

Carbon – Uranium – Zirconium

Pierre Perrot

Introduction

Investigations of the phase equilibria up to 2200°C by [1957Kie, 1957Now1, 1958Bro, 1958Now, 1963Rud1] using X-ray diffraction showed that UC and ZrC form a continuous solid solution. The solid solution is observed both from rapid cooling of the liquid mixture and from annealing at temperatures above 500°C [1958Iva]. According to early investigations [1957Now2, 1958Now], lattice parameter of this solid solution shows a slightly negative deviation from Vegard's law. However, subsequent work [1961Iva, 1963Rud1, 1965Kut, 1968Nic] indicated that Vegard's law holds for this phase within experimental uncertainties. Using a disappearing-filament optical pyrometer, [1958Bro] measured the liquidus curve along the UC–ZrC section. The partial isothermal section at 1700°C within the composition range bounded by C, UC, and ZrC was determined by [1961Ben] using XRD technique. The whole isothermal section at 1700°C was constructed by [1975Hol] using the literature data, supplemented with approximate thermodynamic calculation. Based on XRD technique, [1968Nic] measured the phase relations at 1700, 1900 and 2000°C within the U–Zr–UC–ZrC subsystem.

Binary Systems

The adopted C–Zr phase diagram is due to [1995Fer] who considered the experimental data of [1993But]. The C–U and U–Zr phase diagrams are taken from [2001Che] and [2004Che], respectively. It should be noted that C–U diagram essentially the same as in [Mas2] and U–Zr diagram differs from the one presented in [Mas2]. In the temperature range relevant to the known C–U–Zr equilibria it differs by the position of the L+ β two phase domain.

Solid Phases

The solid phases are presented in Table 1.

Quasibinary Systems

The quasibinary system UC–ZrC_{0.81} established by [1993But, 1994But] is shown in Fig. 1. The miscibility gap at temperatures below 1378°C calculated by [1982Ogo] has not been confirmed experimentally.

Isothermal Sections

The isothermal section at 1700°C presented in Fig. 2 is mainly based on [1961Ben, 1968Nic, 1975Hol]. In order to be consistent with the accepted binaries, the presented isothermal section is slightly modified. This section is in qualitative agreement with the observations of [1968Ale] who measured lattice parameters of the carbides resulting from the reaction between UC and Zr. In the work of [1968Ale], the reaction temperature is not specified. The isothermal sections at 1900 and 2000°C presented by [1968Nic] and the section at 2027°C by [1973Sto] differ from the section at 1700°C in that the ZrC contents of the solid solution (U,Zr)C in equilibrium with the C and UC₂ are reported to be relatively large (68 ± 2 mol% ZrC at 1900°C, 77 ± 2 mol% ZrC at 2000°C, and 78 mol% ZrC at 2027°C), compared with the value of 61 ± 3 mol% ZrC at 1700°C. Several isothermal sections above 2200°C are presented by [1993But], who performed graphical and numerical curve fitting of self-consistent thermodynamic and phase diagram data available in the literature. Figures 3 to 8 show the isothermal sections at 2200, 2410, 2480, 2600, 2850, and 3000°C established by [1993But], respectively. The isothermal section at 3420°C [1993But] shows that C would be in equilibrium with a liquid phase containing approximately 80 at.% C, below which there is a single liquid phase region.

Temperatue – Composition Sections

The vertical section UC₂–ZrC reported by [1973Sto, 1993But] is presented in Fig. 9.

Thermodynamics

The excess Gibbs energy of mixture for the solid solution (U,Zr)C has been evaluated by [1963Rud1, 1963Rud2] using a regular solution model applied to the observed phase relationship. The following expression may be used in the temperature range 1700–1900°C: $\Delta_{\text{mix}}G^{\text{XSJ}} = \alpha x_{\text{UC}}x_{\text{ZrC}}$ with $\alpha = 25.2 \text{ kJ}\cdot\text{mol}^{-1}$. A more precise measurement using the time-of-flight mass spectrometer [1971Hoc] yields a value of $28.0 \pm 2.4 \text{ kJ}\cdot\text{mol}^{-1}$ at 1960°C for α . This value is close to that for the (γ U, β Zr) body centered solid solution. This later value for α leads to a critical point of 1411°C for the solid solution (U,Zr)C, which agrees reasonably with the value of 1378°C calculated by [1982Ogo]. High temperature mass spectrometry was used by [1973Sto] to measure the activities of U and Zr in the (U,Zr)C solid solution in equilibrium with C and UC₂. The solid solution between ZrC and UC was found to be ideal at 1917°C with an increasingly positive enthalpy of mixing as temperature increases. The stability of the solution apparently results from the metal-carbon interactions with a repulsive contribution from the metal-metal interactions above 1917°C.

