

Iron – Uranium – Zirconium

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Introduction

The first experimental study of the Fe–U–Zr system was performed by [1965Wal] and partial isothermal section at 800°C was constructed. The detailed investigation of phase equilibria in the Fe–U–Zr system was undertaken by [1999Nak1]. The authors [1999Nak1] melted 17 alloy compositions in arc furnace under Ar atmosphere. The alloys were annealed between 800 and 580°C for 6–180 d and quenched in water. The phase equilibria were investigated by electron probe microanalysis (EPMA). The temperatures of phase transformations were determined by differential thermal analysis (DTA). [1999Nak2] carried out diffusion couple experiments at 635–715°C and determined phases that form in the reaction zone.

The first assessment of thermodynamic functions was performed by [1994Pel]. However occurrence of ternary phases in the system was not taken into account. [1998Kur] derived thermodynamic parameters for the Fe–U–Zr system based on binary description and adjusted parameters for two ternary phases (one ternary phase was not known at the time). His description was improved by [1999Nak1] by involving more experimental data obtained in their own work and taking into account all ternary phases.

The available experimental data and calculations were reviewed and critically evaluated by [2003Rag]. The information about experimental and theoretical investigation of the Fe–U–Zr system is presented Table 1.

Binary Systems

The phase diagram of the Fe–U binary system is accepted from the thermodynamic assessment of [2003Cha]. This diagram is derived by Calphad method taking into account experimental phase equilibrium data and measured thermodynamic properties. The calculated phase diagram agrees with the diagram from the review of [1993Oka]. The Fe–Zr binary system is accepted from experimental study of [2002Ste]. In this study it was shown that previously reported phase $\text{Fe}_{23}\text{Zr}_6$ in fact is stabilized by oxygen and is not an equilibrium phase. The U–Zr phase diagram accepted from [Mas2] originates from review of [1989She].

Solid Phases

The polymorphic modifications of Fe practically do not dissolve any U and Zr. The bcc continuous solid solution of (γ U) and (β Zr) can dissolve up to 8 at.% Fe in Zr rich area. In the Fe_2U cubic C15 Laves phase can be dissolved up to 5 at.% Zr. The cubic Fe_2Zr C15 Laves has homogeneity range of 27.5–34.4 at.% Zr in the binary Fe–Zr system and dissolves up to 7 at.% U. The FeU_6 tetragonal phase can dissolve up to 5 at.% Zr. The tetragonal phase FeZr_2 stable between 780 and 951°C in the binary Fe–Zr system can dissolve up to 10 at.% U. The FeZr_3 orthorhombic phase practically does not dissolve U and it is stable below 851°C.

There are three ternary compounds in the Fe–U–Zr system (τ_1 , τ_2 , τ_3) according to experimental data of [1999Nak1, 1999Nak2]. The crystal structure data for these phases are not known. The homogeneity ranges of τ_1 and τ_2 phases were determined by [1999Nak1] as 33–50 at.% Zr at constant Fe content of 33 at.% for τ_1 phase and as 21–25 at.% Zr at constant Fe content of 6 at.% for τ_2 phase. The τ_3 phase has practically constant composition of $\text{Fe}_{0.5}\text{U}_{0.18}\text{Zr}_{0.32}$ and it is stable up to at least 895°C. The τ_2 phase decomposes to τ_1 and (γ U, β Zr) at 726°C and the τ_1 phase melts at 933°C [1999Nak1].

Crystallographic data of all solid phases are given in Table 2.

Invariant Equilibria

Invariant equilibria in the Fe–U–Zr system were calculated by [1994Pel] for two limiting cases of mutual solubility of Fe_2U and Fe_2Zr . Experimental study of [1999Nak1] showed that ternary phases, which were not taken into account by [1994Pel] form equilibria with the liquid phase and therefore equilibria calculated by [1994Pel] do not correspond to the equilibrium state.

