Oxygen – Uranium – Zirconium

Pierre Perrot

Introduction

The O-U-Zr system is an important part of the corium, mixture formed at high temperatures between nuclear fuel and other materials (steel, zircaloy, control rods) which may interact with the concrete during an hypothetical severe nuclear accident [1990Rel]. The mixture $U_{0.6}Zr_{0.4}O_2$ which corresponds to 23 mass% ZrO_2 is generally used to model the behavior of corium at high temperatures [2004Asm] and, for this reason, the UO_2-ZrO_2 system has been thoroughly investigated. A first tentative UO_2-ZrO_2 phase diagram was proposed by [1953Lam], reproduced by [1956Lan], and then by [1960Eva] which melted the oxides in a solar furnace then annealed the mixture at 1350°C. An extended range of solid solution of each component was observed, but the stabilisation of fluorite like γZrO_2 by UO_2 was not recognised. The hypothesis of a continuous solid solution in the whole composition range above 1950°C was introduced by [1958Wol]. However, the existence of the high temperature modification of ZrO_2 (the fluorite type γZrO_2) was clearly established by [1963Coh] and the stability of the $\gamma(U,Zr)O_2$ solid solution was put into evidence in the high temperature range. Using experimental informations available to date, [1996Yas] presented a Calphad assessment of the UO_2-ZrO_2 system. More precise experimental determinations of the O-U-Zr phase equilibria at 1000 and 1400°C were presented by [1985Yam, 1990Yam] and [1987Yam], respectively. In order to understand the reactions between the UO_2 fuel and the zircaloy cladding, the Zr-UO_2 reactions have been investigated at 1000-1400°C by [1988Miy], at 2000-2200°C by [1994Hay, 1997Ola], 2300-2500°C by [1996Hay] and 2500-2975°C by [1998Gue] leading to the representation of the O-U-Zr phase equilibria between 1000 and 2500°C used in the thermodynamic assessment carried out by [2004Che]. Experimental investigations are summarized in Table 1.

A first thermodynamic assessment using all the available experimental informations has been carried out by [1998Che]. Unfortunately, experimental information was not fully consistent. Using new activity measurements and experimental results on the O-U binary system, [2004Che] carried out a critical assessment on which the present report is based. The tentative diagram at 2227°C (2500 K) proposed by [1985Hag] analyzing the Three Mile Island core accident is in a good qualitative agreement with the calculations of [2004Che].

Binary Systems

The three binary systems are accepted from the Calphad assessment of [1998Che, 2004Che]. A precise model of the solid and liquid oxide solutions taking into account the oxygen vacancies in the O-U system may be found in [2002Gue]. This model is used in the thermodynamic description of the O-U-Zr system presented by [2004Che]. It should be noted that the U-Zr diagram calculated in [2004Che] differs from the one presented in [Mas2], however, in the temperature range relevant to the known O-U-Zr equilibria, it is basically the same.

Solid Phases

The solid phases are presented in Table 2. UO_2 dissolves 0.38 mol% αZrO_2 at the eutectoid temperature of 1110°C [1967Rom, 1990Das]. The solubility of UO_2 in βZrO_2 presents a retrograde behavior, increasing from 2.8 mol% at 1110°C up to a maximum of 20 mol% around 1750°C. The reactions between ZrO_2 and U_3O_8 have been investigated by [1970Ver]. The presence of U_3O_8 lowers the α-β transition temperature of ZrO_2. Besides, under 150 bar of oxygen pressure and 650°C during 200 h, the following phases are formed: UO_{3-x}, having an orthorhombic lattice and a hexagonal $(U,Zr)O_x$ ones whose compositions are unfortunately not given.

Quasibinary Systems

The quasibinary system UO_2-ZrO_2 assessed by [2004Che] is shown in Fig. 1 with characteristics of the invariant phase equilibrium indicated in Table 3. The former UO_2-ZrO_2 phase diagrams [1953Lam, 1960Eva] presented a miscibility gap in the liquid region, which is not acknowledged in the assessment carried out by [1996Yas] and other authors [1998Gue, 2004Asm].

Isothermal Sections

The isothermal section at 1100, 1600, 2000, 2200, 2400, 2600 and 2800°C as proposed by [2004Che] are given in Figs. 2, 3, 4, 5, 6, 7 and 8, respectively. The sections may be used to explain the observations reported by [1970Bar] on the behavior of UO_2-Zr mixtures between 1600 and 2500°C. The results indicate the presence of the $(U,Zr)O_2$ solid solution, U-Zr alloys and liquid phases.

Temperature – Composition Sections

Figure 9 presents the vertical section UO_2-Zr [2004Che] which is an important tool for predicting the behavior of UO_2 based nuclear fuel on Zr based cladding material.