The heat content of the solid solution U_{1-x}Zr_xC ($x < 0.05$) between 500 and 2500°C has been measured by [1969Boc]. The dissolution of Zr in UC increases slightly the heat content of the solid solution. A more precise description of the solid solutions is obtained by [1982Oga] who took into account the homogeneity ranges of the carbides.

Notes on Materials Properties and Applications

Because of its excellent nuclear and high temperature properties, the C–U–Zr system is attractive as a basis for high temperature nuclear fuels. The (U,Zr)C solid solution and (U,Zr)C + C composite materials may be materials of choice for the manned mission to Mars because of their excellent nuclear properties and thermal stability.

The penetration rate of UC in various metals at 400°C has been investigated by [1962Kat]. The UC–Zr system is considered as a “rapid” reacting system, because the penetration depth is higher than 50 μm in 10 days.

The influence of small additions of C on the morphology and mechanical properties of U–Zr alloys has been investigated by [1962Cra]. In view of application of such alloys as nuclear fuels, the effect of irradiation is also discussed.

Miscellaneous

The average thermal linear expansion coefficients in the temperature range of 25 to 1000°C has been measured for different compositions of the solid solution [1965Kem, 1969Boc] and were found to be $6.4\cdot 10^{-6} \text{ K}^{-1}$ for pure ZrC, $7.28\cdot 10^{-6} \text{ K}^{-1}$ for the composition U_{0.3}Zr_{0.7}C_{0.97} [1965Kem], $10.64\cdot 10^{-6} \text{ K}^{-1}$ for the composition U_{0.9}Zr_{0.17}C and $10.8\cdot 10^{-6} \text{ K}^{-1}$ for pure UC [1969Boc].

References

- [1957Kie] Kieffer, R., Benesovsky, F., Nowotny, H., “About the Production of Uranium Monocarbide and its Behavior Compared with Other High Melting Carbide” (in German), *Planseeber. Pulvermet.*, **5**, 33–35 (1957) (Experimental, Phys. Prop., 7)
- [1957Now1] Nowotny, H., Wittman, A., “Structure of Metalloid-Containing Phases in Alloys” (in German), *Radex Rundsch.*, **5-6**, 693–707 (1957) (Phase Relations, Cryst. Structure, Review, 39)
- [1957Now2] Nowotny, H., Kieffer, R., Benesovsky, F., Laube, E., “The Partial Systems: UC–TiC, –ZrC, –VC, –NbC, –TaC, –Cr₃C₂, –Mo₂C, and –WC” (in German), *Monatsh. Chem.*, **88**, 336–343 (1957) (Cryst. Structure, Experimental, 13)