Liquidus, Solidus and Solvus Surfaces

Liquidus surface of the Fe-U-Zr system was calculated by [1994Pel]. However, two liquidus surfaces derived by [1994Pel] for the above mentioned cases are not reproduced in the present evaluation because they are in contradiction with experimental data of [1999Nak1] (see also chapter “Thermodynamics”).

Isothermal Sections

Isothermal sections at 580, 700 and 800°C were constructed based on experimental investigation by [1999Nak1]. The isothermal sections at these temperatures are presented in Figs. 1-3. They are redrawn from review of [2003Rag]. In this work [2003Rag] deleted the $\text{Fe}_{23}\text{Zr}_6$ phase taking into account data of [2002Ste] for the binary Fe-Zr system. The FeZr_2 phase was omitted at 580°C also based on the results of [2002Ste]. Experimentally indicated solubility of U in FeZr_2 at 800°C by [1999Nak1] is taken into account. The isothermal section at 700°C (Fig. 2) is redrawn here from [1999Nak1] making the same corrections as [2003Rag] made at 580°C. The main difference between the phase diagram at 580 and 700°C relates to phase transformations in the U-Zr system. The δ phase is not stable at 700°C and $(\gamma\text{U},\beta\text{Zr})$ solid solution decomposes into two phases (γ' and γ_2'') of different compositions (miscibility gap).

[1994Pel] calculated isothermal sections at 1000 and 1300°C considering two possible cases of complete solubility and zero mutual solubility between Fe_2Zr and Fe_2U . The isothermal sections at 1000 and 1300°C are presented at Figs. 4 and 5. They are tentatively redrawn from [1994Pel] taking into account limited mutual solubility of Fe_2Zr and Fe_2U and excluding Fe_3Zr as a non-equilibrium phase.

Thermodynamics

[1994Pel] computed ternary phase equilibria in the ternary system using the thermodynamic description from their own works. The intermediate phase δ in the U-Zr system was omitted, while the Fe_3Zr phase was included. The solubility of U in (Fe) and of Fe in (αZr) was neglected. The excess Gibbs energies in ternary liquid and solid phases were calculated from binary values using the Kohler and Toop equations, respectively. The liquidus surface and isothermal sections were calculated considering two limiting cases of complete solubility and zero solubility between Fe_2Zr and Fe_2U . Ternary phases were not considered by [1994Pel]. According to experimental data of [1999Nak1] ternary phases come to an equilibrium with liquid, thus the liquidus calculated by [1994Pel] seems to be in contradiction with data of [1999Nak1]. Also, Fe_3Zr is not an equilibrium phase according to the binary Fe-Zr system of [2002Ste] accepted in the present evaluation.

In the thermodynamic assessment of [1998Kur] two ternary phases τ_1 and τ_2 were taken into account. The calculations were based on the thermodynamic description of the binary systems. The Gibbs energies of τ_1 and τ_2 phases were adjusted to reproduce exactly the experimental tie lines in the ternary system. The phase τ_3 was not known when the work of [1998Kur] was performed. The experimental data of [1965Wal] for the partial isothermal section at 800°C and the results obtained at the first stages of experimental investigation of [1999Nak1] were used. The new thermodynamic calculations of isothermal sections was performed by [1999Nak1] using experimental results obtained in their own work. The τ_3 phase found by [1999Nak1] was included in calculations. The calculated results are in a good agreement with experimental data except for the Zr rich corner. Authors assumed that annealing time was not enough to reach equilibrium in experiments with Zr rich alloys.

Notes on Materials Properties and Applications

A metallic Pu-U-Zr alloy fuel has been recognized as a candidate for advanced fast reactor fuel. One of the key issue is a compatibility of fuel alloy with Fe based cladding materials. During irradiation the fuel alloy swells and comes into a contact with the cladding and metallurgical reactions occur at the fuel alloy - cladding interface. The authors of [2000Oga] conducted diffusion couple experiments at 650°C to study the influence of Pu content to liquid phase formation in the reaction zone. If a liquid phase is formed, it can degrade cladding integrity. The experiments showed the Pu content in $(\text{U,Pu})_6\text{Fe}$ phase is crucial factor in determining the conditions of liquid formation. Using Calphad technique a thermodynamic database for the

