction	T [°C]	Type	Phase	Composition (at.%)		
				C	Ru	U
L + (Ru) \rightleftharpoons η + (C)	~1700	U ₁	L	~17	~61	~22
L + (C) \rightleftharpoons η + τ	1475 \pm 25	U ₂	L	~17	~58	~25

Table 4: Thermodynamic Data of Reactions

Reaction	T [°C]	Quantity, per mole of atoms [kJ, mol, K]	Comment
URu ₃ + 2Ru + (2 + x)C \rightleftharpoons URu ₃ C _{x} + 2Ru + 2C	587 - 797	$\Delta G = -222.32 - 0.029 \cdot T \pm 4.187$	[1970Hol], emf
URu ₃ + 0.7C \rightleftharpoons URu ₃ C _{0.7}	767 - 867	$\Delta G = -192.6 + 0.025 \cdot T \pm 4.1$	[1991Kle1], emf
1/3 {5U + 5.3C + URu ₃ C _{0.7} \rightleftharpoons 3U ₂ RuC ₂ }	747 - 927	$\Delta G = -380.2 + 0.0525 \cdot T \pm 3.6$	[1991Kle1], emf

Table 5: Thermodynamic Properties of Single Phases

Phase	Temperature Range [°C]	Quantity, per mole of atoms [kJ, mol, K]	Comment
URu ₃ C _{x}	727	$^f\Delta H^\circ = -222319 \pm 12560.4$	[1970Hol], emf
	727	$^f\Delta S^\circ = -29.3 \pm 8.4$	[1970Hol], emf
	727	$^f\Delta G^\circ = -251627 \pm 4186.8$	[1970Hol], emf
	827 ($x = 0.7$)	$^f\Delta G^\circ = -189800$	[1991Kle1], emf
U ₂ RuC ₂	827	$^f\Delta G^\circ = -155540$	[1991Kle1], emf