- [1958Bro] Brownlee, L.D., “The Pseudo-Binary Systems of Uranium Carbide with Zirconium Carbide, Tantalum Carbide, and Niobium Carbide”, *J. Inst. Met.*, **87**(2), 58-61 (1958) (Phase Diagram, Crys. Structure, Experimental, 16)
- [1958Iva] Ivanov, V.E., Badajeva, T.A., “Phase Diagrams of Certain Ternary Systems of Uranium and Thorium”, *2nd Internat. Conf. on the Peaceful Uses of Atomic Energy, Geneva*, Paper A/CONF.15/P/2043, **6**, 139-155 (1958) (Phase Diagram, Phase Relations, Review, 2)
- [1958Now] Nowotny, H., Kieffer, R., Benesovsky, F., “Preparation of UC and its Relation to the Carbides of Refractory Transition Metals” (in French), *Rev. Metall.*, **55**(5), 453-458 (1958) (Crys. Structure, Experimental, 11)
- [1961Ben] Benesovsky, F., Rudy, E., “On the Systems U-Zr(Hf, Nb, Ta)-C” (in German), *Planseeber. Pulvermet.*, **9**, 65-76 (1961) (Phase Diagram, Crys. Structure, Experimental, 11)
- [1961Iva] Ivanov, O.S., Alekseeva, Z.M., “Investigation of the UC-ZrC, UC-ThC and ThC-ZrC Systems”, in “*Structure of Alloys in Some Systems with Uranium and Thorium*”, (in Russian), Gosatomizdat, Moscow, 438-449 (1961) (Crys. Structure, Experimental, Mechan. Prop., 4)
- [1962Cra] Craik, R.L., Birch, D., Fizzotti, C., Saraceno, F., “Phase Equilibria in Uranium-Rich Binary Alloys Containing Molybdenum and Zirconium and the Effect of Ternary Additions of Carbon”, *J. Nucl. Mater.*, **6**(1), 13-25 (1962) (Phase Diagram, Phase Relations, Mechan. Prop., Morphology, 17)
- [1962Kat] Katz, S., “High Temperature Reactions between Refractory Uranium Compounds and Metals”, *J. Nucl. Mater.*, **6**, 172-181 (1962) (Experimental, Phase Relations, Thermodyn., 21)
- [1963Rud1] Rudy, E., Benesovsky, F., “Stability of UC₂ and the C-Stable Regions in the Systems of UC with ZrC, HfC, NbC and TaC” (in German), *Monatsh. Chem.*, **94**, 204-224 (1963) (Phase Relations, Thermodyn., 19)
- [1963Rud2] Rudy, E., “Thermodynamics of the Phase Formation in Ternary Systems. II”, *Z. Metallkd.*, **54**, 213-223 (1963) (Phase Diagram, Thermodyn., 23)
- [1965Kem] Kempter, C.P., Merryman, R.G., “Thermal Expansion of a Uranium Monocarbide-Zirconium Monocarbide Solid Solution”, *J. Chem. Phys.*, **43**(5), 1736-1738 (1965) (Crys. Structure, Experimental, 14)
- [1965Kut] Kutka, J., Quaeck, I., Schenk, M., “Diffusion Studies in the C-U-Zr System. Investigation of a U-Zr Mixed Carbide” (in German), *J. Nucl. Mater.*, **15**, 129-132 (1965) (Crys. Structure, Diffusion, Experimental, 5)
- [1968Ale] Alekseeva, Z.M., “The Phase Composition of UC-Zr and Zr-ThC Alloys and the Relative Affinity of C for Zr, Th, and U” in “*Fiz. Khim. Splavov i Tugoplavkikh Soedineniy*” (in Russian), Ivanov, O.S. (Ed.), Nauka, Moscow, 136-139 (1968) (Crys. Structure, Mechan. Prop., Phase Relations, Experimental, 3)
- [1968Nic] Nickel, H., Inanc, Oe., Lücke, K., “On the Knowledge of the U-Zr-C System” (in German), *J. Nucl. Mater.*, **28**, 79-92 (1968) (Phase Relations, Crys. Structure, Experimental, 15)
- [1969Boc] Bocker, S., Boucher, R., “Some Properties of the Uranium Carbide with Small Additions of Zirconium” (in French), *J. Nucl. Mater.*, **33**(1), 30-39 (1969) (Crys. Structure, Mechan. Prop., 23)
- [1971Hoc] Hoch, M., Hapase, M.G., Yamauchi, S., “Thermodynamic Properties of Ternary Refractory Carbides. II. Zirconium-Uranium-Carbon and Zirconium-Hafnium-Carbon”, *J. Electrochem. Soc.*, **118**(9), 1503-1507 (1971) (Thermodyn., Experimental, 20)
- [1973Sto] Storms, E.K., Griffin, J., “Thermodynamic and Phase Relationships of the Zirconium-Uranium-Carbon System”, *High Temp. Sci.*, **5**, 423-437 (1973) (Crys. Structure, Experimental, Phase Diagram, Thermodyn., 15)
- [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, Thermodyn., Review, 47)
- [1982Oga] Ogawa, T., “Application of an Extended Regular Solution Model to Carbides of Group IVb, Vb and Actinide Metals”, *Scr. Metall.*, **16**(7), 781-785 (1982) (Calculation, Thermodyn., Phase Relations, 21)
- [1982Ogo] Ogorodnikov, V.V., Ogorodnikova, A.A., “Calculation of the Phase Diagrams for Pseudo-binary Systems of Cubic Transition Metal Monocarbides”, *Russ. J. Phys. Chem.*, **56**(11), 1749-1751 (1982), translated from *Zh. Fiz. Khim.*, **56**(11), 2852-2854, (1982) (Calculation, Phase Diagram, Thermodyn., 13)
- [1984Hol1] Holleck, H., “Ternary Carbide Systems of Actinoids with the Transition Metals of 4. to 8. Groups”, *J. Nucl. Mater.*, **124**, 129-146 (1984) (Crys. Structure, Phase Diagram, Review, 78)
- [1984Hol2] 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, Review, 91)
- [1993But] Butt, D.P., Wallace, T.C., “The U-Zr-C Ternary Phase Diagram Above 2473 K”, *J. Am. Ceram. Soc.*, **76**(6), 1409-1419 (1993) (Phase Diagram, Experimental, Thermodyn., *, #, 35)
- [1994But] Butt, D.P., Wallace, T.C., “A Simple Method for Calculating Two-Phase Equilibria in Ternary Systems”, *Calphad*, **18**(1), 1-7 (1994) (Calculation, Phase Relations, Thermodyn., Phase Diagram, 7)
- [1995Fer] Fernandez-Guillermot, A., “Analysis of Thermochemical Properties and Phase Stability in the Zirconium-Carbon System”, *J. Alloys Compd.*, **217**, 69-89 (1995) (Phase Diagram, Thermodyn., Assessment, #, 128)
- [2001Che] Chevalier, P.Y., Fischer, E., “Thermodynamic Modelling of the C-U and B-U Binary Systems”, *J. Nucl. Mater.*, **288**, 100-129 (2001) (Thermodyn., Calculations, Phase Relations, #, 97)
- [2004Che] Chevalier, P.Y., Fischer, E., Cheynet, B., “Progress in the Thermodynamic Modelling of the O-U-Zr Ternary System”, *Calphad*, **28**(1), 15-40 (2004) (Thermodyn., Calculations, Phase Relations, #, 92)

