# Nitrogen – Uranium – Zirconium

*Pierre Perrot*

## Introduction

Investigations of the N-U-Zr system by X-ray diffraction [1965Far] showed that the UN-ZrN quasibinary gives a solid solution up to at least 10 mass% Zr whereas [1968Hol1] observed at 1800 and 2000°C a continuous solid solution between pure ZrN and $U_{0.8}Zr_{0.2}N$. The (U,Zr)N solid solution was observed in the whole composition range [1968Hol2] by heating mechanical mixtures during 72 h at 2000°C. The UN-Zr and the (U,Zr)-$N_2$ reactions at 1000°C were investigated respectively by [1962Kat] and [1994Aka, 1997Oga, 2001Aka].

## Binary Systems

The N-Zr system has been assessed by [1994Gri] which proposed for ZrN a sublimation point of 3410°C and a melting point of 3670°C under 6 MPa of nitrogen pressure, which is 427°C higher than the melting point estimated by [Mas2]. Later, the N-Zr system was optimized by calculation using Calphad method [2004Ma], leading to a lower melting point of the ZrN phase. Consequently, the phase diagram proposed by [1994Gri] has been retained in this assessment. The N-U diagram has been updated by [1997Oka], and then thermodynamically assessed by [2000Che]. The U-Zr diagram is accepted from the Calphad assessment of [2004Che].

## Solid Phases

The solid phases are presented in Table 1. The (γU,βZr) solid solution is stable above the eutectoid point at 606°C and 80 at.% Zr. Nitrogen has the effect to increase the (αZr)-(βZr) equilibrium temperature. The nitrogen solubility in the (βZr) phase at 660°C presents a maximum at a composition of 80 at.% U and 425 ppm N [1958Bau]. The nitrogen content of the (αZr) phase in equilibrium with the (βZr) phase is 19 ppm N at the same temperature.

## Quasibinary Systems

The solidus and liquidus temperatures of the (U,Zr)N quasibinary system are shown in Fig. 1. The figure is drawn from the diagram proposed by [2003The] modified to take into account two facts: the accepted melting temperature of UN is 2789°C and the temperature of 3410°C is not the true melting temperature of ZrN, but the temperature at which ZrN loses its nitrogen under 1 bar of nitrogen pressure.

## Isothermal Sections

The isothermal section at 1000°C showing some isobaric curves is given in Fig. 2. A three-phase triangle in the diagram is characterized by a nitrogen pressure at equilibrium. The nitrogen pressure in equilibrium with the mixture $\alpha U_2N_3$-$\beta U_2N_3$-$U_{0.1}Zr_{0.9}N$ is between 0.1 and 1 bar at 1000°C. The diagram, mainly from [1975Hol] has been modified to be coherent with the accepted binary systems. This diagram agrees with the observations of [1962Kat, 1994Aka]. An UN-Zr mixture heated during 168 h at 1000°C shows the formation of a ZrN phase identified by metallographic examination [1962Kat]. The reactions between (U,Zr) alloys and nitrogen was investigated by electron-probe microanalysis and X-ray diffraction between 800 and 1000°C under nitrogen pressures of 0.19 and 20 kPa [1994Aka]. The scales are mainly composed of $U_2N_3$, ZrN and (αZr) having dissolved N. Similar observations are also reported by [1997Oga]. The solubility of U in ZrN or in Zr having dissolved N is negligible [2001Aka].

### Thermodynamics

The (U,Zr)N solid solution has been described at 1000°C with a regular model: $\Delta_{mix}G^{xs} = \alpha\, x_{UN}\, x_{ZrN}$ with $\alpha = 18.4$ kJ·mol$^{-1}$. The solid solution may exhibit a miscibility gap under a critical point estimated at 830°C [1975Hol].

### Notes on Materials Properties and Applications

UN used as fuel in a fast transmutation reactor, or (U,Zr)N when ZrN is used as a diluent, offers enhanced performances compared to the conventional oxide fuel [2003The]. It presents higher thermal conductivity, good sodium compatibility and, in case of fuel reprocessing, higher solubility in nitric acid.
The compatibility of UN with cladding materials such as Zr and zircaloy has been tested by [1966Pri] by compressing UN and Zr discs between 400 and 1350°C for periods up to 5000 h. Below 700°C, the reaction products have a low rate of growth and were identified as a mixture of (U,Zr)N solid solution and U rich alloy.

