Thorium – Uranium – Zirconium

Olga Fabrichnaya

Introduction

Th-U-Zr alloys are important materials for fuel of nuclear reactors [1959Iva, 1967Far, 1968Far1, 1968Far2, 1969Far]. Thorium fuel cycle system has great advantages of resource abundance, less production of transuranium elements and applicability to thermal breeder reactor [1995Yam]. A substantial increase in the ^{233}U isotopic content of the fuel during irradiation demonstrated the attractiveness of Th as a fertile material [1967Far]. Among the systems of ordinary uranium alloys, attention was attracted by metals that possess a high solubility in (γU) and a relatively small cross section for capturing thermal neutrons, such as Zr [1958Iva]. That is why phase relations between solid phases in the Th-U-Zr system are of particular interest. The experimental studies made in the Th-U-Zr system are summarized in Table 1. Carlson [1950Car] investigated the liquidus surface in the concentration range adjacent to the Th-U binary system with Zr contents up to 33 mass%. According to the results of [1950Car] there is no ternary eutectic in the uranium corner of the Th-U-Zr system. Murray [1958Mur] studied the effect of Zr (up to 19 at.%) on the extension of a miscibility gap in the liquid and eutectic temperature found in the Th-U binary system. [1960Mur] studied influence of 2 at.% U addition on the miscibility gap in the bcc phase of the Th-Zr system and demonstrated that U increases the maximal temperature of the miscibility gap and widens its size. Detailed experimental investigations of phase diagrams in the Th-U-Zr system were performed by [1958Iva, 1959Iva, 1961Bad, 1972Bad, 1972Iva] using XRD, microstructural and thermal analysis and hardness measurements. Phase relations between solid phases in the Th-U-Zr system were studied by [1961Bad] at 550-1000°C. The details of this experimental study are reported in [1972Iva]. Liquidus and solidus surfaces were constructed by [1972Bad] using thermal analysis. An early review of phase relations and properties of Zr alloys including the Th-U-Zr alloys can be found from [1963Dou].

Binary Systems

The binary Th-U phase diagram is accepted from the evaluation of [1985Pet]. For the U-Zr system the evaluation of [1989She] is accepted in the present work. The phase diagram of the Th-Zr system is accepted as presented by [1959Bad, 1972Bad] with corrections applied for the temperature of the α-β transition of Th. The phase diagrams of the U-Zr and Th-Zr systems are presented in Figs. 1 and 2.

Solid Phases

The (βZr) forms a continuous solid solution with γU in the U-Zr binary system and with βTh in the Th-Zr binary system. Th and U themselves have limited mutual solubility in solid state. The only binary phase δ is found in the U-Zr system. The summary of solid phases is given in Table 2, showing that no ternary phases have been reported for the Th-U-Zr system.

Invariant Equilibria

The invariant reactions involving solid phases, Table 3, were derived from [1958Iva, 1959Iva, 1961Bad] From their experimental data it was possible to suggest a reaction scheme, taking into account modified temperatures of U_1 and E_3 reactions and the U-Zr binary phase relations as accepted in the present work. The corrected reaction scheme is shown in Fig. 3.

Liquidus, Solidus and Solvus Surfaces

The liquidus and solidus surfaces were experimentally obtained by [1972Bad] using thermal analysis with subsequent study of the microstructure. The results show a three-phase equilibrium L+(αTh)+(γU) which extends from binary Th-U system into a ternary as temperature increases. There should be another

three-phase equilibrium L+(βTh)+(αTh) which extends from binary system into a ternary as the temperature increases. However, this reaction was not indicated by [1972Bad]. The liquidus surface shown in Fig. 4 is from [1972Bad] with univariant reaction L+(βTh)+(αTh) tentatively indicated by dash lines. [1958Mur] presented a part of the liquidus surface in the U rich corner up to 50 at.% Th which is in a good agreement with the results of [1972Bad].
The solidus surface of the Th-U-Zr ternary system is constructed by [1972Bad] based on experimental studies. The region of Zr rich γ solid solution decreases continuously from the Zr corner to concentration of about 60 at.% Zr. Below this Zr composition the γ-surface contracts and comes close to the binary U-Zr and Th-Zr systems. The remainder of the solidus surface is characterized by the presence of the three-phase equilibrium L+(αTh)+(γU). The boundary of this surface is shown by a dashed line, as obtained from thermal and microstructural analysis. The solidus surface is presented in Fig. 5. A projected solvus surface can be found at [1958Iva, 1959Iva, 1961Bad] constructed on the base of their experimental phase studies.

Isothermal Sections

The isothermal sections were constructed by [1961Bad] based on data of microstructural, X-ray diffraction analysis and hardness measurements of alloys quenched from 1000, 960, 930, 915, 800, 750, 700, 640 and 550°C. The results of [1961Bad] are included in Figs. 6 to 14.

Temperature – Composition Sections

[1960Mur] found a miscibility gap in the γ phase for the binary Th-Zr system and in the Th-U-Zr system at 2 at.% U. It was demonstrated that U as well as other additives resulted in expanding the miscibility gap and in raising its maximum temperature, Fig. 15.