Table 1: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
C (graphite) < 3827	<i>hP4</i> <i>P6₃/mmc</i> C (graphite)	<i>a</i> = 246.12 <i>c</i> = 670.9	at 25°C [Mas2]
C (diamond)	<i>cF8</i> <i>Fd$\bar{3}m$</i> C (diamond)	<i>a</i> = 356.69	high pressure phase
(α U) < 668	<i>oC4</i> <i>Cmcm</i> α U	<i>a</i> = 285.37 <i>b</i> = 586.95 <i>c</i> = 495.48	at 25°C [Mas2] dissolves ~1 at.% Zr at 617°C
(β U) 776 - 668	<i>tP30</i> <i>P4₂/mnm</i> β U	<i>a</i> = 1075.9 <i>c</i> = 565.6	at 25°C [Mas2] dissolves ~2 at.% Zr at 693°C

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(α Zr) < 1360	<i>hP2</i> <i>P6₃/mmc</i> Mg	$a = 323.16$ $c = 514.75$	at 25°C [Mas2]
(γ U, β Zr)	<i>cI2</i> <i>Im$\bar{3}m$</i> W		solid solution (γ U, β Zr)
(γ U) 1135 - 776		$a = 352.4$	[Mas2]
(β Zr) 1855 - 863		$a = 360.90$	β Zr dissolves ~1 at.% C at 1805°C
η , UZr ₂ < 617	<i>hP3</i> <i>P6/mmm</i> AlB ₂	$a = 503$ $c = 308$	65 to 78 at.% Zr [2004Che]
(U,Zr)C	<i>cF8</i> <i>Fm$\bar{3}m$</i> NaCl		
U _{0.5} Zr _{0.5} C		$a = 482.2$	[1984Hol1, 1984Hol2]
δ , UC < 2515		$a = 495.97 \pm 0.4$	stoichiometric UC from 47 to 66 at.% C miscibility gap (critical point at 2050°C, 45 at.% C) [1993But, 2001Che]
ZrC < 3427		$a = 469.6$	33 to 50 at.% C [1995Fer] at 50 at.% C [1961Ben]
ζ , U ₂ C ₃ < 1833	<i>cI40</i> <i>I$\bar{4}3d$</i> Pu ₂ C ₃	$a = 808.9$	60 at.% C [1993But, 2001Che]
ϵ , UC ₂ 1762 - 1477	<i>tI6</i> <i>I4/mmm</i> CaC ₂	$a = 351.90 \pm 0.11$ $c = 597.87 \pm 0.17$	62 to 65.5 at.% C [Mas2] UC _{1.78} [2001Che]
		$a = 352.41 \pm 0.05$ $c = 599.62 \pm 0.08$	UC _{2.00} [2001Che]
δ , UC ₂ 2434 - 1762	<i>cF12</i> <i>Fm$\bar{3}m$</i> CaF ₂ ?	$a = 545.0$	actually, “ δ ,UC ₂ ” phase represents the δ ,UC phase in equilibrium with graphite [1993But, 2001Che]

Fig. 1: C-U-Zr.
The UC-ZrC_{0.81}
quasibinary phase
diagram showing
solidus and liquidus
temperature data for
the (U_yZr_{1-y})C_x
solid solutions