### References

[1958Bau] Bauer, A.A., Beatty, G.H., Rough, F.A., "The Constitution of Zirconium-Uranium Alloys Containing Oxygen or Nitrogen", *Trans. Met. Soc. AIME*, **212**(12), 801-808 (1958) (Phase Relations, Experimental, 5)

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

[1965Far] Farkas, M.S., Pardue, W.M., Martin, R.L., Stoltz, D.L., Kizer, D.E., Veigel, N.D., Townley, C.W., Pfeifer, W.H., Barnes, R.H., Wright, T.R., Chubb, W., Speidel, E.O., Berry, W.E., Lemmon, A.W., Rough, F.A., "Fuel and Fertile Materials - Uranium Metal and Alloys - Plutonium - Thorium - Metal-Ceramic Fuels - Coated-Particle Fuel Materials - Uranium Oxides - Carbide and Nitride Fuels - Mechanism of Corrosion of Fuel Alloys - Fuel-Water Reactions - Basic Studies", *Reactor Mater.*, **8**(1), 1-17 (1965) (Crys. Structure, Electr. Prop., Phase Relations, Review, 88)

[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, Phase Diagram)

[1968Hol1] Holleck, H., Wagner, W., "Ternary Oxides, Nitrides and Carbides of U-Ce-Zr", *Thermodynamics of Nuclear Materials, Vienna*, 667-681 (1968) (Experimental, Phase Relations, 15)

[1968Hol2] Holleck, H., Smailos, E., Thuemmler, F., "Solid Solution Formation in Quasi-Binary Systems of UN and the Mononitrides", *Monatsh. Chem.*, **99**(3), 985-989 (1968) (Crys. Structure, Phase Relations, Experimental, 10)

[1975Hol] Holleck, H., "Ternary Phase Equilibria in the Systems Actinide-Transition Metal-Carbon and Actinide-Transition Metal Nitrogen", *Thermodynamics of Nuclear Materials.,* Proc. Symp., 4$^{th}$, Vienna, October 21-25, 1974, International Atomic Energy Agency, Vienna, Austria, **2**, 213-264 (1975) (Crys. Structure, Phase Diagram, Phase Relations, Review, Thermodyn., 47)

[1994Aka] Akabori, M., Itoh, A., Ogawa, T., Ugajin, M., "Reactions Between U-Zr Alloys and Nitrogen", *J. Alloys Compd.*, **213/214**, 366-368 (1994) (Phase Relations, Interface Phenomena, Experimental, 6)

[1994Gri] Gribaudo, L., Arias, D., Abriata, J., "The N-Zr (Nitrogen-Zirconium) System", *J. Phase Equilib.,* **15**(4), 441-449 (1994) (Phase Diagram, Phase Relations, Thermodyn., Review, #, 29)

[1997Oga] Ogava, T., Akabori, M., Kobayashi, F., Haire, R.G., "Thermochemical Modeling of Actinide Alloys Related to Advanced Fuel Cycles", *J. Nucl. Mater.*, **247**, 215-221 (1997) (Phase Relations, Thermodyn., Review, 39)

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

[2001Aka] Akabori, M., Itoh, A., Ogawa, T., "Formation of Nitrides at the Surface of U-Zr Alloys", *J. Nucl. Mater.*, **289**, 342-345 (2001) (Phase Relations, Interface Phenomena, Experimental, 6)

[2003The] Thetford, R., Mignanelli, M., "The Chemistry and Physics of Modelling Nitride Fuels for Transmutation", *J. Nucl. Mater.*, **320**(1-2), 44-53 (2003) (Phase Diagram, Phys. Prop., Experimental, #, 51)

[2004Che] Chevalier, P.Y., Fischer, E., Cheynet, B., "Progress in the Thermodynamic Modelling of the O-U-Zr Ternary System", *Calphad,* **28**(1), 15-40 (2004) (Thermodyn., Calculation, Assessment, #, 92)

[2004Ma] Ma, X., Li, C., Bai, K., Wu, P., Zhang, W., "Thermodynamic Assessment of the Zr-N System", *J. Alloys Compd.*, **373**, 194-201 (2004) (Phase Relations, Review, Calculation, Thermodyn., 40)