Notes on Materials Properties and Applications

The Th-2.5U-1.0Zr (mass%) alloy fuel elements were being irradiated under water-cooled power-reactor conditions [1968Far1, 1968Far2, 1969Far]. After 403 thermal cycles, the fuel exhibited a 3.8% swelling, as determined by measuring weight and volume of fuel elements in water. The fuel temperatures were maintained between 350 and 600°C with surface temperature of 295°C. No evidence of warpage, bowing or distortion was noted [1969Far]. When given a postirradiation anneal at 800°C for 100 h, the fuel incurred 22.5% total swelling because of the release of fusion gas [1968Far2].
Hydrogen absorption properties of Th-U-Zr alloys were investigated for the purpose of developing of a new hydride nuclear fuel [1994Yam, 1995Yam, 1997Yam1, 1997Yam2, 1998Yam]. The hydrogen absorption properties of four Th-U-Zr alloys with composition of 2:1:6, 1:1:4, 1:2:6 and 1:4:10 (U:Th:Zr ratios) were examined at temperatures from 500 to 900°C and hydrogen pressures from 100 to 10^5 Pa. Regarding the microstructure, the alloy hydrides consisted of three phases: (αU), ZrH_{2-x} and $ThZr_2H_{7-x}$, which were finely and homogeneously mixed with each other probably due to formation from one solid solution phase stable at high temperatures [1997Yam1, 1997Yam2]. To get the properties of H-Th-U-Zr alloys, which are needed to utilize them for nuclear fuel, changes in the dimensions and weights of the alloys on hydrogenation and in microstructure and hardness on neutron irradiation to $7.4 \cdot 10^{23}$ $n \cdot m^{-2}$ were examined. The hydrogenated alloys show high apparent densities and high durability forirradiation, which promotes the use of these alloys for a new type of nuclear fuel [1998Yam].
The hardness of Th-U-Zr alloys quenched from 640°C was studied by [1961Bad] to determine the two-phase field boundaries. It is worth noting that γ solid solutions quenched from stable state harden when tempered at 400-550°C, due to the decay of phases formed. The maximum hardness is reached on tempering at 400°C. Increasing the tempering temperature leads to a decrease in hardness of the alloys [1958Iva].
Information about investigations of the Th-U-Zr materials properties is summarized in Table 4.

Miscellaneous

A metastable ω phase with hexagonal structure forms in the Zr rich region [1958Iva, 1972Iva]. On hardening from 1000°C the γ phase undergoes different transformations depending on compositions.

The (αU) phase forms in U rich compositions, the (αZr) phase forms in Zr rich regime along with metastable ω phase, which is characteristic of hardened alloys of binary U-Zr system. By increasing the Th and U contents the γ phase is preserved on hardening.

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Table 1: Investigations of the Th-U-Zr Phase Relations, Structures and Thermodynamics

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1950Car]	Thermal analysis	Liquidus surface adjacent to Th-U system at Zr up to 33 at.%
[1958Mur]	Thermal analysis, metallographic study, XRD of arc melted alloys and thermal couples after annealing	Annealing at 1000 and 1050°C, thermal analysis up to 1450°C. Influence of Zr (up to 19 at.%) to liquid miscibility gap and eutectic in Th-U system (up to 50 at.% Th)
[1960Mur]	Metallographic method	920-1000°C 40-65 at.% Zr, bcc miscibility gap at 2 at.% U

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1961Bad]	Equilibration and quenching, characterization by XRD and microstructural analysis	1000, 960, 930, 915, 800, 750, 700, 640, 550°C - isothermal sections
[1972Bad]	Thermal analysis, microstructural analysis	Liquidus and solidus surfaces 1075-1800°C

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(αTh) < 1360°C $(Th_{100-x-y}U_xZr_y)$	*cF*2 $Fm\overline{3}m$ Cu	*a* = 508.45	at *x* = 0 and *y* = 0 [1985Pet] dissolves up to 14 at.% Zr and 6.8 at.% U
γ, $(Th_{100-x-y}U_xZr_y)$	*cI*2 $Im\overline{3}m$ W		(βTh) dissolves up to 12.2 at.% U and from 0 to 100 at.% Zr (γU) dissolves up to 2.5 at.% Th and from 0 to 100 at.% Zr
(βTh) 1755 - 1360		*a* = 411	at *x* = 0 and *y* = 0 [1985Pet]
(βZr) 1855 - 863		*a* = 360.9	at y = 100 and *x* = 0 [1989She]
(γU) 1135 - 776		*a* = 352.4	at *x* = 100 and *y* = 0
(αU) < 668	*oC*4 *Cmcm* αU	*a* =285.37 *b* = 586.95 *c* = 495.48	pure U, at 25°C [Mas2] dissolves up to 0.5 at.% Zr and < 0.05 at.% Th
(βU) 776 - 668	*tP*30 $P4_2/mnm$ βU	*a* = 1075.9 *c* = 565.6	pure U [Mas2] dissolves up to 1.1 at.% Zr and 0.1 at.% Th
(αZr) < 863	*hP*2 $P6_3/mmc$ Mg	*a* = 323.17 *c* = 514.76	pure Zr dissolves 0.4 at.% U and 2 at.% Th
δ $(U_{100-x}Zr_x)$ < 617°C	*hP*3 *P*6/*mmm* AlB_2	 *a* = 503 *c* = 308	63-78 at.% Zr at 66.67 at.% Zr [1989She] dissolves up to 4 at.% Th
ω	*h**	-	Metastable. Form in the Zr rich region [1958Iva, 1972Iva]

Table 3: Invariant Equilibria

Reaction	T [°C]	Type	Phase	Composition (at.%)		
				Th	U	Zr
$\gamma_U \rightleftharpoons (\alpha Th) + \gamma_{Zr} + (\beta U)$	~680	E_1	-	-	-	-
$(\beta U) \rightleftharpoons (\alpha U) + (\alpha Th) + \gamma_{Zr}$	~650	E_2	-	-	-	-
$(\alpha Zr) + \gamma_{Zr} \rightleftharpoons (\alpha Th) + \delta$	~605	U_1	-	-	-	-
$\gamma_{Zr} \rightleftharpoons (\alpha U) + (\alpha Th) + \delta$	~600	E_3	-	-	-	-