Thermodynamics

The heat of solution of O in U-Zr liquid alloys have been measured at 2000°C by [1995Ola1]. The stronger binding of O in the solid oxides compared to that of the liquid metals results in heat of solution of O larger than the heat of fusion of pure metals or pure oxides. The activity of oxides in the solid solution $\gamma(Zr,U)O_2$, was measured by mass spectrometry coupled with a Knudsen' effusion cell between 1930 and 2375°C [1997Sto] for the ZrO_2 rich mixtures, and between 1727 and 2225°C in the whole concentration range [2001Bai]. The solid solutions present, above 2225°C an ideal behavior and below that temperature, a positive deviation towards ideality. At lower temperature (1100°C), the $(Zr,U)O_2$ solutions may also be described by a regular model: $\Delta G^{xs} = \alpha\ x_{UO2}\ x_{ZrO2}$ [2004Kin]. The interaction parameters α are respectively 8428, 32234, 32717 and 31386 $J \cdot mol^{-1}$ for the liquid, cubic (fluorite), tetragonal and monoclinic solutions.

Notes on Materials Properties and Applications

Liquefaction of UO_2 by molten Zircaloy is one of the signal events in a severe fuel damage accident in a light water reactor [1997Ola] and considerable efforts have been devoted to the modelling of the process. By quenching the UO_2-ZrO_2 melts at 2500°C, [2004Asm] showed that no separation of the corium melts can be observed under conditions of heavy accident. The vaporization of U_3O_8-ZrO_2 mixtures in a Knudsen' cell towards 2100°C [1984Bel] leads mainly to the formation of the gaseous species UO_2.

The system $U_xZr_{1-x}O_2$ ($0.1 < x < 0.9$) has been found [1962Joh] to exhibit two modes of electrical conductivity: in low temperature region (< 1200°C), the conductivity is mainly electronic and in high temperature region (1200-2000°C), the conductivity is mainly ionic and proceeds by oxygen vacancies. The electrical conductivity in both regions obeys the Arrhenius' law:

$\sigma_L / (\Omega^{-1}\ cm^{-1}) = (0.1 \text{ to } 1) \exp(-3\,000 / T)$ ($T \lesssim 1200$°C)

$\sigma_H / (\Omega^{-1}\ cm^{-1}) = (10^3 \text{ to } 10^6) \exp(-18\,500 / T)$ ($1200 < T < 2000$°C)

The thermal conductivity of these solid solutions is also described by [1967Far] with two different equations, depending on the temperature range, above or below 1650°C. These equations take also into account the irradiation supported by the solid solution.

The solid solutions $U_xZr_{1-x}O_2$ ($x > 0.78$) show an antiferromagnetic transition [1985Hin] with a linear dependence of the Neel temperature on concentration and a critical concentration of 22 mol% ZrO_2.

The density of the $U_{0.6}Zr_{0.4}O_2$ melts, measured between 2700 and 3100°C [2003Asm] is given by the following expression: $\rho(T) / g \cdot cm^{-3} = 7.0 - 4.5 \cdot 10^{-4}\ [(T/K) - 2973]$. This particular mixture, which corresponds to 23 mass% ZrO_2 is generally used for modelling the corium.

Miscellaneous

Reinterpreting former observations [1961Eva] showed that the α-β transition of the $(U,Zr)O_2$ solid solution is of the martensitic type. A mixture β + γ of the $(U,Zr)O_2$ solid solution was shown to be transformed into an homogeneous, metastable cubic form γ $(U,Zr)O_2$ under irradiation [1965Ber]. The process of homogenization can be described by a diffusion constant $D = 3.32 \cdot 10^{-14}$ $cm^2 \cdot s^{-1}$, which indicates that a single fission event homogenizes a volume containing $1.66 \cdot 10^7$ atoms. Irradiation is known to have a marked influence on the physical properties of materials [1965Far], for instance, it may decrease the melting point of oxides by several tens of degrees.

When heated in an accident, UO_2 begin to react with the Zr cladding resulting in formation of the multilayer structure consisting of U, Zr and their oxides [1991Ves]. The diffusion of O is the limiting process of the reaction. The kinetics of dissolution of UO_2 in liquid Zr at 2000°C has been described [1995Ola2] by a two-stage model. In the first stage, the saturation is approached by natural convection mass transfer; in the following stage, where $(U,Zr)O_{2-x}$ precipitates from the melt, oxygen enters the melt as the oxide is reduced to UO_{2-x}. A new method for obtaining high quantities (3 to 10 kg) of ZrO_2-UO_2 melts was proposed by [2003Hon]. Called the "Cold crucible method" or the "Skull melting method", this technique allows the separation of gases, the preparation of high purity material and decrease the heat loss during melting. Induction melting under 50 Hz is possible because the electrical resistivity of a mixture UO_2-ZrO_2 lies around $\sim 4 \cdot 10^{-3}$ Ω cm at the melting point.