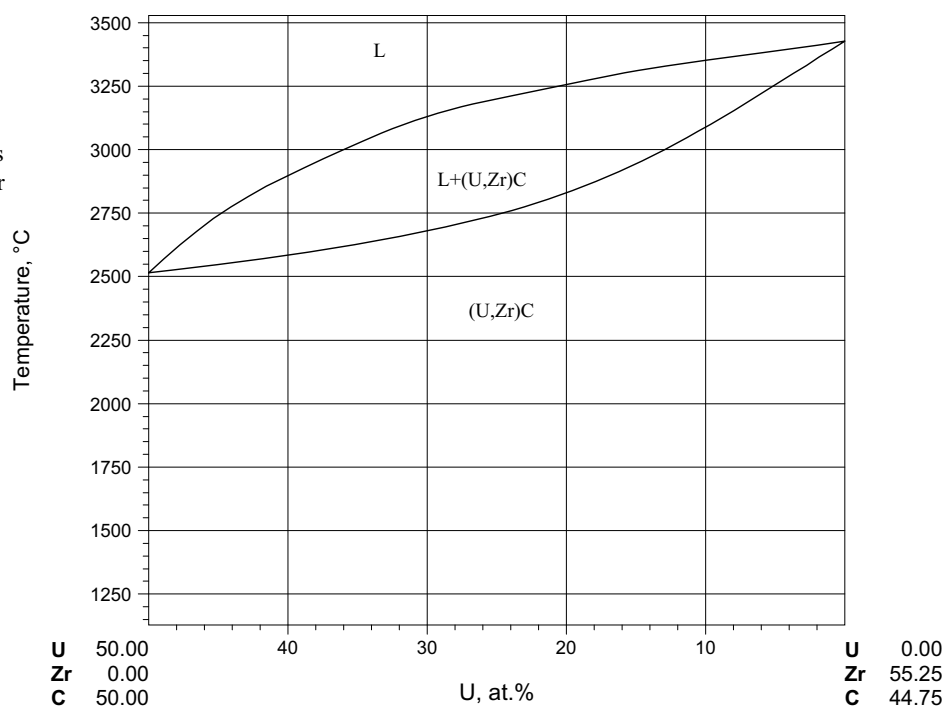


Fig. 2: C-U-Zr.
Isothermal section at
1700°C

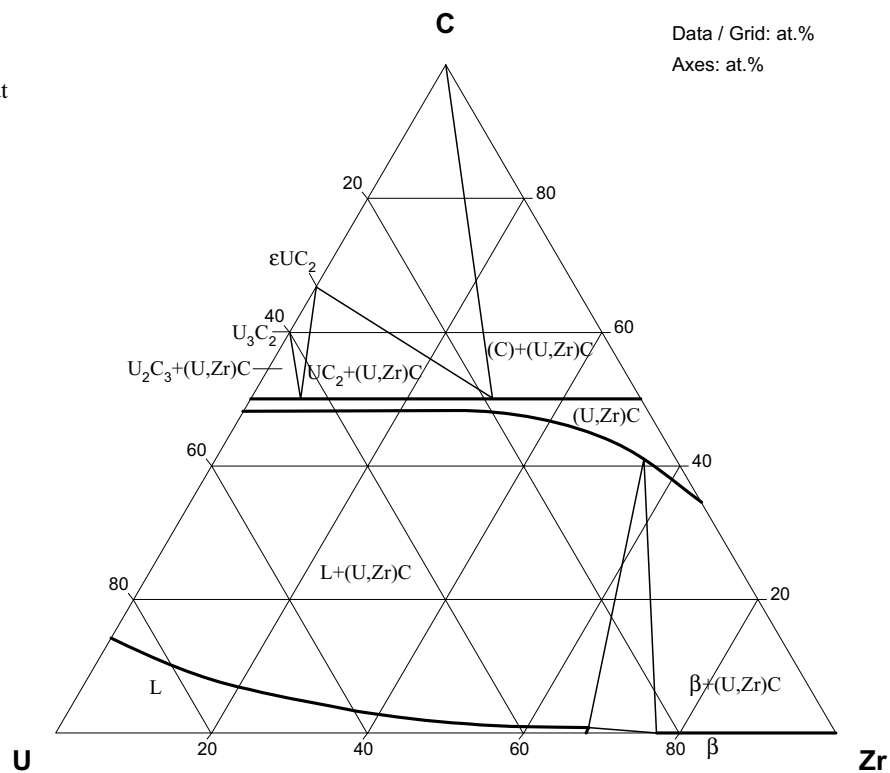


Fig. 3: C-U-Zr.
Isothermal section at
2200°C