quaternary Fe–Pu–U–Zr system was derived by [2001Kur]. [2002Nak] presented phase relation data in the U rich region of the Fe–Pu–U–Zr system from annealing studies of quaternary alloys at 650°C. The samples were studied metallographically and by EPMA. Phase compositions were measured using energy dispersive X-ray detector (EDX). The thermodynamic description of the quaternary system was improved by [2002Nak] by including new experimental data (obtained in the same work) and by introducing the three-sublattice model accounting the solubility of Pu in the τ_2 phase. Predicted phase relations at other temperatures than 650°C are compared with the results of DTA and the applicability of calculated phase diagrams in other temperature regions was confirmed. [2005Nak] calculated phase diagrams for the U–Pu–Zr–Fe system at 800°C based on the established thermodynamic description [2002Nak].

The metallurgical interdiffusion zones at the interface between irradiated or unirradiated U–Pu–Zr metal fuel and stainless steel cladding at elevated temperatures in literature [1990Tsa, 1993Coh, 1994Sar] were analyses and interpreted using the calculated phase diagrams.

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

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1994Pel]	CALPHAD	Isothermal sections at 1100, 1300°C, liquidus surfaces for case ideal and zero solubility between Fe ₂ U and Fe ₂ Zr
[1998Kur]	CALPHAD	Isothermal section and potential diagram (activity of U vs activity Zr) at 700°C
[1999Nak1]	Arc-melting and annealing for 6-180 days, EPMA (electron probe micro-analysis), DTA (differential thermal analysis), CALPHAD	580, 700 and 800°C isothermal sections
[1999Nak2]	Diffusion couple, EPMA, CALPHAD	635, 650, 700, 715°C U-23at.% Zr/Fe

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(δFe) (h ₂) 1538 - 1394	<i>cI2</i> <i>Im</i> $\bar{3}m$ W	<i>a</i> = 293.15	[Mas2]
(γFe) (h ₁) 1394 - 912	<i>cF4</i> <i>Fm</i> $\bar{3}m$ Cu	<i>a</i> = 364.67	at 915°C [V-C2, Mas2]