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Table 1: Investigations on the O-U-Zr Phase Relations, Structure and Thermodynamics

Reference	Experimental Technique	Temperature/Composition/Phase Range Studied
[1957Och]	X-ray diffraction	U_3O_8-ZrO_2 (tentative)
[1958Bau]	Metallographic examination	O-U-Zr system at 660°C (< 66.7 at.% O)
[1958Wol]	X-ray diffraction on samples quenched from 2300°C	UO_2-ZrO_2 (tentative)
[1960Dou]	Chemical analysis, partitioning of U and O between α and βZr	1095°C, > 85 at.% Zr
[1960Eva]	X-ray diffraction after melting and annealing	UO_2-ZrO_2 at 1350 and 2500°C (tentative phase diagram)
[1962Joh]	Electrical conductivity measurements	UO_2-ZrO_2, 500-2000°C
[1963Coh]	X-ray and metallographic techniques	UO_2-ZrO_2, 1200-2350°C, cubic-tetragonal equilibrium
[1967Rom]	Chemical analysis	UO_2-ZrO_2, 600-1130°C, phase equilibria
[1970Ver]	X-ray diffraction	U_3O_8-ZrO_2, 650°C, oxidation under 150 bar O_2
[1984Bel]	Mass spectrometry measurements	U_3O_8-ZrO_2, 2100°C
[1985Hin]	Magnetic susceptibility measurements	UO_2-ZrO_2, 2-298 K
[1985Yam, 1990Yam]	X-ray diffraction	O-U-Zr diagram at 1000°C
[1987Yam]	X-ray diffraction of Zr-ZrO_2-UO_2 mixtures	O-U-Zr diagram at 1400°C
[1988Miy]	X-ray diffraction of Zr-UO_2 mixtures	O-U-Zr diagram at 1000 and 1400°C
[1994Hay]	X-ray diffraction of Zr-UO_2 mixtures	O-U-Zr diagram, 2000-2200°C
[1995Ola1]	Dissolution calorimetry	Liquid alloy - oxide equilibrium, 2000°C
[1996Hay]	Metallography, SEM and EDX analysis of Zr-UO_2 mixtures	U-Zr-O equilibria at 2300-2500°C Schematic Zr(O)-UO_2 diagram
[1997Sto]	Activity measurements by Knudsen' effusion cell	ZrO_2-UO_2 (< 50 at.% UO_2) 1930-2375°C
[1998Che, 2004Che]	Calphad assessment	The whole diagram up to 2800°C, 0.1 MPa
[1998Gue]	Quenched from the melts, SEM, EDS, WDS analysis	O-U-Zr equilibria at 2500-2975°C
[1998Ves]	Morphological observations, mechanism analysis	Liquid Zr-solid $(Zr,U)O_2$ reactions 1900-2000°C
[2001Bai]	Multiple Knudsen Cell mass spectrometric method	ZrO_2-UO_2, 1727-2225°C

Reference	Experimental Technique	Temperature/Composition/Phase Range Studied
[2003Asm]	Density measurements by a pycnometric method	UO_2-ZrO_2, 2700-3100°C
[2004Asm]	Quenching from the melts	UO_2-ZrO_2 (1.2 < U/Zr < 1.6) at 2500°C
[2004Kin]	Calphad assessment	UO_2-ZrO_2, 1000-3200°C