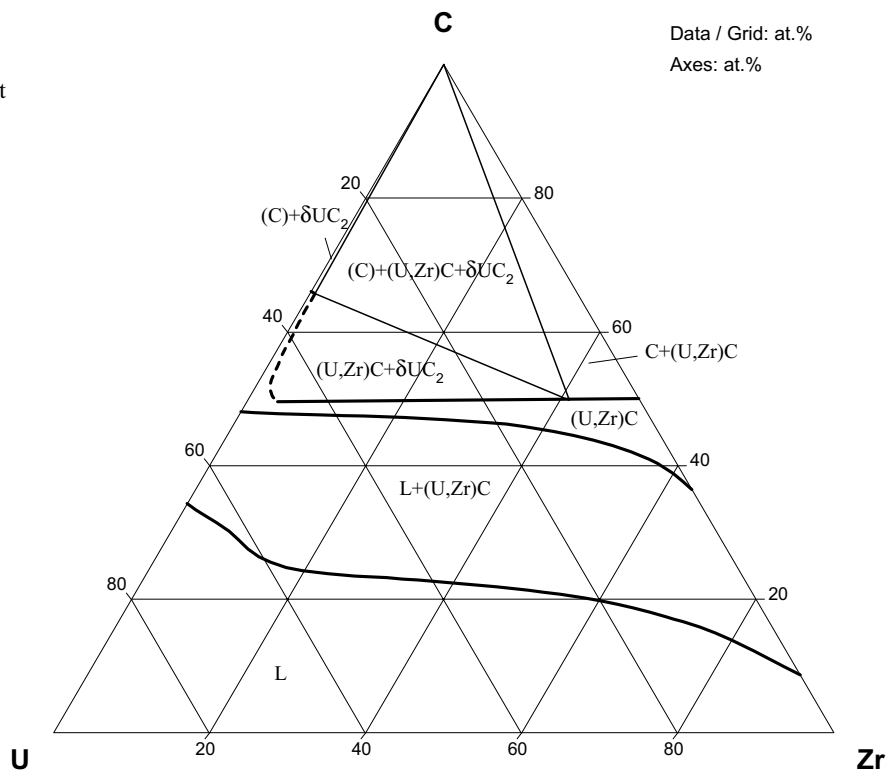


Fig. 4: C-U-Zr.
Isothermal section at
2410°C

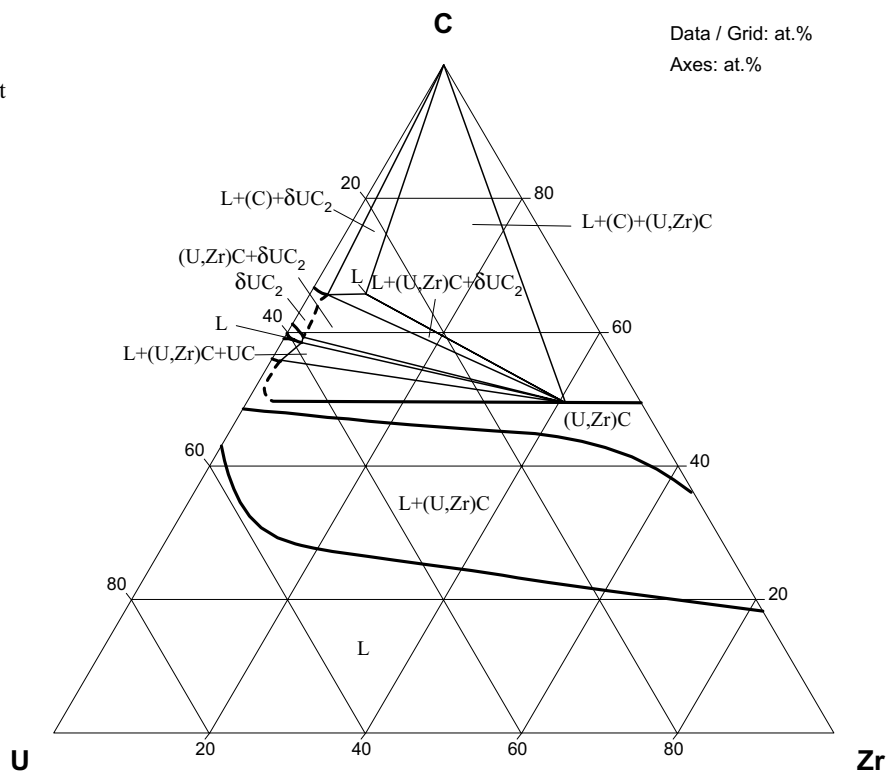


Fig. 5: C-U-Zr.
Isothermal section at
2480°C