(αFe) < 912	<i>cI2</i> <i>Im</i> $\bar{3}m$ W	<i>a</i> = 286.65	at 25°C [Mas2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(εFe)	<i>hP2</i> <i>P6₃/mmc</i> Mg	<i>a</i> = 246.8 <i>c</i> = 396.0	at 25°C, 13 GPa [Mas2]
(αU) < 668	<i>oC4</i> <i>Cmcm</i> αU	<i>a</i> = 285.37 <i>b</i> = 586.95 <i>c</i> = 495.48	up to 0.05 at.% Fe and up to 0.5 at.% Zr at 25°C, pure U [Mas2]
(βU) 776 - 668	<i>tP30</i> <i>P4₂/mnm</i> βU	<i>a</i> = 1075.9 <i>c</i> = 565.6	up to 0.3 at.% Fe and up to 1.1 at.% Zr at 720°C, pure U [V-C2]
γ, (γU,βZr) (γU) 1135 - 762 (βZr) 1855 - 775	<i>cI2</i> <i>Im$\bar{3}m$</i> W	<i>a</i> = 352.4 <i>a</i> = 360.9	up to 1.3 at.% Fe in U rich area and up to 4.2 at.% Fe in Zr rich area, maximal Fe ~7 at.% pure U [Mas2] pure Zr [Mas2]
(αZr) < 863	<i>hP2</i> <i>P6₃/mmc</i> Mg	<i>a</i> = 323.16 <i>c</i> = 514.75	up to 0.4 at.% U at 25°C pure Zr [Mas2]
Fe ₂ Zr < 1673	<i>cF24</i> <i>Fd$\bar{3}m$</i> Cu ₂ Mg	<i>a</i> = 702 to 709	27.5-34.4 at.% Zr, 0-7 at.% U [2002Ste]
Fe ₂ Zr 1345 - 1240	<i>hP24</i> <i>P6₃/mmc</i> MgNi ₂	<i>a</i> = 495 <i>c</i> = 1614	26.5-27 at.% Zr [2002Ste]
FeZr ₂ 951 - 780	<i>tI12</i> <i>I4/mmc</i> Al ₂ Cu	<i>a</i> = 638 <i>c</i> = 560	66.7-67.2 at.% Zr and up to ~10 at.% U at 66.7 at.% Zr and 0% U [2002Ste]
FeZr ₃ ≤ 851	<i>oC16</i> <i>Cmcm</i> BRe ₃	<i>a</i> = 332 <i>b</i> = 1100 <i>c</i> = 882	74.8-75.4 at.% Zr [2002Ste]
FeZr ₂	<i>cF96</i> <i>Fd$\bar{3}m$</i> NiTi ₂	<i>a</i> = 1221	O-stabilized [2002Ste]
Fe ₂₃ Zr ₆	<i>cF116</i> <i>Fm$\bar{3}m$</i> Mn ₂₃ Th ₆	<i>a</i> = 1172	O-stabilized 20.6-21.6 at.% U [2002Ste]
Fe ₂ U < 1236	<i>cF24</i> <i>Fd$\bar{3}m$</i> Cu ₂ Mg	<i>a</i> = 705.5	[V-C2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
FeU ₆ < 831	<i>tI</i> 28 <i>I4/mcm</i> MnU ₆	<i>a</i> = 1024.99 <i>c</i> = 525	[V-C2]
δ, UZr ₂ < 617	<i>hP</i> 3 <i>P6/mmm</i> AlB ₂	<i>a</i> = 503 <i>c</i> = 308	63-78 at.% Zr at 66.67 at.% Zr [1989She]
* τ ₁ , Fe ₃₃ U _{67-x} Zr _x < 933	-	-	33-50 at.% Zr [1999Nak1]
* τ ₂ , Fe ₆ U _{92-x} Zr _x ? - 726	-	-	21-25 at.% Zr [1999Nak1]
* τ ₃ , Fe ₅₀ U ₁₈ Zr ₃₂ < 895	-	-	[1999Nak1]