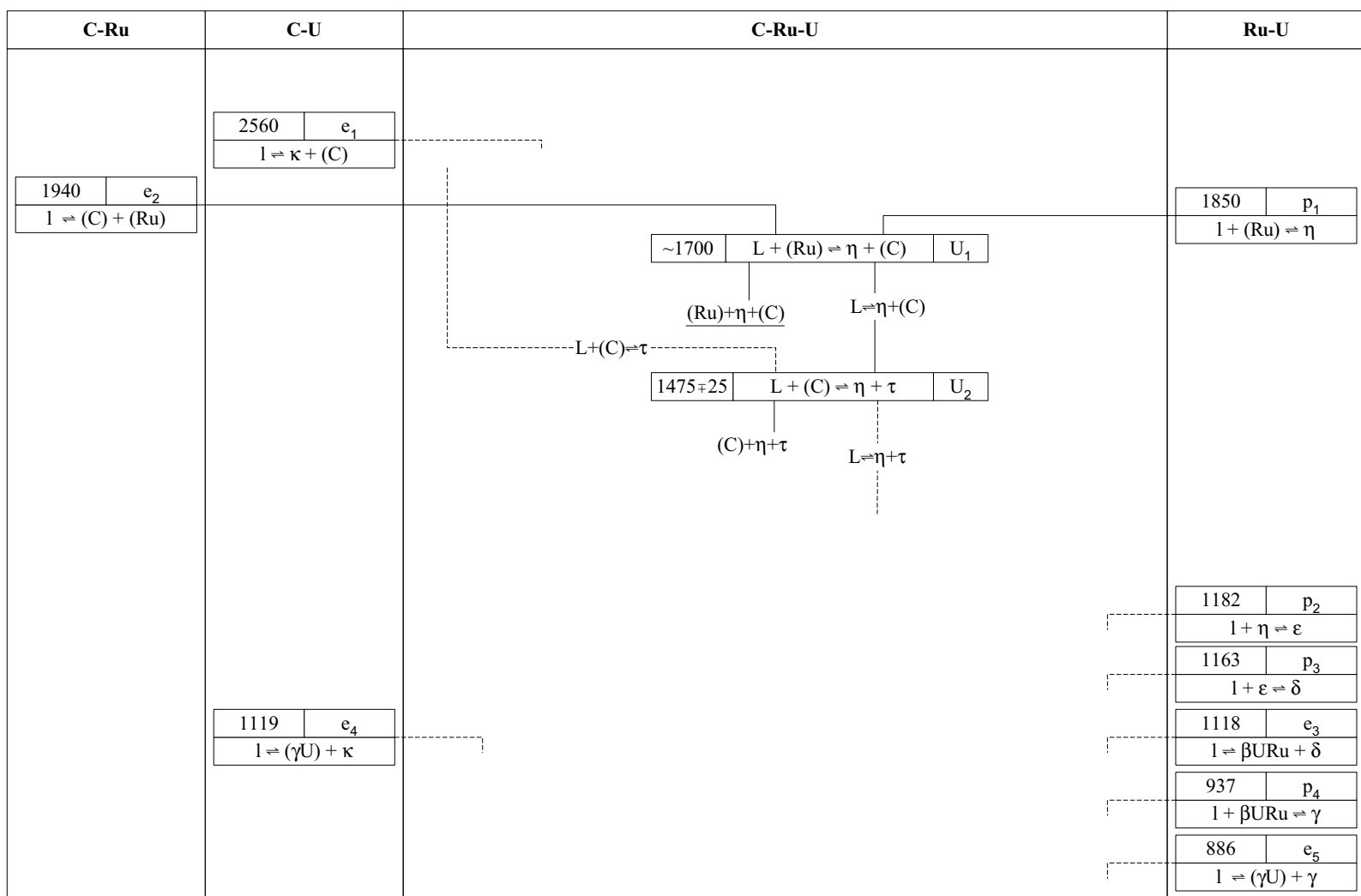


Fig. 1: C-Ru-U. Partial reaction scheme

Fig. 2: C-Ru-U.
Partial liquidus
surface projection

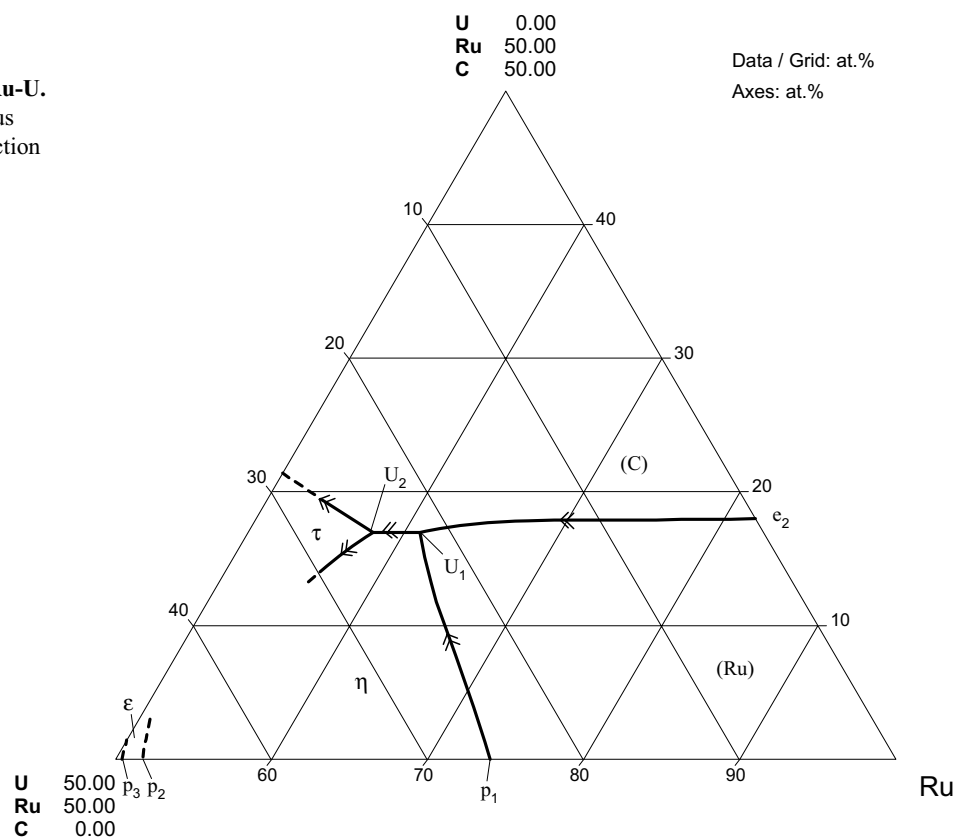