Table 4: Investigations of the Th-U-Zr Materials Properties

Reference	Method/Experimental Technique	Type of Property
[1961Bad]	Quenched alloys at 640°C	Hardness
[1968Far1, 1968Far2, 1969Far]	Test in thermal cycling 350-600°C by weighing in water; alloys Th-2.5U-1.0Zr (mass%)	Swelling
[1998Yam]	Hydrogen pressure 100 kPa and 800°C Micro-hardness and density measurement for H-Th-U-Zr alloys	Vickers microhardness, density

Fig. 1: Th-U-Zr.
Phase diagram of the U-Zr system

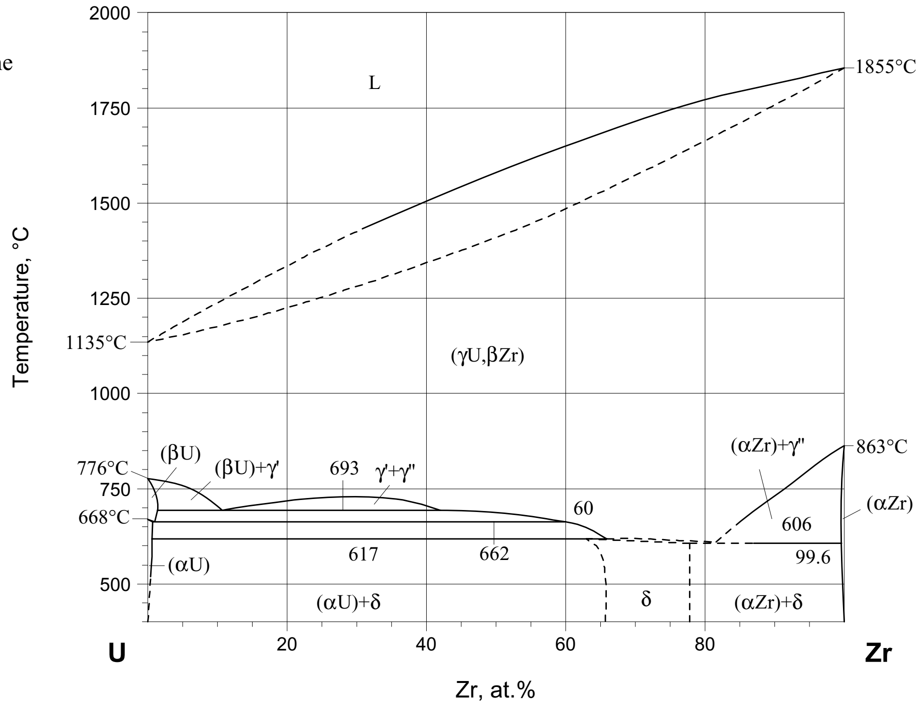
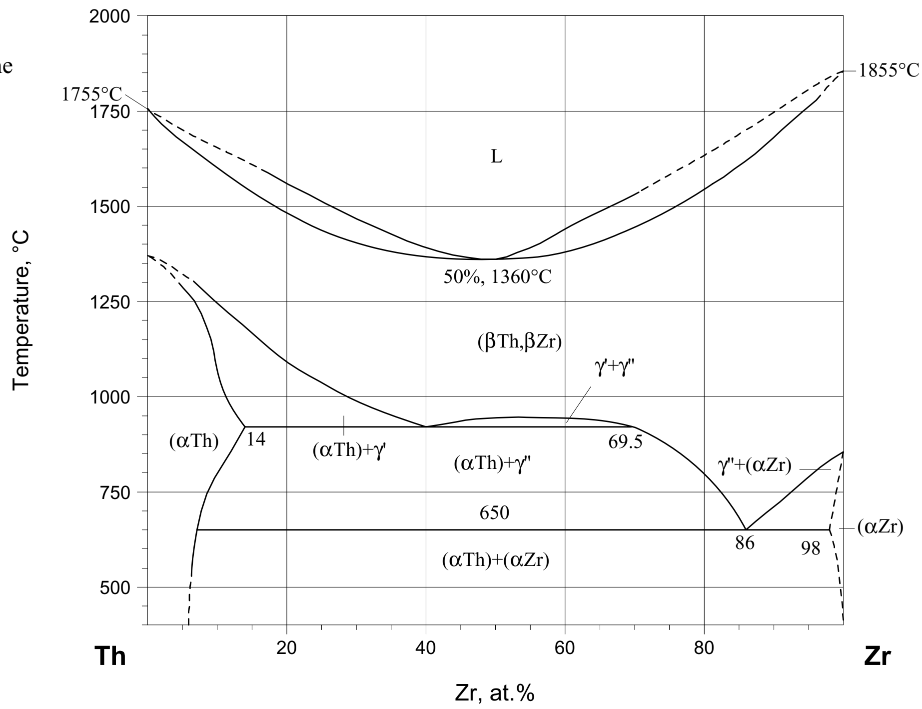