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(αU) < 668	*oC*4 *Cmcm* αU	 *a* = 285.37 *b* = 586.95 *c* = 495.48	dissolves up to 1.5 at.% Zr at 660°C [1998Che] pure αU at 25°C [Mas2]
(βU) 776 - 668	*tP*30 $P4_2/mnm$ βU	 *a* = 1075.9 *c* = 565.6	dissolves up to 2 at.% Zr at 695°C [1998Che] pure βU at 25°C [Mas2]
(αZr) < 2173	*hP*2 $P6_3/mmc$ Mg	 *a* = 323.16 *c* = 514.75	dissolves up to 31.3 at.% O at 2097°C [2004Che] pure αZr at 25°C [Mas2]
(γU,βZr) 1970 - 612	*cI*2 $Im\bar{3}m$ W		continuous solid solution between γU and βZr. βZr dissolves 10.4 at.% O at 1970°C [2004Che]
(γU) 1135 - 776		*a* = 352.4	pure γU [Mas2]
(βZr) 1885 - 866		*a* = 360.90	pure βZr [Mas2]
δ, UZr_2 < 617	*hP*3 *P6/mmm* AlB_2	*a* = 503 *c* = 308	65 to 78 at.% Zr [2004Che]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
γ, $(UO_2)_{1-x}(\gamma ZrO_2)_x$ < 2852	*cF*12 *Fm*$\bar{3}$*m* CaF_2		continuous solid solution between UO_2 and γZrO_2. $0 \le x \le 1$
UO_2 < 2852		*a* = 547.0	*x* = 0 UO_2 contains from 62.5 (at 2425°C) to 66.7 at.% O [2004Che]
		a = 547 – 26.0 *x*	$(UO_2)_{1-x}(\gamma ZrO_2)_x$ annealed at 1700°C (*x* < 0.5) [1993Kle]
γZrO_2 2710 - 1483		*a* = 527.2	γZrO_2 contains from 61.6 (at 2097°C) to 66.7 at.% O [1963Coh, 2004Che] *x* = 1
U_4O_9 < 1123	*cI*832 *I*$\bar{4}$3*d* or *I*4$_1$32	*a* = 2176	[2004Che]
U_3O_8 < 1870	*oC*44 *Cmcm*	*a* = 706.9 *b* = 1144.5 *c* = 830.3	[2004Che]
UO_3 < 669	*cP*4 *Pm*$\bar{3}$*m* ReO_3	*a* = 414.6	[2004Che]
αZrO_2 < 1205	*mP*12 *P*2$_1$/*c* αZrO_2	*a* = 517 *b* = 522 *c* = 533 β = 99.46	[1963Coh, 2004Che] dissolves 0.2 mol% UO_2 at ~ 1110°C [1967Rom]
βZrO_2 2377 - 1126	*tP*6 *P*4$_2$/*nmc* HgI_2	*a* = 508.4 *c* = 517.0	[1963Coh, 2004Che] dissolves 2.8 mol% UO_2 at ~ 1110°C [1967Rom]

Table 3: Invariant Equilibria

Reaction	*T* [°C]	Type	Phase	Composition (at.%)		
				O	U	Zr
L ⇌ γ	2562	congruent	L	66.7	13.3	20.0
			γ	66.7	13.3	20.0
βZrO_2 ⇌ γ + αZrO_2	1126	e	βZrO_2	66.7	4	29.3
			γ	66.7	32.1	1.2
			αZrO_2	66.7	0	33.3