Fig. 3: C-Ru-U.
Isothermal section at
1300°C

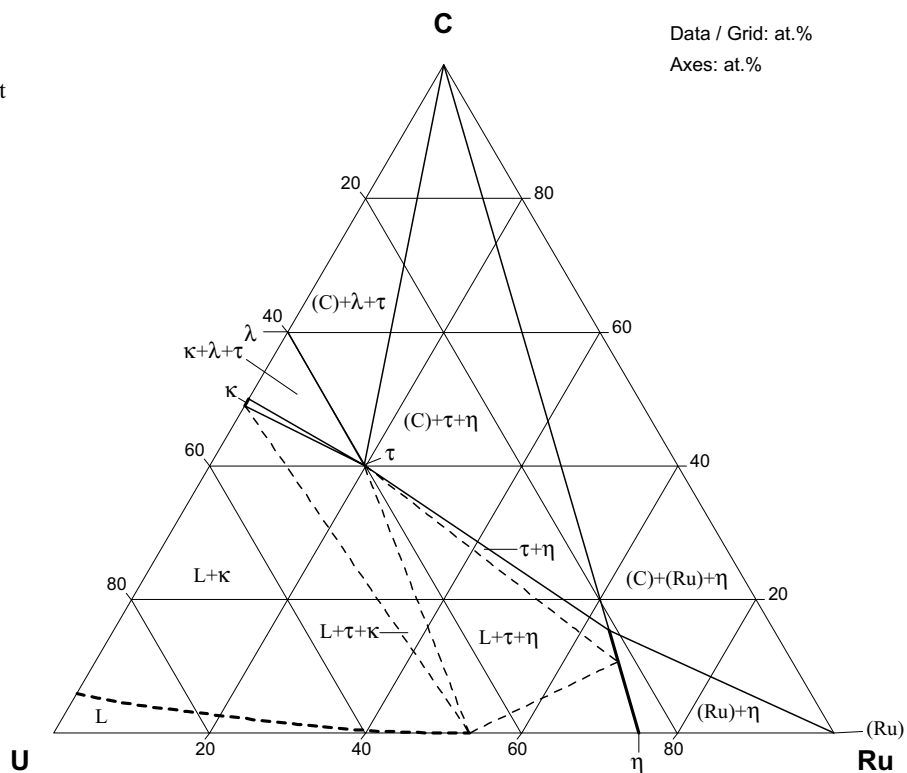


Fig. 4: C–Ru–U.
Isothermal section at
1000°C

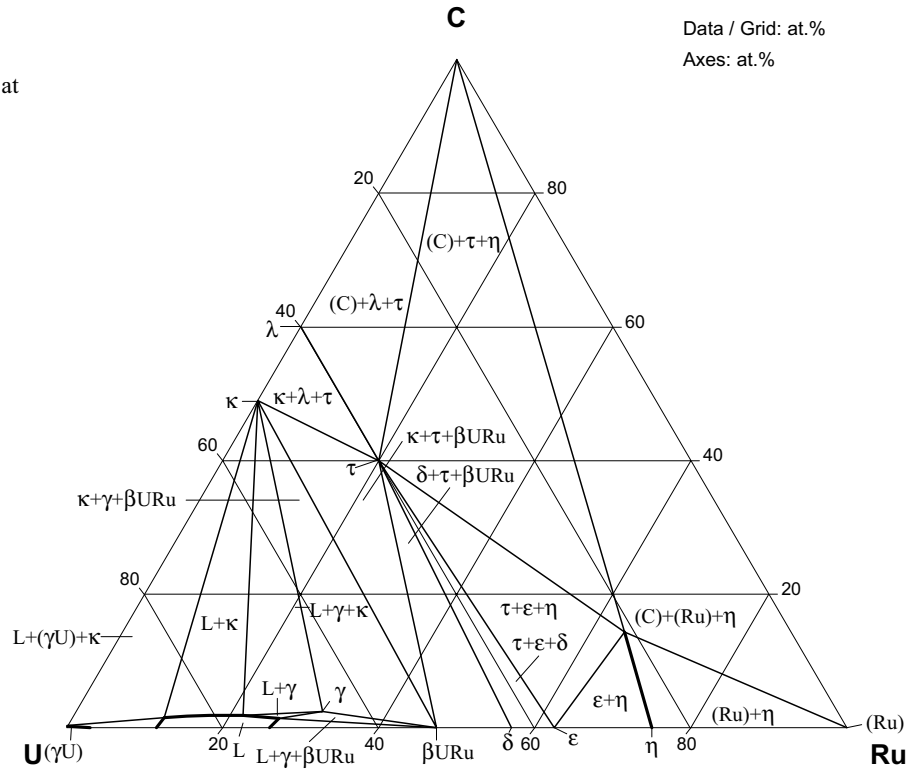


