Iron – Nitrogen – Uranium

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Introduction

The investigations of this ternary system are devoted only to the phase diagram of the quasibinary system Fe-UN [1962Kat, 1963Bri, 1966Pri, 1971Guh, 1974Imo].
According to the thermodynamic calculations UN does not react with Fe. The solid-solid reactions of Fe with UN were investigated at elevated temperatures by [1962Kat, 1966Pri]: UN samples showed no signs of reaction after 500 h at 1000°C. [1963Bri] indicated that the system Fe-UN was found to be of simple eutectic type and the eutectic contains 48.5 mass% Fe and crystallizes at 1430 ± 10°C. The later investigations showed that the eutectic temperature is equal to 1395 ± 5°C, eutectic composition being at 49 mass% Fe [1971Guh].
[1974Imo] confirmed that Fe and UN are compatible under the following conditions: at 1000°C in 0.4-33.3 kPa of nitrogen, and at 1400°C in 44 kPa of nitrogen. As the lattice parameter of UN remained unchanged it was suggested that the solubility of Fe in UN is very small. By heating a mixed powder of Fe and UN at 1400°C in a vacuum of 0.013 Pa for 5 h, UFe_2 was formed, but the reaction did not occur at 1220°C by heating for 25 h [1974Imo].
Powdered UFe_2 interacts with UN at 1000°C in 40 kPa of nitrogen for 5 h forming U_2N_3 and Fe [1974Imo]: $4UFe_2 + 3N_2 \rightleftharpoons 2U_2N_3 + 8Fe$. Thus there seem to exist as equilibrium the next reactions: $UN + 2Fe \rightleftharpoons UFe_2 + 1/2N_2$ (1) and/or $2U_2N_3 + 8Fe \rightleftharpoons 4UFe_2 + 3N_2$ (2). The equilibrium pressure for the reaction (1) was estimated to be 0.003 Pa at 1220°C and 0.133 Pa at 1400°C. Therefore the formation of UFe_2 is practically impossible below 1400°C and the liquid appears in the Fe-UN quasibinary system at higher temperature [1971Guh].
Investigations of the system are listed in Table 1.

Binary Systems

Binary systems Fe-N, Fe-U and N-U are accepted from [Mas2].

Solid Phases

There are no data about existence of ternary compounds in the Fe-N-U system. Crystallographic data of all unary phases and binary compounds are listed in Table 2.

Quasibinary Systems

The Fe-UN system was constructed using the data of [1963Bri] and [1971Guh] and it is seen that this quasibinary system is of simple eutectic type with no evidence of solid solubility (Fig. 1).

Invariant Equilibria

The temperature of 1395°C and the liquid composition of 49 mass% Fe (68.44Fe-15.79U(at.%)) are accepted from [1971Guh] for the three-phase invariant eutectic reaction L $\rightleftharpoons$ UN + (γFe).

Notes on Materials Properties and Applications

Dispersions of UN in Fe have been examined as potential fuel elements for high-temperature nuclear applications [1963Bri]. To localize fission-product damage it is usually required that the structure consists essentially of discrete particles of the uranium compounds dispersed in a metallic uranium-free matrix.

References

[1962Kat] Katz, S., "High Temperature Reactions between Refractory Uranium Compounds and Metals", *J. Nucl. Mater.*, **6**(2), 172-181 (1962) (Experimental, Phase Relations, Thermodyn., 21)

[1963Bri] Briggs, G., Guha, J., Barta, J., White, J., "Systems of UC, UC_2, and UN with Transition Metals", *Trans. Brit. Ceram. Soc.*, **62**, 221-246 (1963) (Experimental, Morphology, Phase Diagram, Phase Relations, 18)

[1966Pri] Price, D.E., Moak, D.P., "The Compatibility of Uranium Nitride with Potential Cladding Metals", *Trans. Amer. Nucl. Soc.*, **9**, 418 (1966) (Experimental, Phase Relations, 0)

[1971Guh] Guha, J.P., "Phase Equilibrium Relationships in the System UN-UC-Fe", *J. Nucl. Mater.*, **41**, 187-194 (1971) (Experimental, Phase Diagram, Phase Relations, 15)