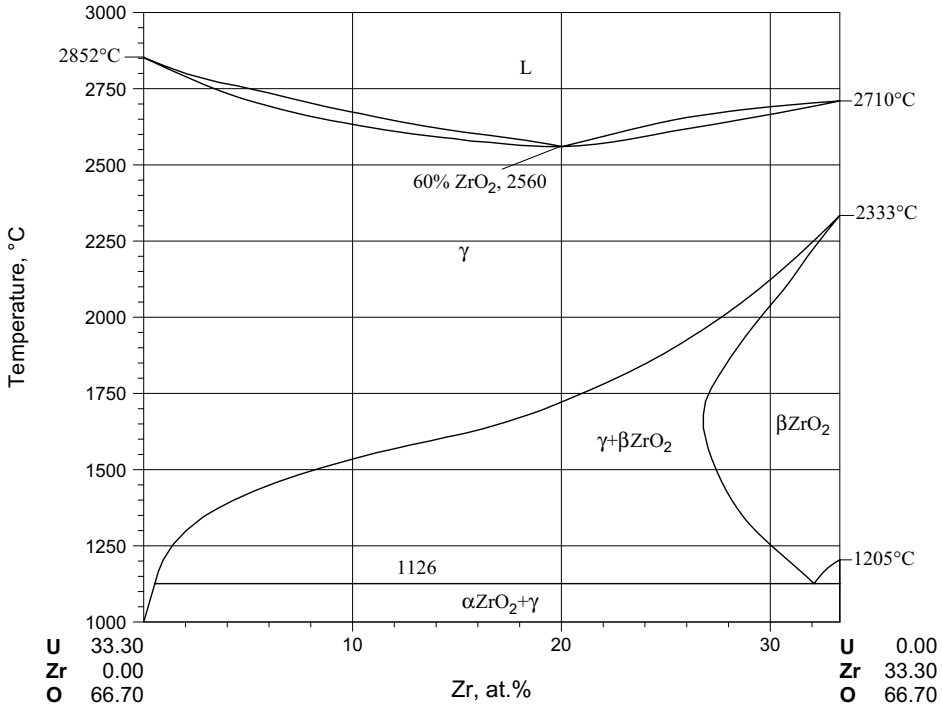

Fig. 1: O-U-Zr. The UO_2-ZrO_2 quasibinary system

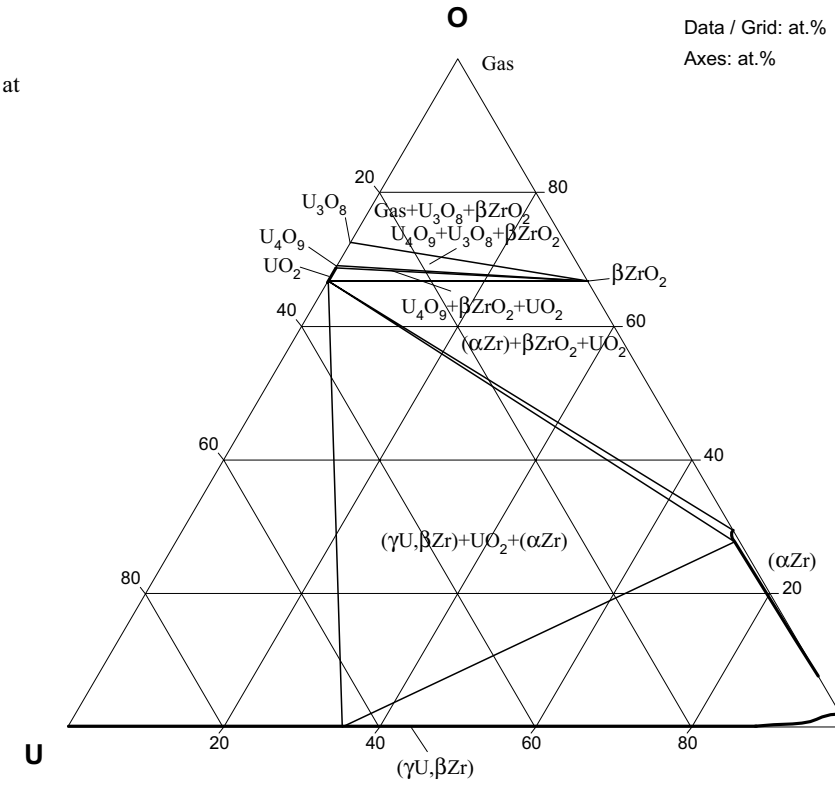

Fig. 2: O-U-Zr. Isothermal section at 1100°C