Fig. 2: Th-U-Zr.
Phase diagram of the Th-Zr system



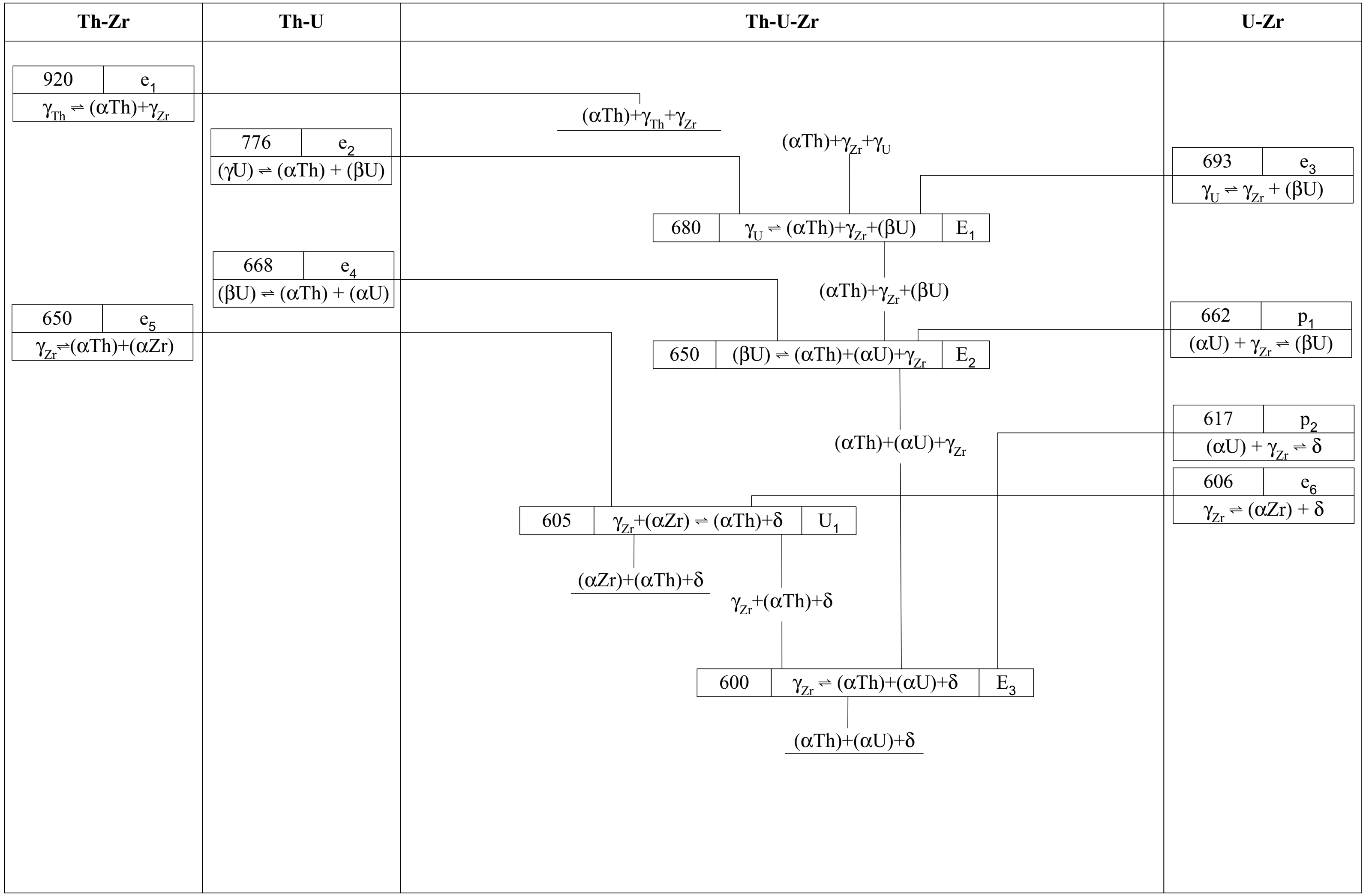


Fig. 3: **Th-U-Zr.** Partial reaction scheme

Fig. 4: Th-U-Zr.
Liquidus surface projection

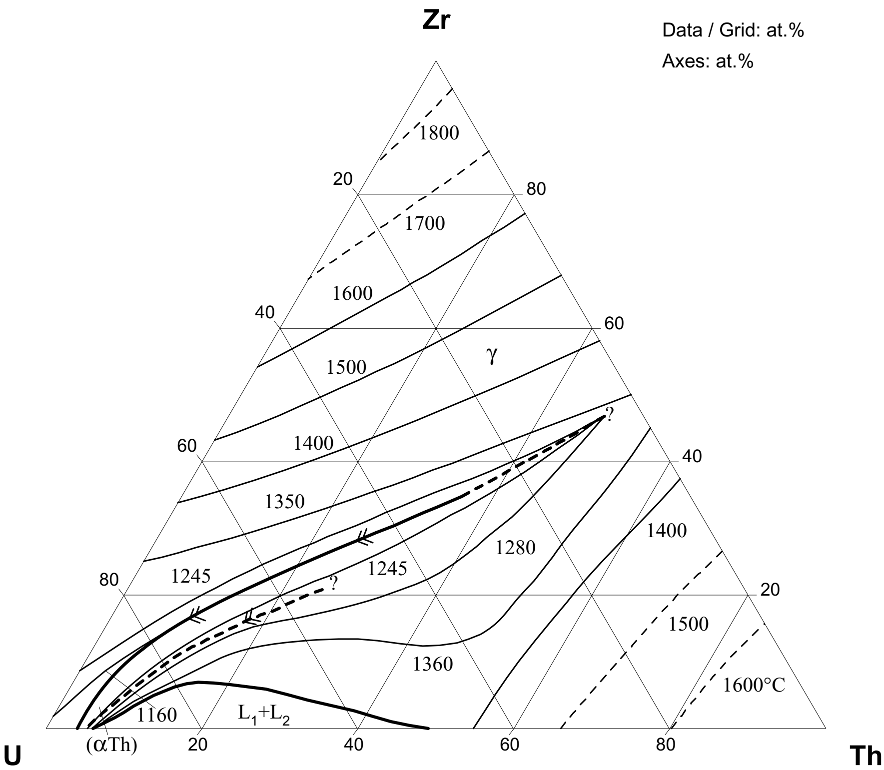