[1974Imo] Imoto, S., Namba, S., "Thermodynamics Applied to Compatibility of UN with Ni, Cr and Fe", *J. Nucl. Mater.*, **51**, 106-111 (1974) (Experimental, Phase Relations, Thermodyn., 20)

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

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1962Kat]	XRD, metallography	1000°C / Fe-UN
[1963Bri]	XRD, metallography	1250-1900°C / Fe-UN
[1966Pri]	Metallography	400-1350°C / Fe-UN
[1971Guh]	XRD, metallography	Fe-UN
[1974Imo]	XRD, measurements of equilibrium pressures of nitrogen	up to 1400°C / Fe-UN

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(εFe)	*hP*2 $P6_3/mmc$ Mg	*a* = 246.8 *c* = 396.0	at 25°C, 13 GPa [Mas2]
(δFe) 1538 - 1394	*cI*2 $Im\overline{3}m$ W	*a* = 293.15	[Mas2]
(γFe) 1394 - 912	*cF*4 $Fm\overline{3}m$ Cu	*a* = 364.67	at 915°C [V-C2, Mas2]
(αFe) < 912	*cI*2 $Im\overline{3}m$ W	*a* = 286.65	at 25°C [Mas2]
(γU) 1135 - 776	*cI*2 $Im\overline{3}m$ W	*a* = 352.4	[Mas2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(βU) 776 - 668	*tP*30 $P4_2/mnm$ βU	a = 1075.9 c = 565.6	[Mas2]
(αU) < 668	*oC*4 *Cmcm* αU	a = 285.37 b = 586.95 c = 495.48	at 25°C [Mas2]
Fe_2N $\lesssim$ 500	*hP*9 $P\overline{3}1m$ V_2N	a = 478.7 c = 441.8	[V-C2, Mas2]
Fe_3N	*hP*4 $P6_3/mmc$ NiAs	a = 270.5 c = 437.6	[V-C2] Mineral siderazot
Fe_4N	*cP*5 $Pm\overline{3}m$ $TiCaO_3$	a = 389.6 ± 0.2	[V-C2] Mineral roaldite
Fe_4N < 680	*cF*8 $Fm\overline{3}m$ NaCl	a = 379.0 ± 0.1	[V-C2, Mas2]
Fe_5N_2 (ε-phase)	*hP*4 $P6_3/mmc$ NiAs	a = 274.42 ± 0.04 c = 440.25 ± 0.11	[V-C2]
Fe_8N ?	*tI*18 *I*4/*mmm* Fe_8N	a = 572.0 c = 629.2	[V-C2]
Fe_2U < 1228	*cF*24 $Fd\overline{3}m$ $MgCu_2$	a = 706.29	[V-C2, Mas2]
FeU_6 < 795	*tI*28 *I*4/*mcm* MnU_6	a = 1024.99 ± 0.01 c = 525.00 ± 0.01	at 20 K
		a = 1025.36 ± 0.01 c = 524.84 ± 0.01	at 50 K
		a = 1026.25 ± 0.01 c = 524.58 ± 0.01	at 100 K
		a = 1027.24 ± 0.01 c = 524.36 ± 0.01	at 150 K
		a = 1028.63 ± 0.01 c = 524.10 ± 0.01	at 220 K
		a = 1030.22 ± 0.01 c = 523.86 ± 0.01	at 295 K [V-C2, Mas2]
UN < 2805	*cF*8 $Fm\overline{3}m$ NaCl	a = 488.87 ± 0.03	[V-C2, Mas2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
UN(hp)	*hR** $R\overline{3}m$?	a = 316.9 ± 0.4 c = 864.0 ± 1.4	high-pressure phase at 34 GPa [V-C2]
UN_2	*cF*12 $Fm\overline{3}m$ CaF_2	a = 529.9	[V-C2, Mas2]
βU_2N_3 1352-940	*hP*5 $P\overline{3}m1$ La_2O_3	a = 369.77 ± 0.01 c = 583.3 ± 0.1	[V-C2, Mas2]
αU_2N_3 < 1132	*cI*80 $Ia\overline{3}$ Mn_2O_3	a = 1068.4 ± 0.1	[V-C2, Mas2]
U_4N_7	*cI*96 $Ia\overline{3}$ U_4N_7	a = 1062.8 ± 0.1	[V-C2]

Fig. 1: Fe-N-U. Phase diagram of the quasibinary system Fe-UN