Carbon – Thorium – Zirconium

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Introduction

Investigations of the C-Th-Zr system by X-ray diffraction [1958Iva, 1961Iva] showed that ThC and ZrC present a very low mutual solubility, even in the cast state after 5 days of annealing at 1000°C. The first diagram was presented by [1962Rud] which showed that non stoichiometric ZrC may be in equilibrium with (Th), ThC and ThC_2. Mixtures (Th) + ZrC and (Zr) + ThC have been investigated respectively by [1963Bad] and by [1968Ale]. A more complete investigation carried out at 1500°C by [1975Hol] agrees qualitatively with the preceding one, but gives more accurate information concerning equilibria between ZrC and the Th-Zr alloys. Further reviews [1977Hol, 1984Hol1, 1984Hol2] present the same diagram at 1500°C without any modifications.

Binary Systems

The C-Zr system has been assessed by [1995Fer] which proposes for ZrC a melting point of 3427°C, that is 123 K lower than the melting point accepted by [Mas2]. The C-Th and Th-Zr diagrams are accepted from [Mas2].

Solid Phases

The solid phases are presented in Table 1. ThC may dissolves up to 8 mol% ZrC [1958Iva, 1961Iva] whereas ZrC does not dissolve any measurable amount of ThC even in the cast state after a 5 days period of annealing at 1000°C. These results were confirmed by [1963Bad] which investigated by microscopic and X-ray examination mixtures (Th) + ZrC annealed at 1000°C. This mixture behaves as a quasibinary system of the eutectic type with a eutectic composition at 89 at.% Th. The solubility of ZrC in (Th) does not exceed 0.5 at.%. On the other hand, mixtures (Zr) + ThC has been investigated by [1968Ale] in the solid state, unfortunately without giving the working temperature. The (Zr) + ThC mixture reacts by forming ZrC + Zr-Th alloys at low ThC content (< 20 at.% Th). Pure ZrC appears at higher ThC content in the mixture.

Isothermal Sections

The isothermal section at 1500°C is given in Fig. 1. The diagram, mainly from [1975Hol] has been corrected to take into account the accepted binaries and the solubility of ZrC in ThC observed by [1958Iva, 1961Iva].

Notes on Materials Properties and Applications

Natural Thorium (100 % ^{232}Th), three times more abundant than uranium in earth crust may be used as nuclear fuel. Although not fissile itself, Th-232 will absorb slow neutrons to produce ^{233}U which is fissile. Refractory thorium carbide has been used as fuel element in high temperature (700-800°C) fast breeder reactor. The behavior of ThC with Zr is of greatest interest because Zr is one of the main constituent of cladding materials.

References

[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 Relation, Phase Diagram, Crys. Structure, Experimental, 2)

[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, Mechan. Prop., Morphology, Phase Relations, Experimental, 4)

[1962Rud] Rudy, E., Benesovsky, F., "Investigations of the System Th-Zr-C" (in German), *Monatsh. Chem.*, **93**, 1279-1283 (1962) (Phase Relations, Experimental, Phase Diagram, Crys. Structure, 11)

[1963Bad] Badaeva, T.A., Kuznetsova, R.I., "Constitution of the Th-Zr-C Allloys" in "*Stroenie i Svoistva Splavov Urana, Toriya i Zirkoniya*" (in Russian), Ivanov, O.S., (Ed.), Gosatomizdat, Moscow, 223-226 (1963) (Crys. Structure, Mechan. Prop., Morphology, Phase Relations, Experimental, 1)

[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 "*Fizika Khimiya Splavov i Tugoplavkikh Soedineniy*" (in Russian), Ivanov, O.S. (Ed.), Nauka, Moscow, 136 (1968) (Crys. Structure, Mechan. Prop., Phase Relations, Experimental, 3)

[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 Relations, Phase Diagram, Thermodyn., Review, 47)

[1977Hol] Holleck, H., "On the Constitution of the Systems Thorium-(Zirconium, Niobium, Ruthenium, Rhodium)-Carbon", *J. Nucl. Mater.*, **66**, 273-282 (1977) (Crys. Structure, Experimental, Phase Relations, Thermodyn., 18)

[1984Hol1] Holleck, H., "Ternary Carbide Systems of Actinoids with the Transitions Metals of 4th to 8th Groups", *J. Nucl. Mater.*, **124**, 129-146 (1984) (Crys. Structure, Phase Relations, 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 Relations, Review, 91)

[1995Fer] Fernandez-Guillermet, A., "Analysis of Thermochemical Properties and Phase Stability in the Zirconium-Carbon System", *J. Alloys Compd.*, **217**, 69-89 (1995) (Phase Relations, Thermodyn., Assessment, #, 128)