Fig. 5: Th-U-Zr.
Solidus surface projection

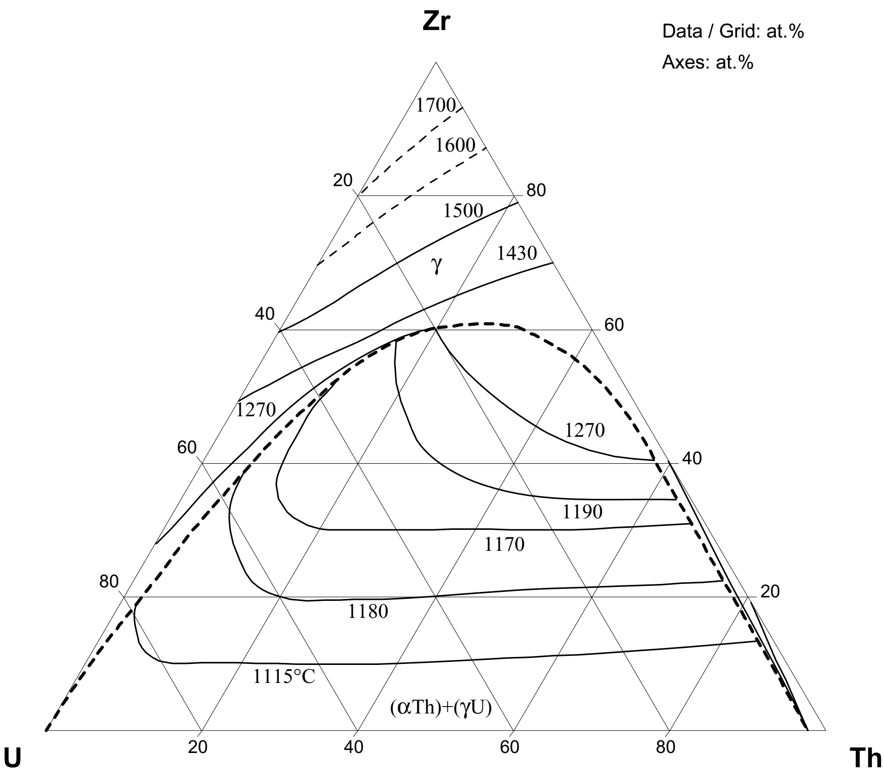


Fig. 6: Th-U-Zr.
Isothermal section at 1000°C

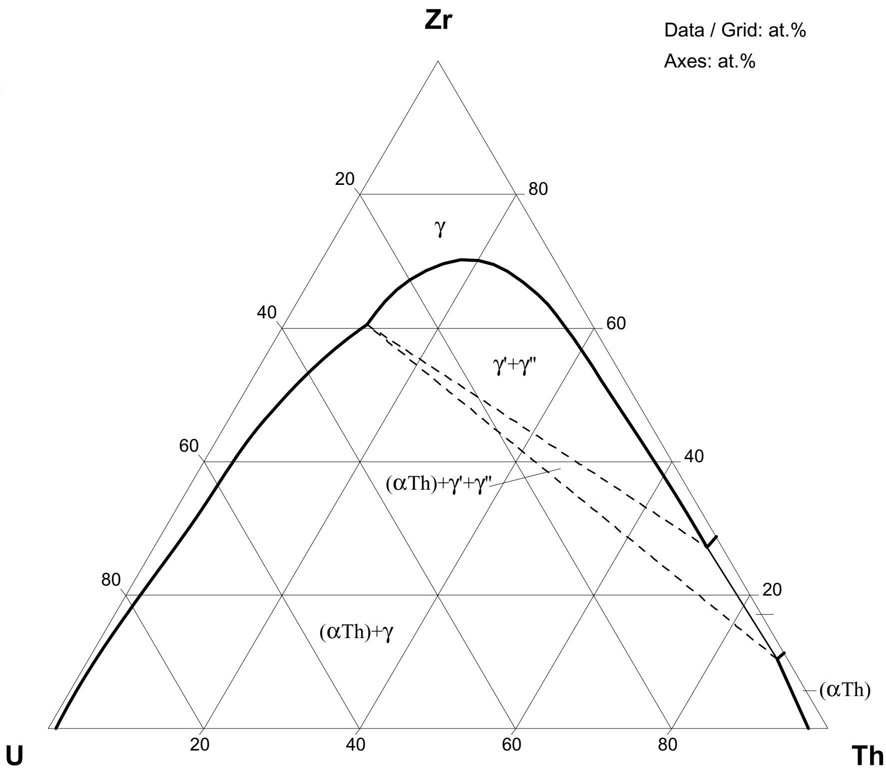


Fig. 7: Th-U-Zr.
Isothermal section at 960°C