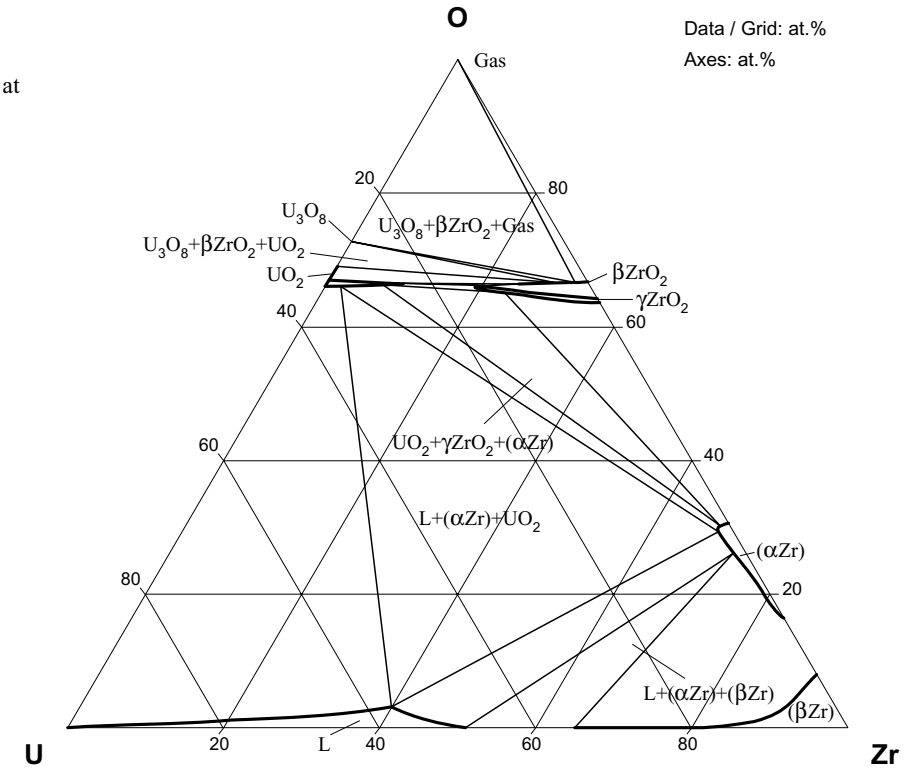

Fig. 3: O-U-Zr. Isothermal section at 1600°C

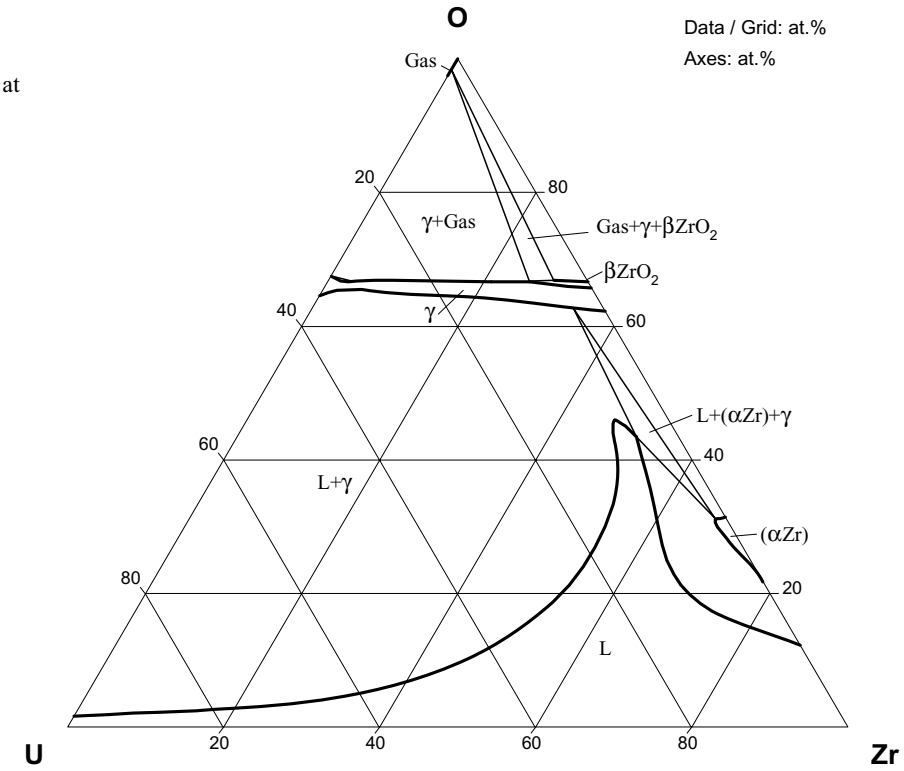

Fig. 4: O-U-Zr. Isothermal section at 2000°C

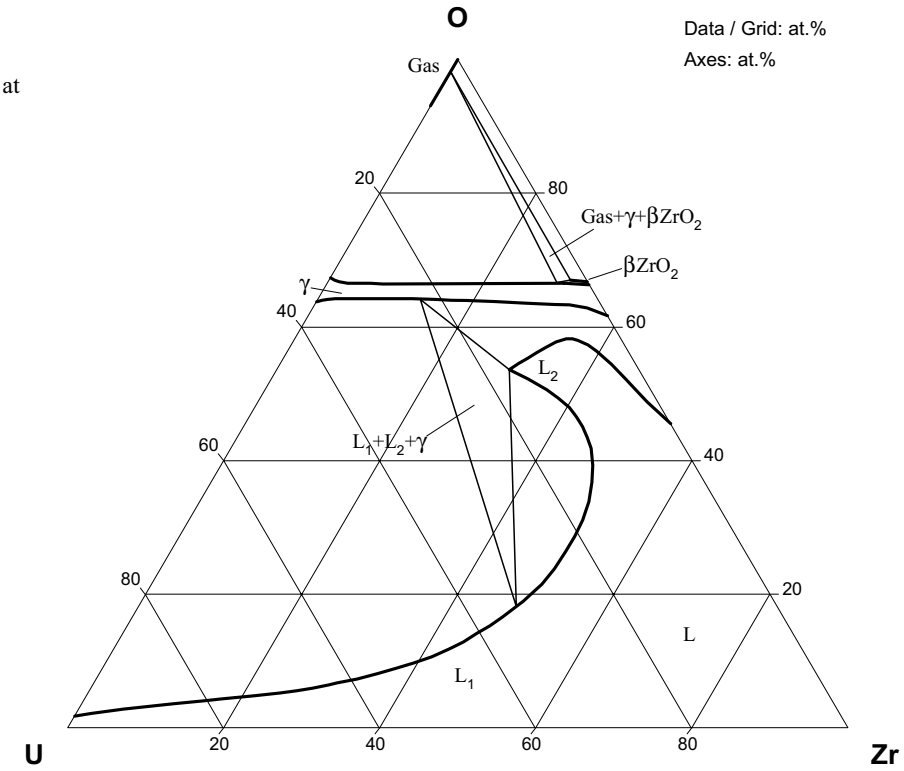

