Oxygen – Thorium – Zirconium

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Introduction

A first tentative ThO_2-ZrO_2 phase diagram was proposed by [1929Ruf], which presented a cigar shaped liquidus and solidus together with a miscibility gap in the γ solid solution with a critical point of 2600°C. However, these features are inconsistent from a thermodynamic point of view. A more careful investigation of this system [1975Sak] using a solar furnace confirms the miscibility gap in the γ phase, but demonstrates the existence of a minimum in the solidus and liquidus lines and both features are thermodynamically consistent. These features were confirmed by [1978Ara] which evaluates the position of the critical point (2400°C and 50 mol% ThO_2), the position of the minimum (2480°C and 28 mol% ThO_2) and precises the shape of the tetragonal domain. The reciprocal solubility of γThO_2 and βZrO_2 at 1400°C has been investigated by [2002Gro]. However, a more recent Calphad assessment [2004Kin] shows that the miscibility gap in the γ solid solution must be metastable and presents a diagram with a large β + γ two-phase domain.

Binary Systems

The Th-Zr system is accepted from [Mas2]. The O-Zr system is accepted from the Calphad assessment of [1998Che, 2004Che]. The O-Th system is accepted from [1998Che].

Solid Phases

The solid phases are presented in Table 1.

Quasibinary Systems

The ThO_2-ZrO_2 phase diagram shown in Fig. 1 is mainly from [2004Kin]. The diagram proposed by [1978Ara] has not been taken into account because it presents, without any experimental evidence, two biphased domains γ + γ'. Actually, the only miscibility gap recognized is metastable with a critical point at 2400°C and 50 mol% ZrO_2. At low temperature, it is acknowledged [1981Pep] that ThO_2 and ZrO_2 shows slight mutual solubility, probably no more than 2 mol% in each end-member.
The solubility of ZrO_2 in γThO_2 and that of ThO_2 in βZrO_2 has been investigated by X-ray diffraction of mixtures $Th_{1-x}Zr_xO_2$ annealed at 1400°C following by a slow cooling [2002Gro]. The crystal parameter of cubic γThO_2 remains constant for $x > 0.05$, which agrees with [2004Kin]. For the higher values of x, [2002Gro] observes the presence of a monoclinic phase $\alpha Th_{0.05}Zr_{0.95}O_2$ together with that of $\gamma Th_{0.95}Zr_{0.05}O_2$, which contradicts the known behavior of αZrO_2. It is probable that the monoclinic α phase observed comes from the slow cooling of the β quadratic phase which is stable at 1400°C.

Thermodynamics

The solid solution γ, $(Th,Zr)O_2$, has been described by [1978Ara] with the approximation of regular solutions: $\Delta_{mix}G^{xs} = \alpha\, x_{ThO2}\, x_{ZrO2}$ with $\alpha = 42890$ J·mol^{-1} for the γ solid solution. Such a value leads for the γ solid solution to a miscibility gap at 50 at.% ZrO_2 and 2306°C, which is 100°C lower than the value proposed by [1978Ara]. An evaluation of the α parameter by [2004Kin] leads to the following values: 8427, 39234, 38717 and 32385 J·mol^{-1}, respectively for the liquid solution, the cubic, tetragonal and monoclinic solid solutions.

Notes on Materials Properties and Applications

Early review of nuclear fuel cycles tended to conclude that uranium fuel cycle currently used in nuclear power plants was more preferable than thorium cycle [2000Bus]. However, Th based fuels are of interest due to the efficiency of creating new fissile materials with high burnup, the abundance of Th and the chemical stability of thoria. Thoria could be considered as a potential base for diluting plutonia. On another hand, opposite to urania, thoria can not react with zirconium cladding because the standard enthalpy of formation of ZrO_2 (–1100 kJ·mol^{-1} at 25°C) is of the same order than that of UO_2 (–1085 kJ·mol^{-1} at 25°C) and higher than that of ThO_2 (–1226 kJ·mol^{-1} at 25°C).

Miscellaneous

Zirconium alloys containing thorium oxide were prepared by arc melting [1971Ske]. The refractory ThO_2 dissolved in the molten zirconium precipitates as a dispersed phase on solidification. The resulting composite presents high temperature (650°C) tensile strength up to twice that of Zircaloy-2.

References

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Table 1: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(αTh) < 1360	*cF*4 $Fm\overline{3}m$ Cu	*a* = 508.42	at 25°C [Mas2] dissolves up to 14.8 at.% Zr at 908°C
(αZr) < 2127	*hP*2 $P6_3/mmc$ Mg	*a* = 323.16 *c* = 514.75	at 25°C [Mas2] dissolves up to 31.3 at.% O at 2097°C [2004Che]
(βTh,βZr) (βTh) 1755 - 1360 (βZr) 1855 - 866	*cI*2 $Im\overline{3}m$ W	 *a* = 411.0 *a* = 360.90	 ($\beta Th_{0.54}Zr_{0.46}$) stable between 908 and 1350°C [Mas2] (βZr) dissolves up to 10.4 at.% O at 1970°C [2004Che]
α, αZrO_2 < 1203	*mP*12 $P2_1/c$ ZrO_2	*a* = 522 *b* = 527 *c* = 538 β = 99.46°	66.6 at.% O [2004Che]
β, βZrO_2 2333 - 1203	*tP*6 $P4_2/nmc$ HgI_2	*a* = 511.9 *c* = 526.0	66.5 to 66.6 at.% O [2004Che]. dissolves ~30 at.% ZrO_2 at 2000°C [2004Kin]
γ, $(Th,Zr)O_2$ γZrO_2 2710 - 1483 ThO_2 < 3390	*cF*12 $Fm\overline{3}m$ CaF_2	*a* = 558.7 *a* = 509 *a* = 559.57	$Th_{0.95}Zr_{0.05}O_2$ [2002Gro] 61 to 66.6 at.% O [2004Che] 65 to 66.6 at.% O [2003Kin]

Table 2: Invariant Equilibria

Reaction	*T* [°C]	Type	Phase	Composition (at.%)		
				O	Th	Zr
L ⇌ γ	2480	min	L γ	9.19 9.19	24.14 24.14	66.67 66.67
β ⇌ γ + α	1157	e	β γ α	2.68 31.03 0.96	30.65 2.30 32.37	66.67 66.67 66.67

Fig. 1: O-Th-Zr. The quasibinary system ThO_2-ZrO_2