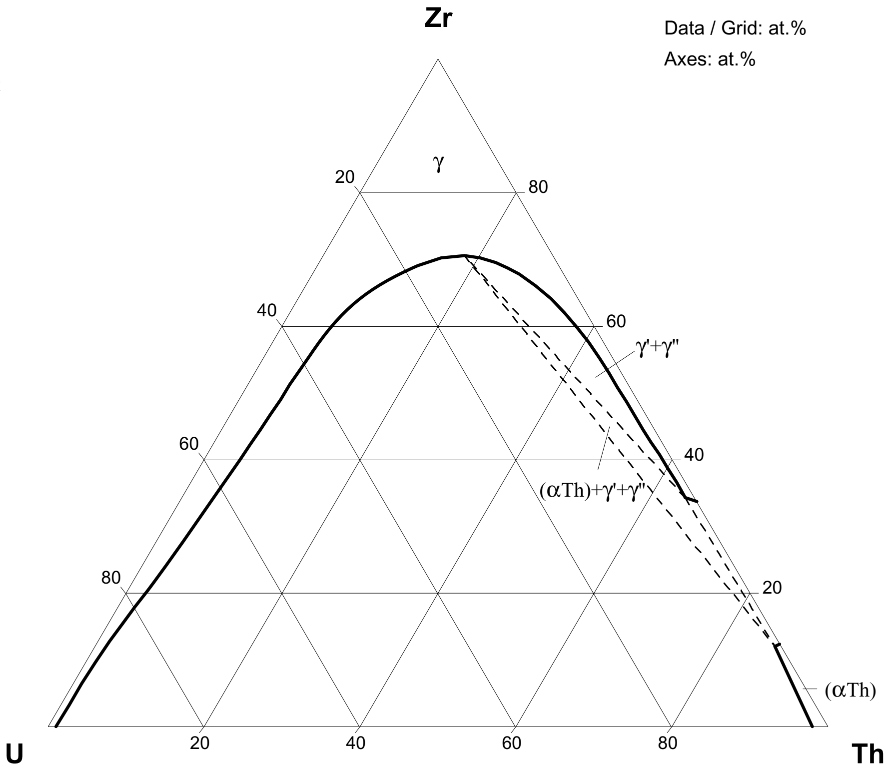


Fig. 8: Th-U-Zr.
Isothermal section at 930°C

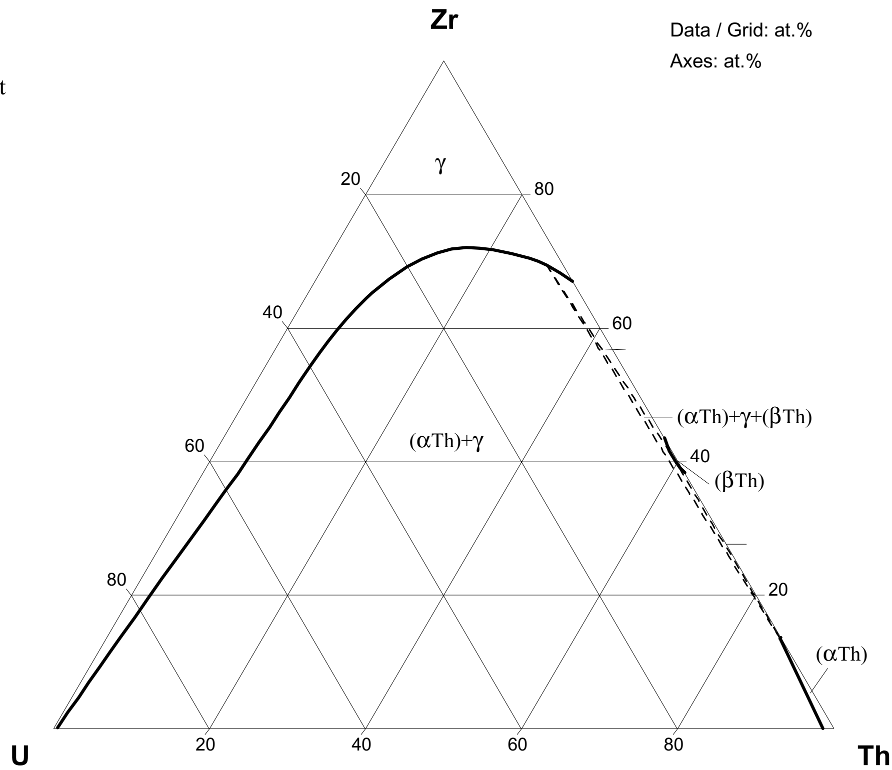


Fig. 9: Th-U-Zr.
Isothermal section at 915°C

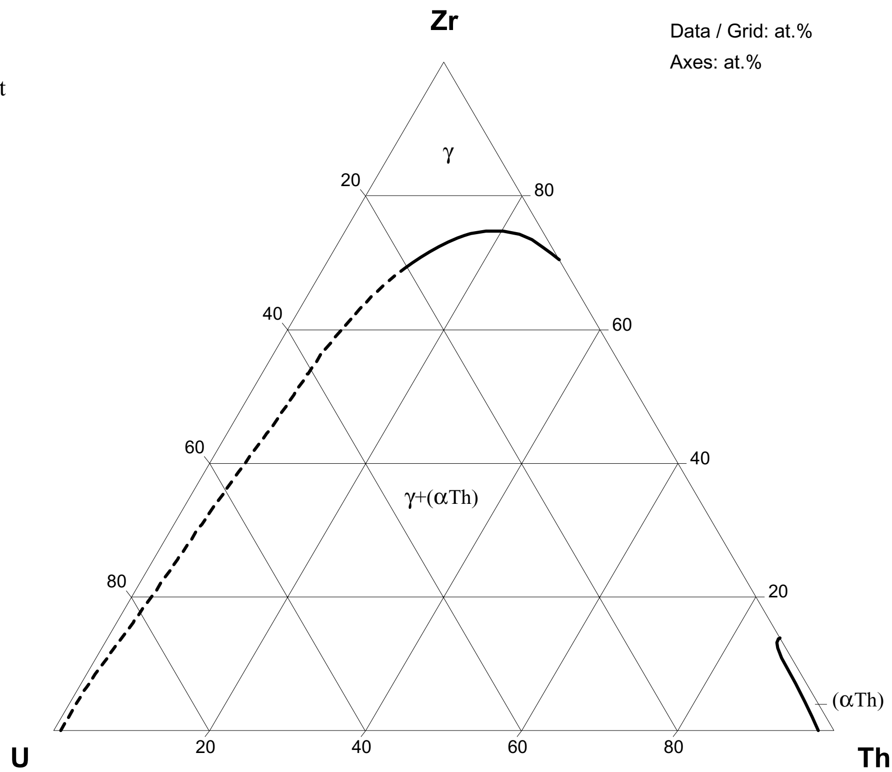


Fig. 10: Th-U-Zr.
Isothermal section at
