Nitrogen – Thorium – Uranium

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Introduction

Investigations of the N-Th-U system by X-ray diffraction have been carried out at 1000°C under nitrogen pressures varying from 10^{-4} to 1 bar [1968Far, 1968Ven] and reproduced by [1975Hol]. The UN-ThN quasibinary system presents a solid solution in the whole composition range, which confirms the observations of [1967Ven].

Binary Systems

The N-Th systems is accepted from [Mas2]. The N-U diagram given by [Mas2] has been updated by [1997Oka], then thermodynamically assessed by [2000Che]. The Th-U system is accepted from the assessment of [1985Pet], reproduced by [Mas2].

Solid Phases

The solid phases are presented in Table 1. The Vegard's law is well obeyed by the (U,Th)N solid solution [1967Ven]. At 1000°C, U may be dissolved into pure ThN (a = 516.19 pm) up to the formation of a solid solution $Th_{0.96}U_{0.02}N_{0.96}$ whose crystal parameter is a = 514.1 pm [1968Ven].

Isothermal Sections

The isothermal section at 1000°C is given in Fig. 1. The diagram, mainly from [1975Hol], has been modified to be coherent with the accepted binaries. The most uranium rich (U,Th)N solid solution in equilibrium with metallic (Th) was found to be $(U_{0.056}Th_{0.944})N_{0.866}$ at 1000°C [1969Fac]. However, taking into account the stoichiometric character of ThN and UN at 1000°C, the composition $(U_{0.056}Th_{0.944})N$ is more probable. Each three-phase triangle in the isothermal section is characterized by a nitrogen pressure at equilibrium. The nitrogen pressure in equilibrium with βU_2N_3, Th_3N_4 and $U_{0.9}Th_{0.1}N$ is ~0.1 bar at 1000°C; the nitrogen pressure in equilibrium with αU_2N_3, βU_2N_3 and Th_3N_4 is ~1 bar at the same temperature.

Thermodynamics

The (U,Th)N solid solution has been described at 1000°C with a regular model: $\Delta_{mix}G^{xs} = \alpha\, x_{UN}\, x_{ThN}$ with α = 11.7 kJ·mol^{-1}. The solid solution probably presents a miscibility gap under a critical point estimated at 430°C [1968Far, 1975Hol].

Notes on Materials Properties and Applications

Alloys N-Th-U are applied as fuel in a fast transmutation reactor in meeting several fuel criteria [1968Ven] such as an operating capability at central fuel temperature of about 800°C.

References

[1967Ven] Venard, J.T., Spruiell, J.E., Cavin, O.B., "Lattice Parameters Across the UN-ThN Pseudobinary", *J. Nucl. Mater.*, **24**, 245-246 (1967) (Crys. Structure, Phase Relations, Experimental, 13)

[1968Far] Farkas, M.S., Daniel, N.E., Askey, D.F., Martin, R.L., Lozier, D.E., Smith, R.A., Veigel, N.D., Barnes, R.H., Wright, T.R., Chubb, W., Markworth, A.J., "Fuel and Fertile Materials - Uranium Metal and Alloys - Plutonium - Thorium - Metal-Ceramic Fuels - Coated-Particle Fuels - Uranium and Thorium Oxides - Carbide and Nitride Fuels - Basic

Studies of Irradiation Effects in Fuel Materials", *Reactor Mater.*, **11**(3), 145-156 (1968) (Phase Diagram, Phase Relations, Review, 66)

[1968Ven] Venard, J.T., Spruiell, J.E., "Phase Relations in the Th-U-N Ternary System at 1000°C", *J. Nucl. Mater.*, **27**, 257-263 (1968) (Experimental, Crys. Structure, Phase Relations, Phase Diagram, 29)

[1969Fac] Fackelmann, J.M., Askey, D.F., Houston, M.D., Martin, R.L., Smith, J.T., Smith, R.A., Barnes, R.H., Wright, T.R., Chubb, W., Lowder, J.T., Rosenberg, H.S., Berry, W.E., Markworth, A.J., "Fuel and Fertile Materials - Uranium Metal and Alloys - Plutonium - Thorium and Its Alloys - Metal-Ceramic Fuels - Uranium and Thorium Oxides - Uranium Carbide, Nitride and Sulfide Fuels - Fuel Reactions Following Loss-of-Coolant Accidents - Mechanism of Corrosion of Fuel Alloys", *Reactor Mater.*, **12**(2), 73-88 (1969) (Phase Relations, Phys. Prop., Thermodyn., Review, 83)

[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)

[1985Pet] Peterson, D.E., "The Th-U (Thorium-Uranium) System", *Bull. Alloy Phase Diagram,* **6**(5), 443-445 (1985) (Phase Relations, Phase Diagram, Crys. Structure, Review, #, 8)