Fig. 1: Fe-U-Zr.
Isothermal section at
580°C

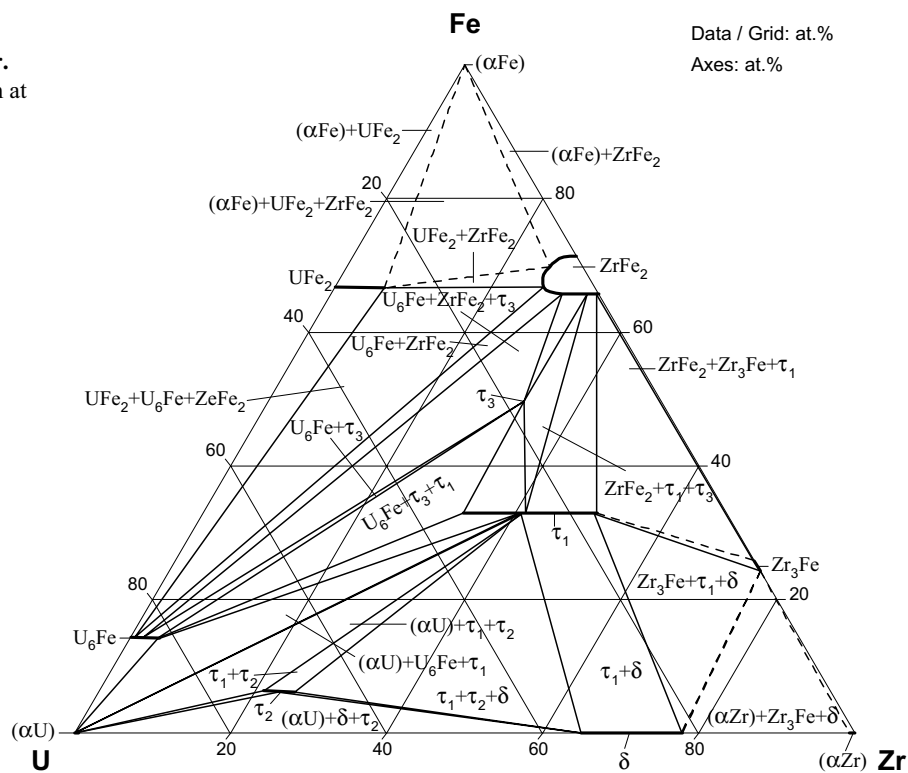


Fig. 2: Fe-U-Zr.
Isothermal section at
700°C

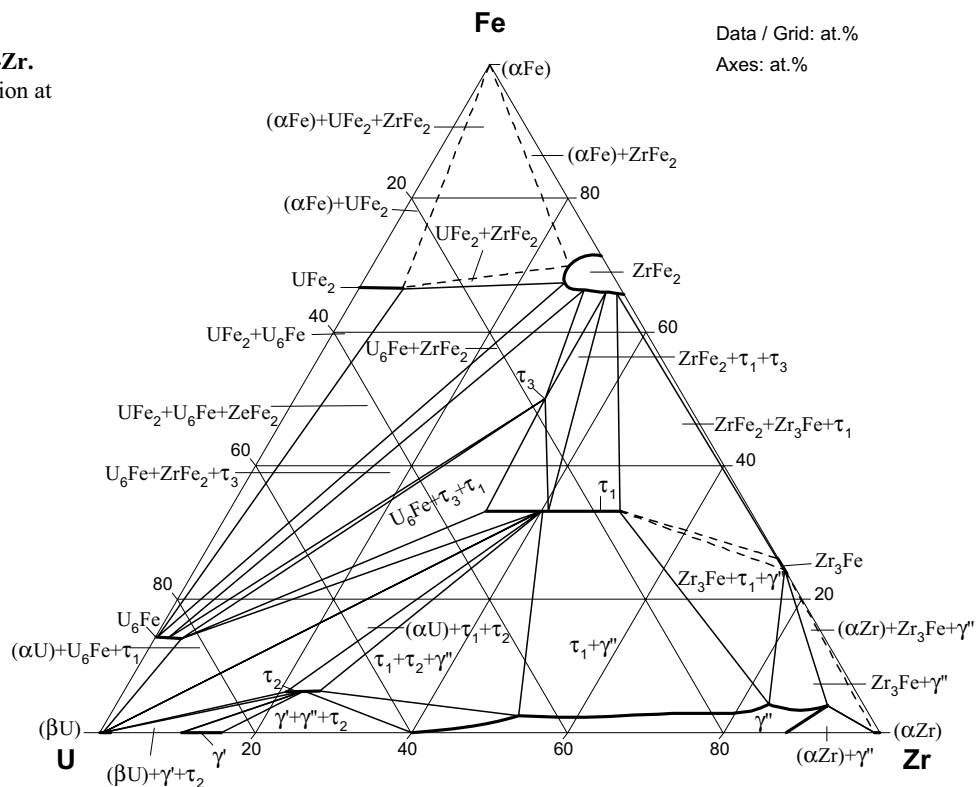


Fig. 3: Fe-U-Zr.