800°C

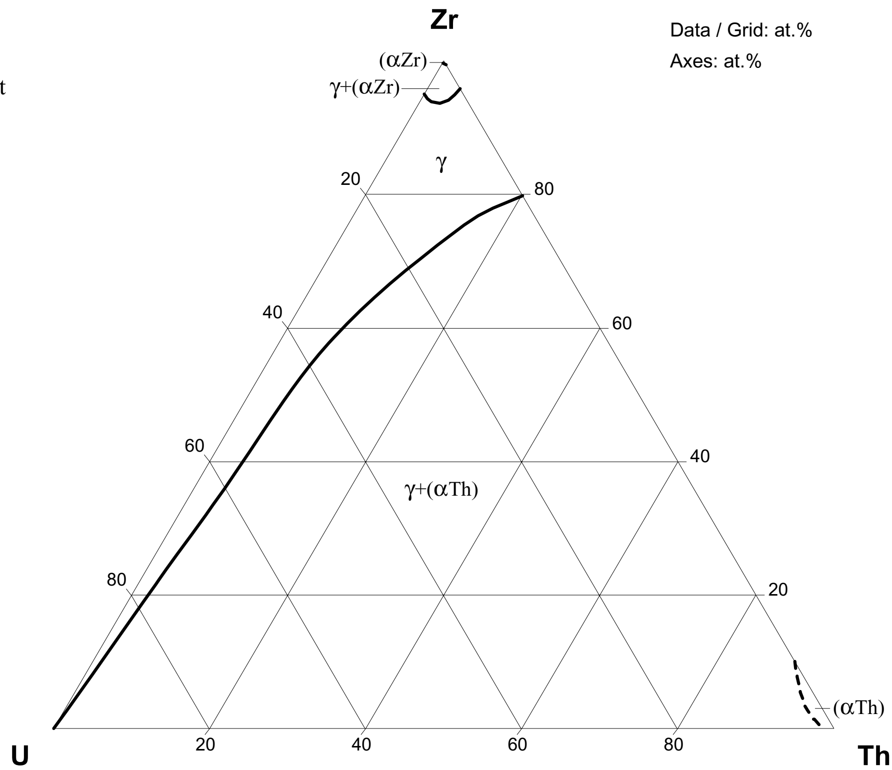


Fig. 11: Th-U-Zr.
Isothermal section at
750°C

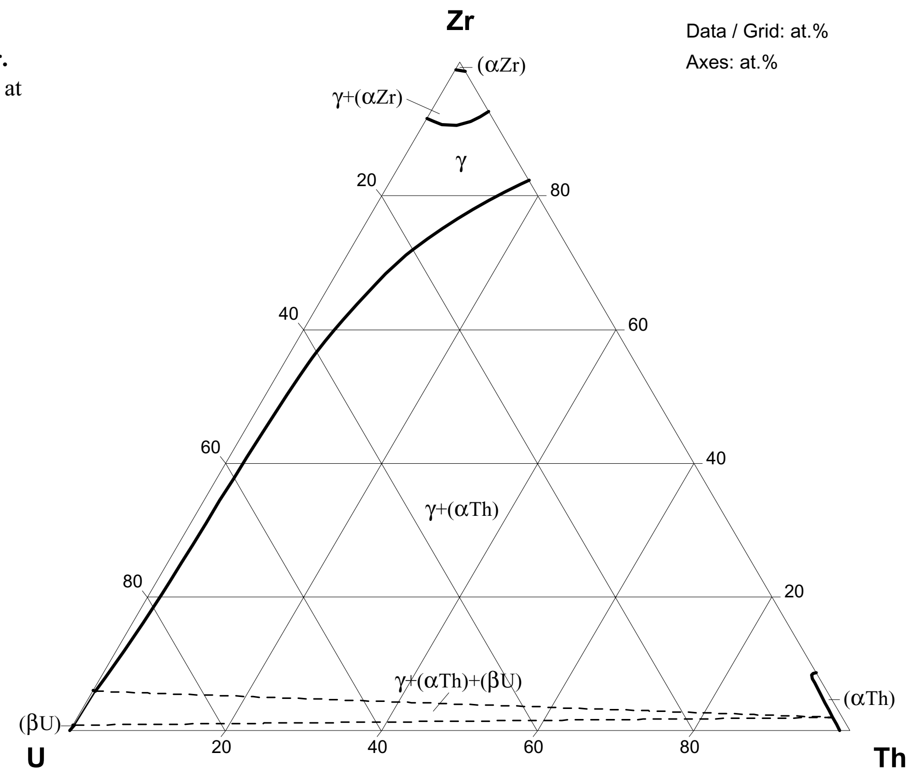


Fig. 12: Th-U-Zr. Isothermal section at 700°C

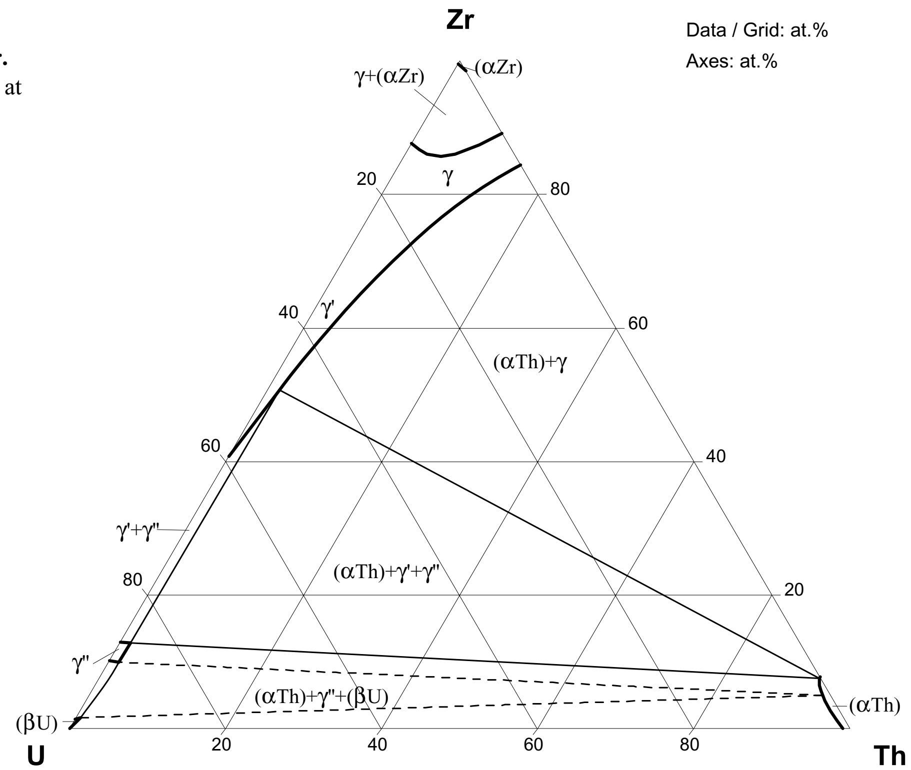