Table 1: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
C (graphite) < 3827	*hP*4 $P6_3/mmc$ C (graphite)	a = 246.12 c = 670.9	at 25°C [Mas2]
C (diamond)	*cF*8 $Fd\bar{3}m$ C (diamond)	a = 356.69	high pressure phase
(αTh) < 863	*cF*4 $Fm\bar{3}m$ Cu	a = 508.42	at 25°C [Mas2] Dissolves up to 14.8 at.% Zr at 908°C
(αZr) < 1360	*hP*2 $P6_3/mmc$ Mg	a = 323.16 c = 514.75	at 25°C [Mas2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
β	*cI*2 *Im*$\bar{3}$*m*		$\beta Th_{0.54}Zr_{0.46}$ stable between 908 and 1350°C [Mas2]
(βTh) 1755 - 1360	W	*a* = 411.0	(βTh) dissolves ~9 at.% C at 1707°C
(βZr) 1855 - 863		*a* = 360.90	(βZr) dissolves ~1 at.% C at 1805°C
ThC_{1-x} < 2500	*cF*8 *Fm*$\bar{3}$*m* NaCl	*a* = 534.0	ThC [1977Hol] Solid solution with (αTh) (critical point at 1140°C, 23 at.% C) and with γThC_2 (critical point at 1850°C, 55 at.% C) [Mas2]
αThC_2 < 1440	*mC*12 *C*2/*c* αThC_2	*a* = 669.2 *b* = 422.3 *c* = 674.4 β = 103.0°	66 at.% C [Mas2]
βThC_2 1495 - 1255	*tP*6 $P4_2/mmc$ βThC_2	*a* = 423.5 *c* = 540.8	63 to 66 at.% C [Mas2]
γThC_2 2610 - 1470	*cP*12 *Pa*$\bar{3}$ FeS_2	*a* = 580.9	Presents a solid solution with (αTh). Two miscibility gaps. Critical points at 1140°C, 23 at.% C and 1850°C, 55 at.% C [Mas2]
ZrC_{1-x} < 3427	*cF*8 *Fm*$\bar{3}$*m* NaCl	*a* = 467.0 *a* = 472.2	33 to 50 at.% C [1995Fer] at 33 at.% C [1962Rud] at 50 at.% C [1977Hol]

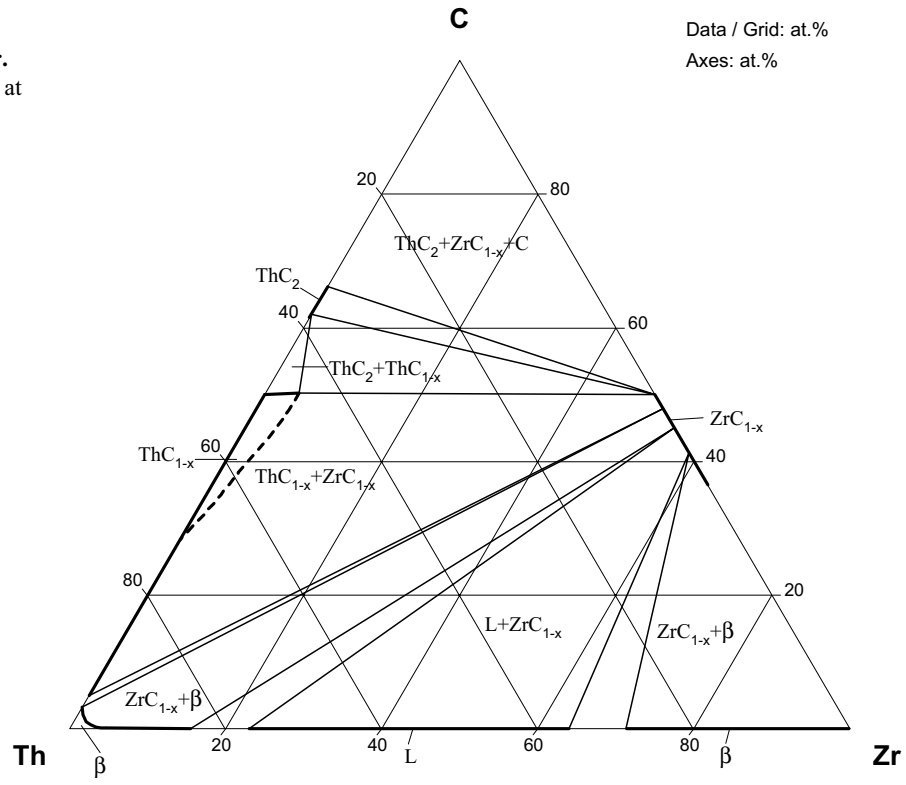

Fig. 1: C-Th-Zr. Isothermal section at 1500°C