Isothermal section at
800°C

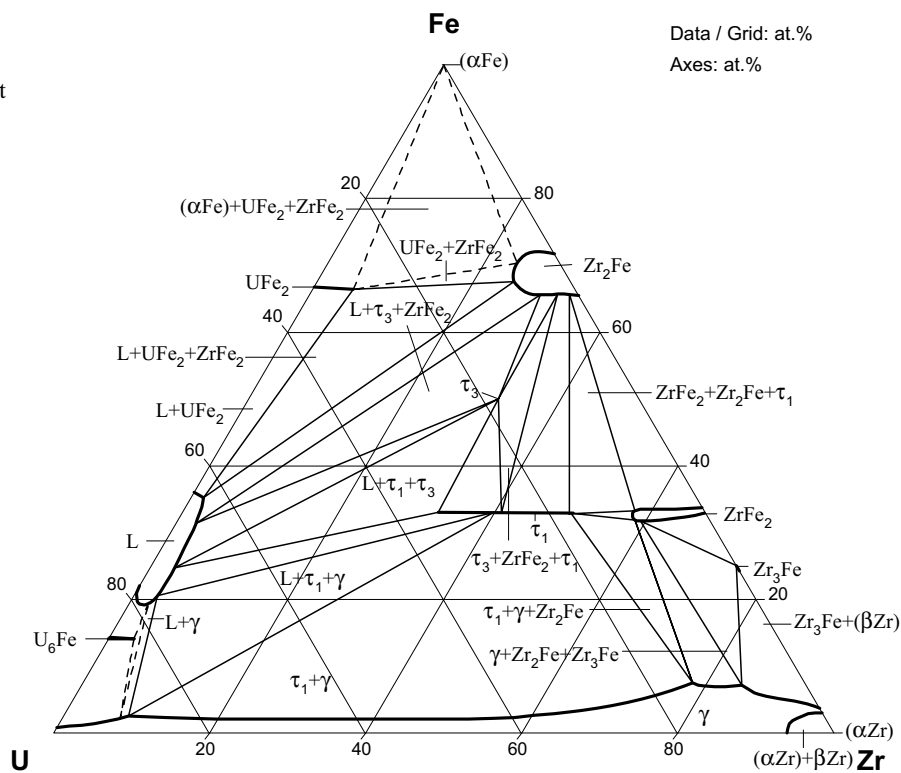


Fig. 4: Fe-U-Zr.
Isothermal section at
1000°C

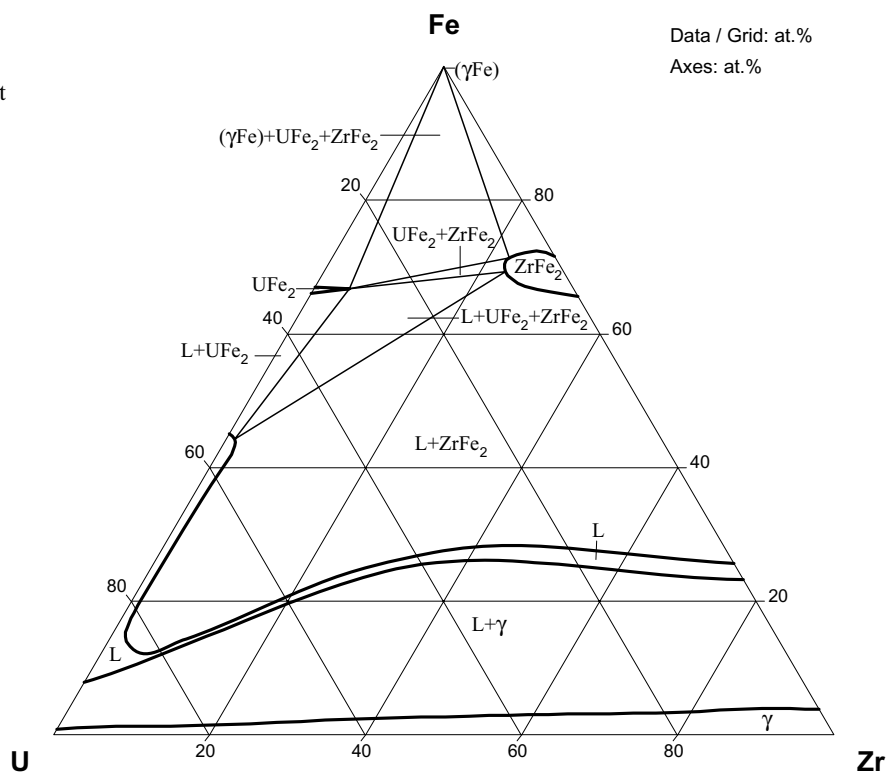


Fig. 5: Fe-U-Zr.
Isothermal section at
1300°C