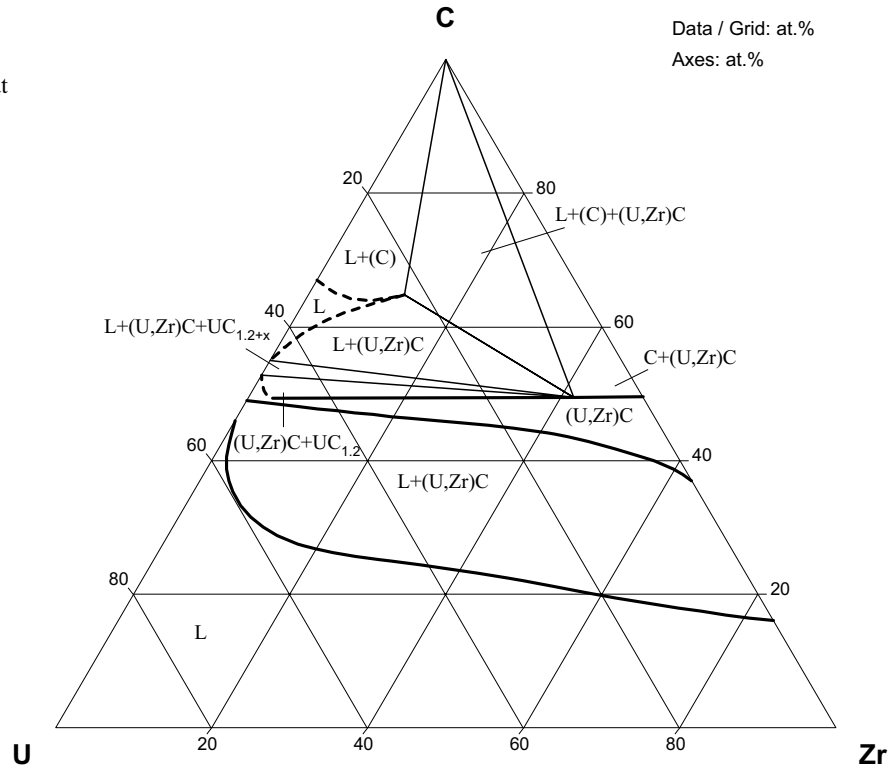


Fig. 6: C-U-Zr.
Isothermal section at
2600°C

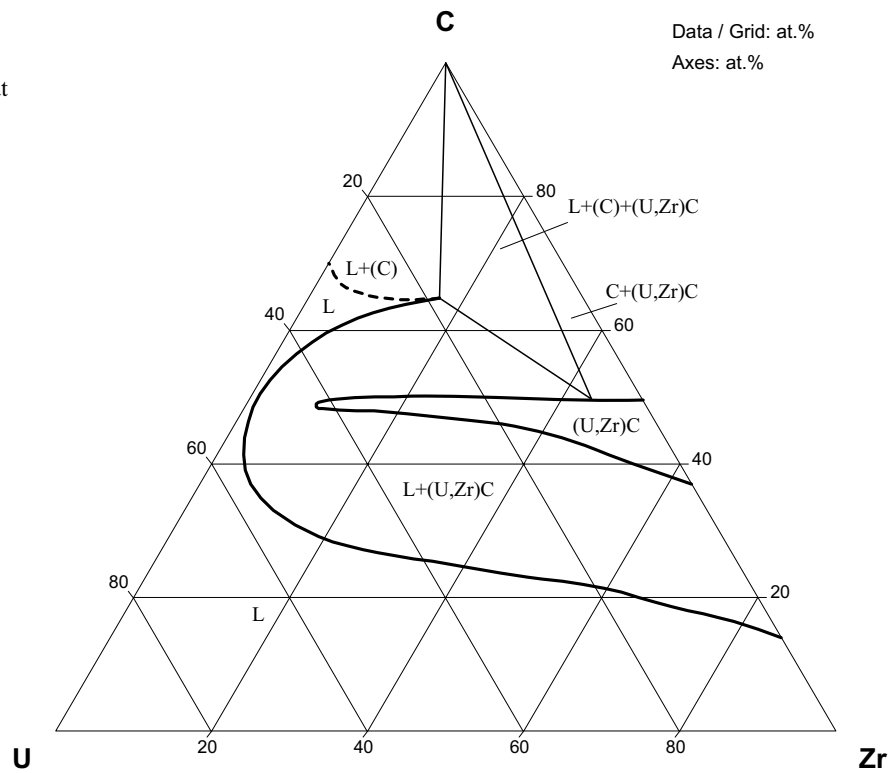


Fig. 7: C-U-Zr.
Isothermal section at
2850°C