[1997Oka] Okamoto, H., "N-U (Nitrogen-Uranium)", *J. Phase Equilib.*, **18**(1), 107 (1997) (Phase Relations, Phase Diagram, Review, #, 1)

[2000Che] Chevalier, P.Y., Fischer, E., Cheynet, B., "Thermodynamic Modelling of the N-U System", *J. Nucl. Mater.*, **280,** 136-150 (2000) (Phase Relations, Phase Diagram, Thermodyn., Assessment, #, 44)

Table 1: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(βTh) 1755 - 1360	*cI*2 $Im\bar{3}m$ W	a = 411.0	(βTh) dissolves up to 12.2 at.% U at 1375°C [Mas2]
(αTh) < 1360	*cF*4 $Fm\bar{3}m$ Cu	a = 508.42	at 25°C [Mas2] dissolves up to 6.8 at.% U at 1270°C
(γU) 1135 - 776	*cI*2 $Im\bar{3}m$ W	a = 352.	(γU) dissolves up to ~2 at.% Th at 1100°C [Mas2]
(βU) 776 - 668	*tP*30 $P4_2/mnm$ βU	a = 1075.9 c = 565.6	at 25°C [Mas2]
(αU) < 668	*oC*4 *Cmcm* αU	a = 285.37 b = 586.95 c = 495.48	at 25°C [Mas2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(U,Th)N $U_{0.5}Th_{0.5}N$	*cF*8 $Fm\bar{3}m$ NaCl	a = 503.2	solid solution [1968Ven]
UN < 2789		a = 488.83	UN melts congruently at 2835°C, 2.5 MPa N_2 [2000Che]
ThN < 2820		a = 516.19	ThN: 46 to 50 at.% N [1967Ven, Mas2]
βU_2N_3 1349 - 776	*hP*5 $P\bar{3}m1$ La_2O_3	a = 370.0 c = 582.5	58.7 at.% N [2000Che]
αU_2N_3 < 1134	*cI*80 $Ia\bar{3}$ Mn_2O_3	a = 1068.2	60 to 64 at.% N. Gradually changes to CaF_2 type with increasing N content [2000Che]
Th_3N_4 < 1900	*hR*21 $R\bar{3}m$ Al_4C_3	a = 387.5 c = 2739	57 at.% N [Mas2, V-C2]

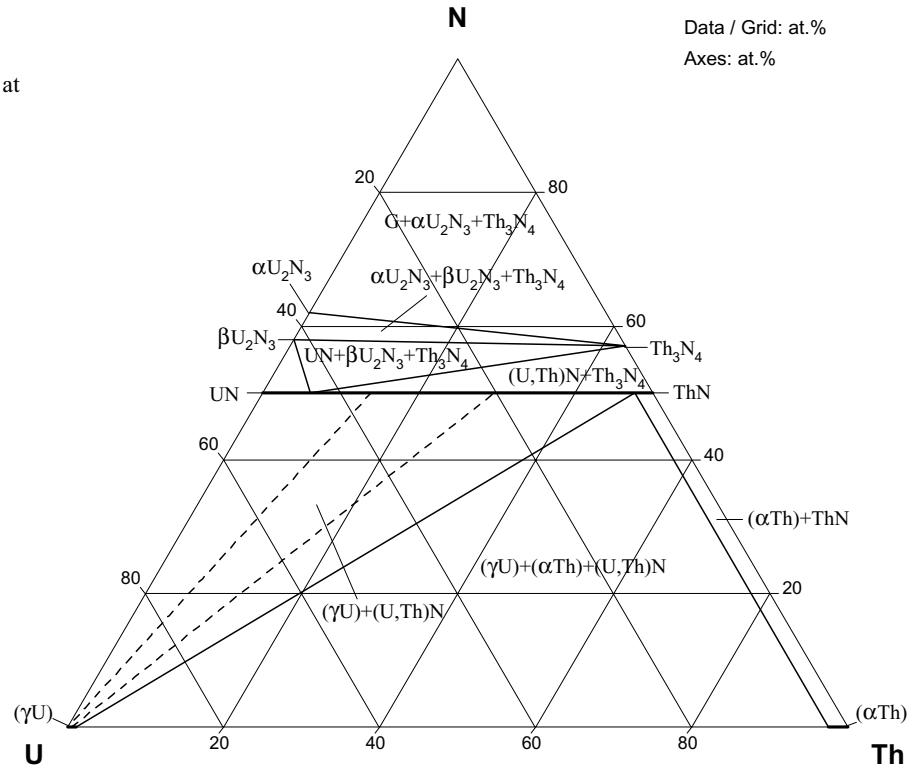

Fig. 1: N-Th-U. Isothermal section at 1000°C