Fig. 5: O-U-Zr. Isothermal section at 2200°C

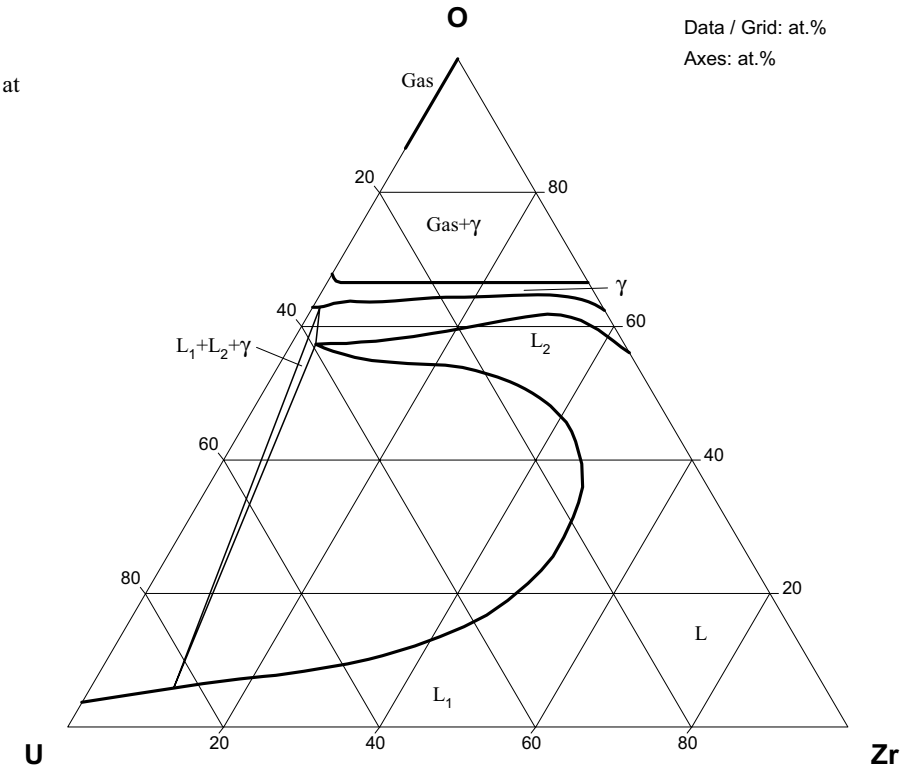

Fig. 6: O-U-Zr. Isothermal section at 2400°C

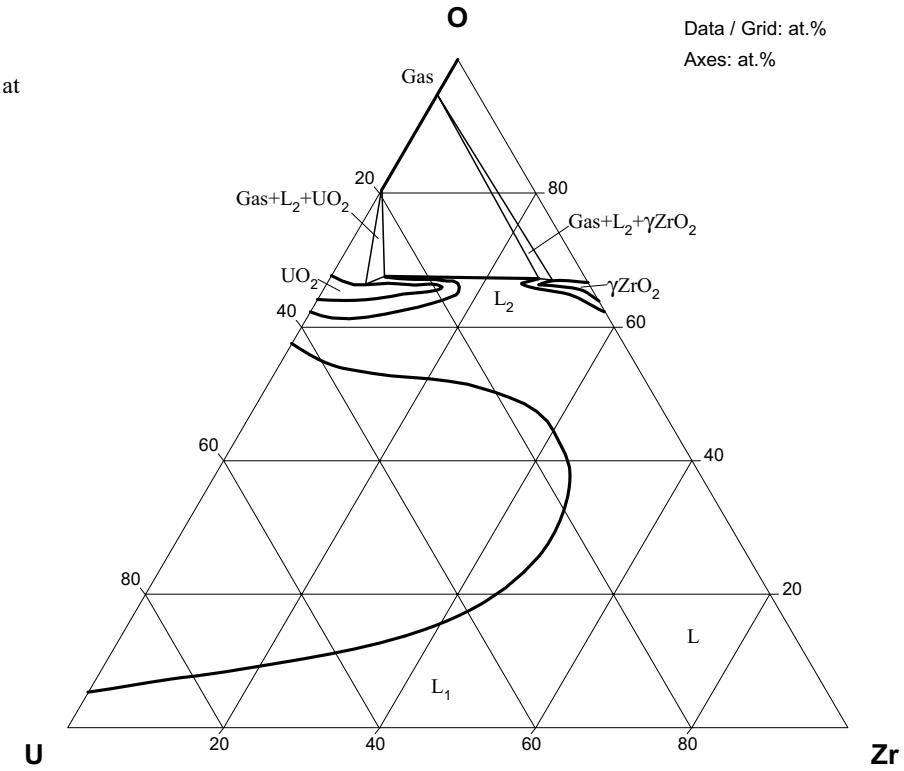