Fig. 13: Th-U-Zr. Isothermal section at 640°C

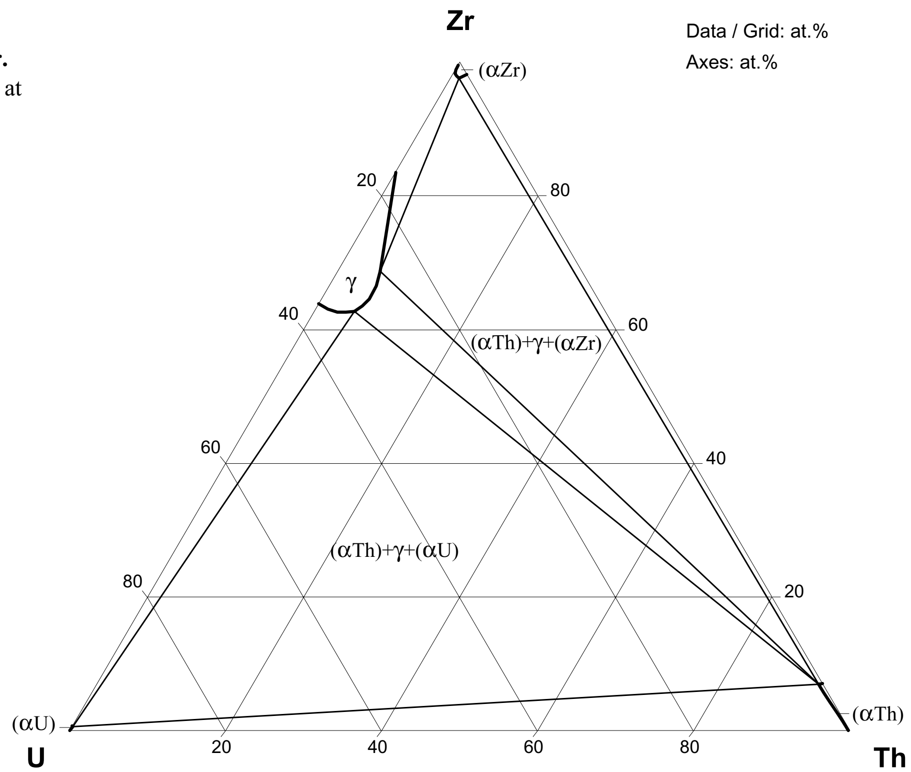


Fig. 14: Th-U-Zr.
Isothermal section at 550°C

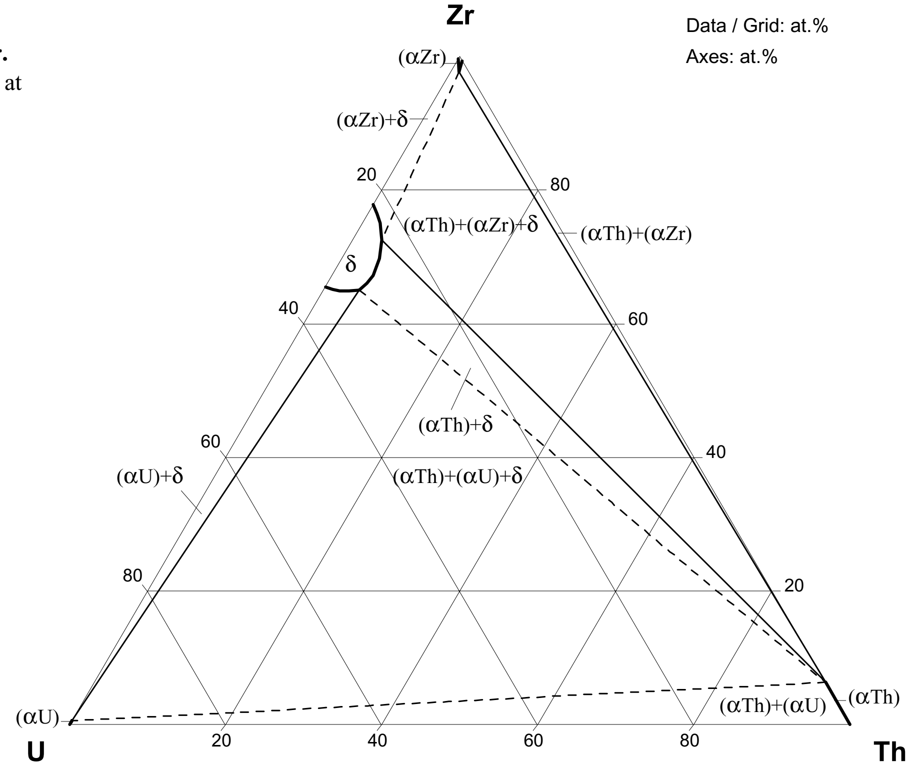


Fig. 15: Th-U-Zr.
Miscibility gap in the γ phase at 0 and 2 at.% U