Fig. 5: C–Ru–U.
Thermal diffusivity of
 U_2RuC_2

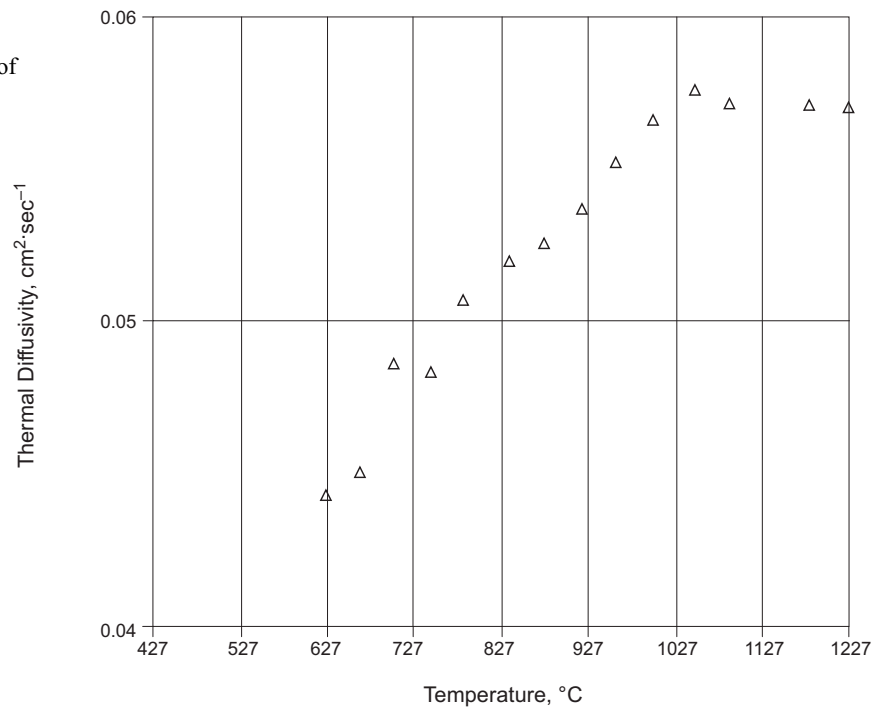


Fig. 6: C-Ru-U.
Thermal conductivity
of U_2RuC_2
normalized to 100%
theoretical density