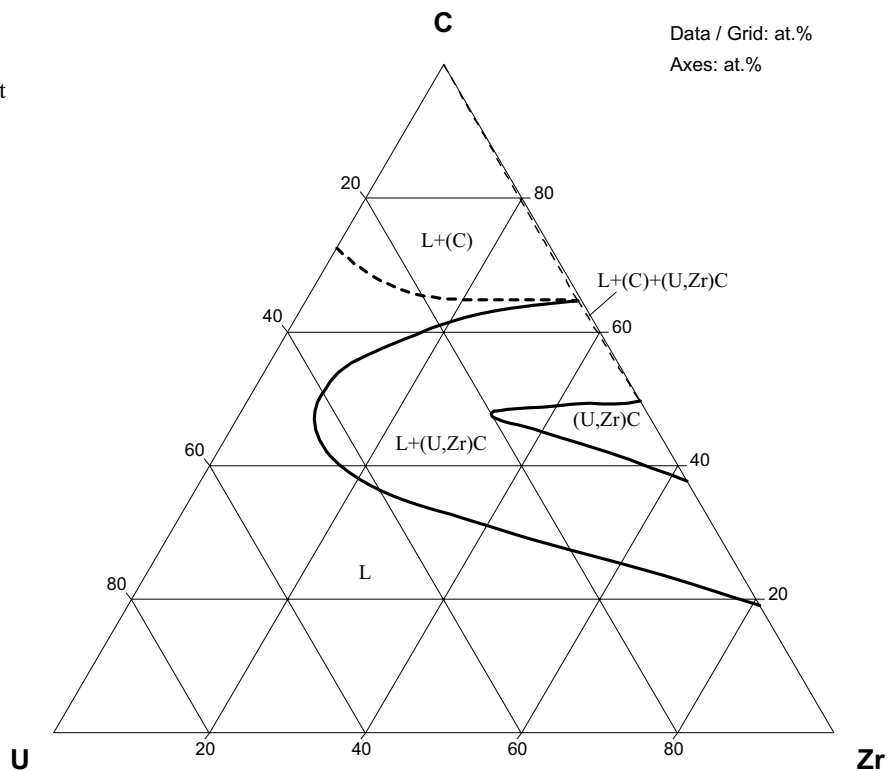


Fig. 8: C-U-Zr.
Isothermal section at
3000°C

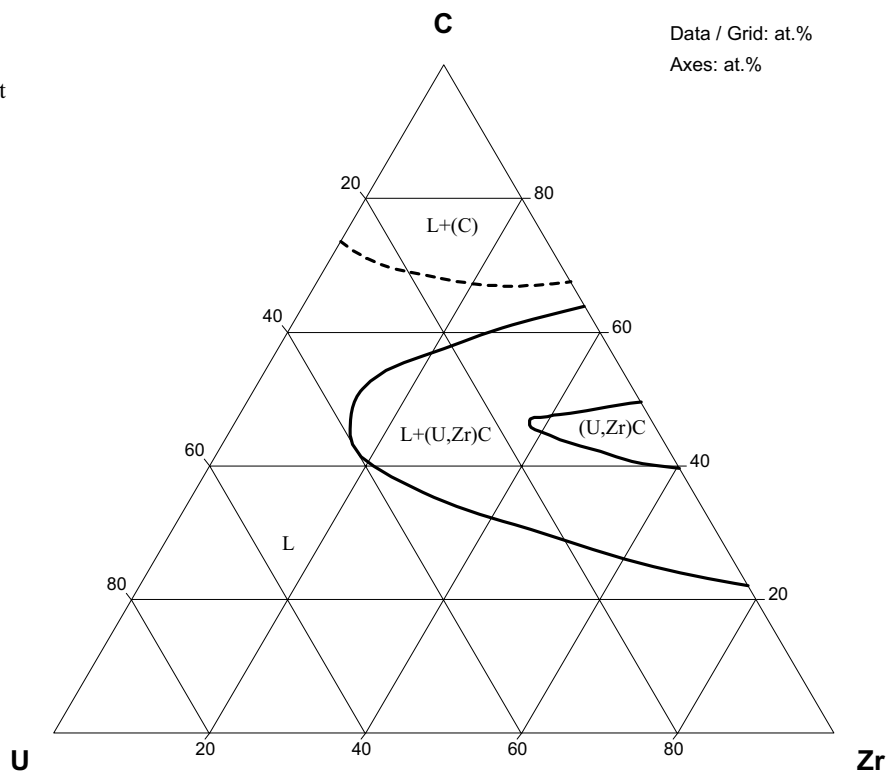


Fig. 9: C-U-Zr.
The vertical section
 $\text{UC}_2\text{-ZrC}$