Fig. 7: O-U-Zr. Isothermal section at 2600°C

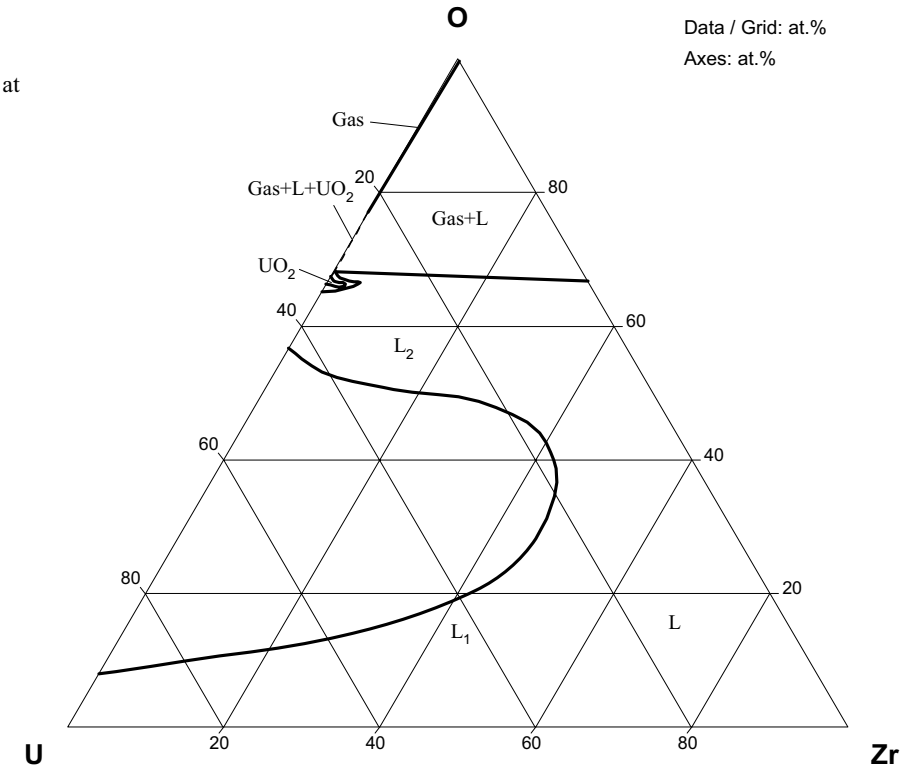

Fig. 8: O-U-Zr. Isothermal section at 2800°C

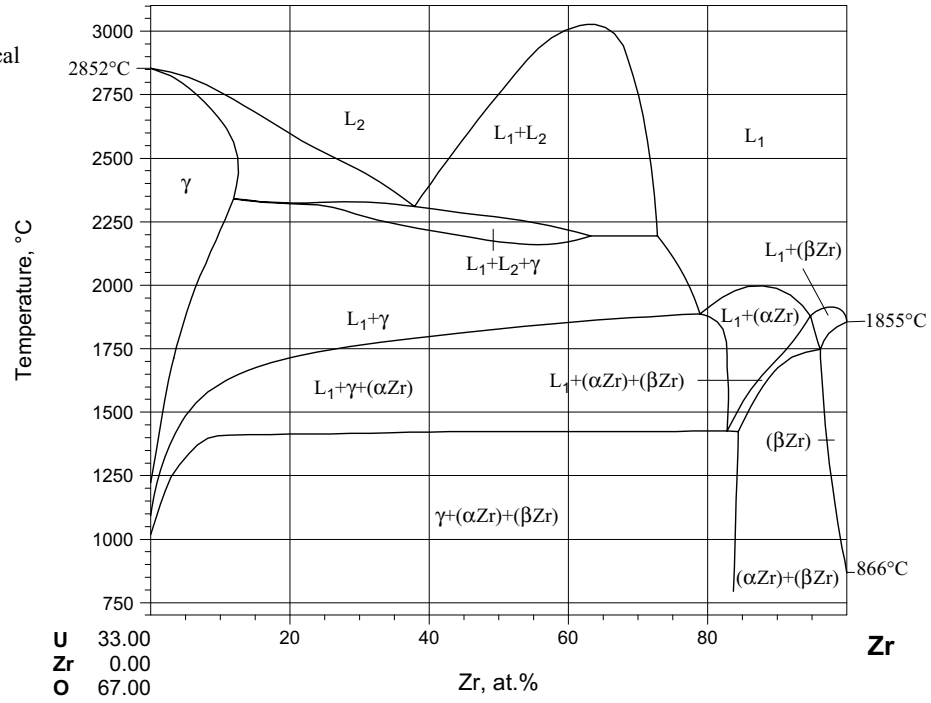

Fig. 9: O-U-Zr. The UO_2 - Zr vertical section