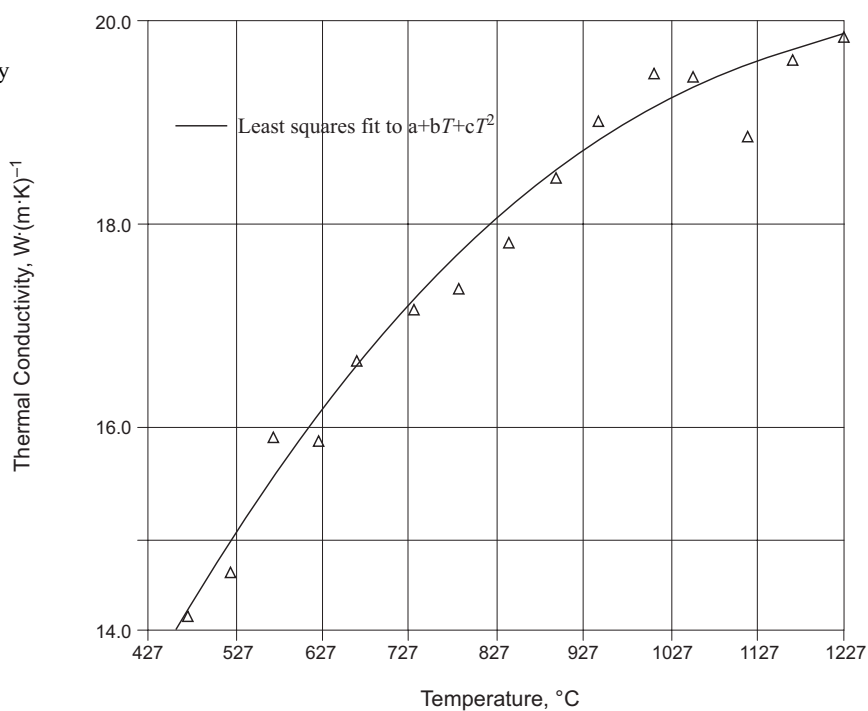


Fig. 7: C-Ru-U.
Magnetic
susceptibility of
 U_2RuC_2 as a function
of temperature,
measured with a
magnetic flux density
of 5 T

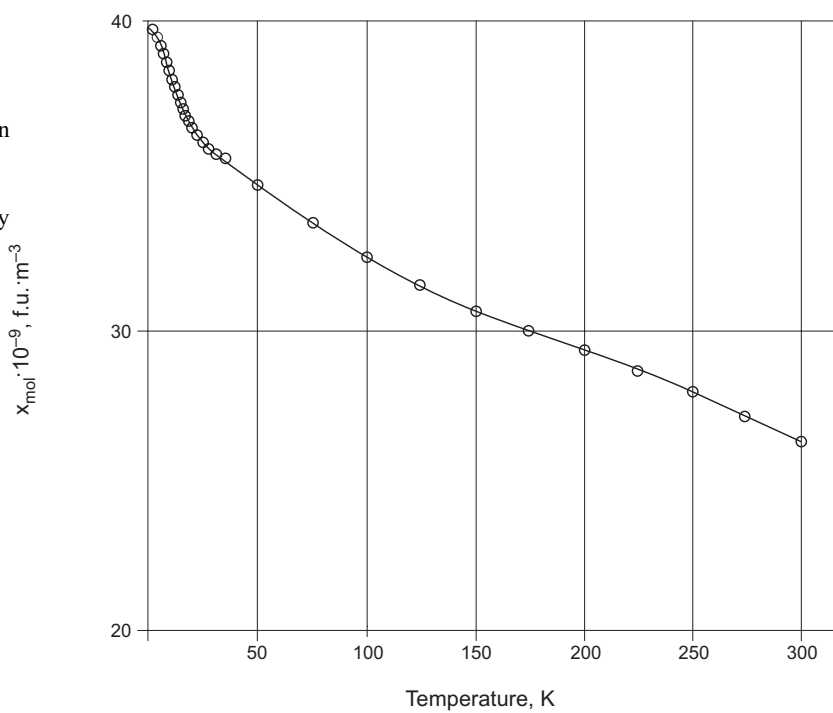


Fig. 8: C-Ru-U.
Lattice parameter of
 URu_3C_x with respect
to C content