**Table 1:** Crystallographic Data of Solid Phases

| Phase/ Temperature Range [°C] | Pearson Symbol/ Space Group/ Prototype | Lattice Parameters [pm] | Comments/References |
|---|---|---|---|
| (αU)<br>< 668 | *oC*4<br>*Cmcm*<br>αU | *a* =285.37<br>*b* = 586.95<br>*c* = 495.48 | at 25°C [Mas2]<br>dissolves ~1 at.% Zr at 617°C [2004Che] |
| (βU)<br>776 - 668 | *tP*30<br>$P4_2/mnm$<br>βU | *a* = 1075.9<br>*c* = 565.6 | at 25°C [Mas2]<br>dissolves ~2 at.% Zr at 693°C [2004Che] |
| (αZr)<br>< 863 | *hP*2<br>$P6_3/mmc$<br>Mg | *a* = 323.16<br>*c* = 514.75 | at 25°C [Mas2]<br>dissolves ~0.5 at.% U at 593°C [2004Che]<br>dissolves 24.7 at.% N at 1988°C [1994Gri] |
| (γU,βZr) | *cI*2<br>$Im\bar{3}m$ | | solid solution (γU,βZr) |
| (γU)<br>1135 - 776 | W | *a* = 352.4 | [Mas2] |
| (βZr)<br>1855 -863 | | *a* = 360.90 | [Mas2] |
| δ, $UZr_2$<br>< 617 | *hP*3<br>*P*6/*mmm*<br>$AlB_2$ | *a* = 502.5<br>*c* = 308.6 | 64.7 to 77.9 at.% Zr [2004Che]<br>[V-C2] |

| Phase/ Temperature Range [°C] | Pearson Symbol/ Space Group/ Prototype | Lattice Parameters [pm] | Comments/References |
|---|---|---|---|
| (U,Zr)N | *cF*8<br>$Fm\bar{3}m$ | | |
| UN<br>< 2789 | NaCl | $a$ = 488.83 | 50 to 66.3 at.% U at 2427 °C [2000Che]<br>UN melts congruently at 2850°C, 2.5 MPa $N_2$ [2000Che] |
| ZrN<br>< 3410 | | $a$ = 457.5 | ZrN: 40 to 50 at.% N. Melts congruently at 3670°C, 6 MPa $N_2$ pressure; [1994Gri] |
| $\beta U_2N_3$<br>1349.1 - 955.2 | *hP*5<br>$P\bar{3}m1$<br>$La_2O_3$ | $a$ = 370.0<br>$c$ = 582.6 | 58.7 at.% N [2000Che] |
| $\alpha U_2N_3$<br>< 1135 | *cI*80<br>$Ia\bar{3}$<br>$Mn_2O_3$ | $a$ = 1068.8 | 60 to 64 at.% N. Gradually changes to $CaF_2$ type with increasing N content [2000Che] |
| $UN_2$ | *cF*12<br>$Fm\bar{3}m$<br>$CaF_2$ | $a$ = 521.0 | high nitrogen pressure phase |

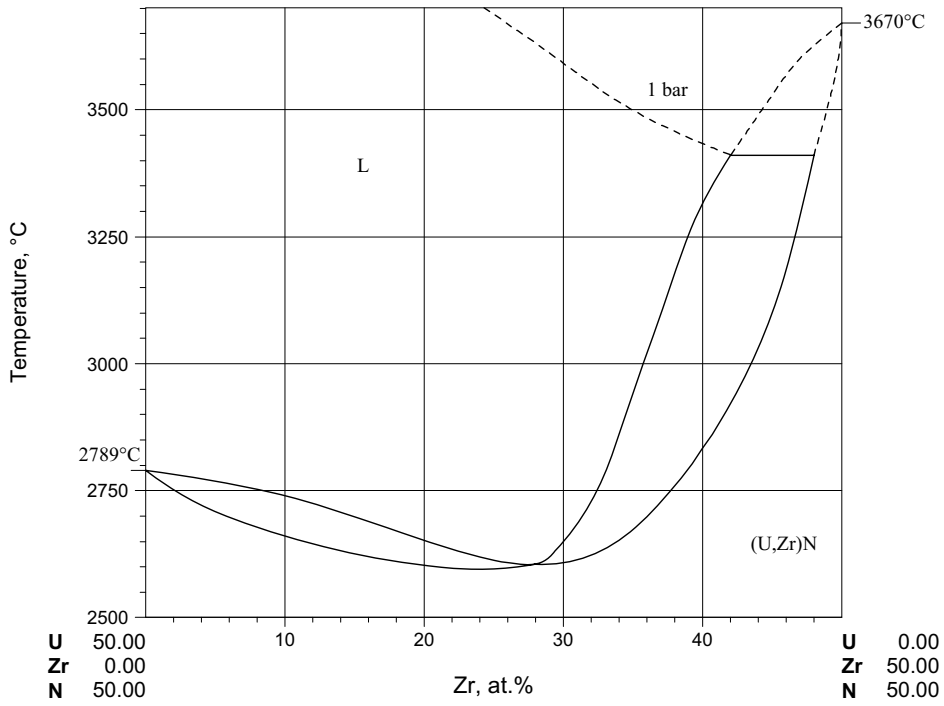


**Fig. 1: N-U-Zr.** The UN-ZrN quasibinary system

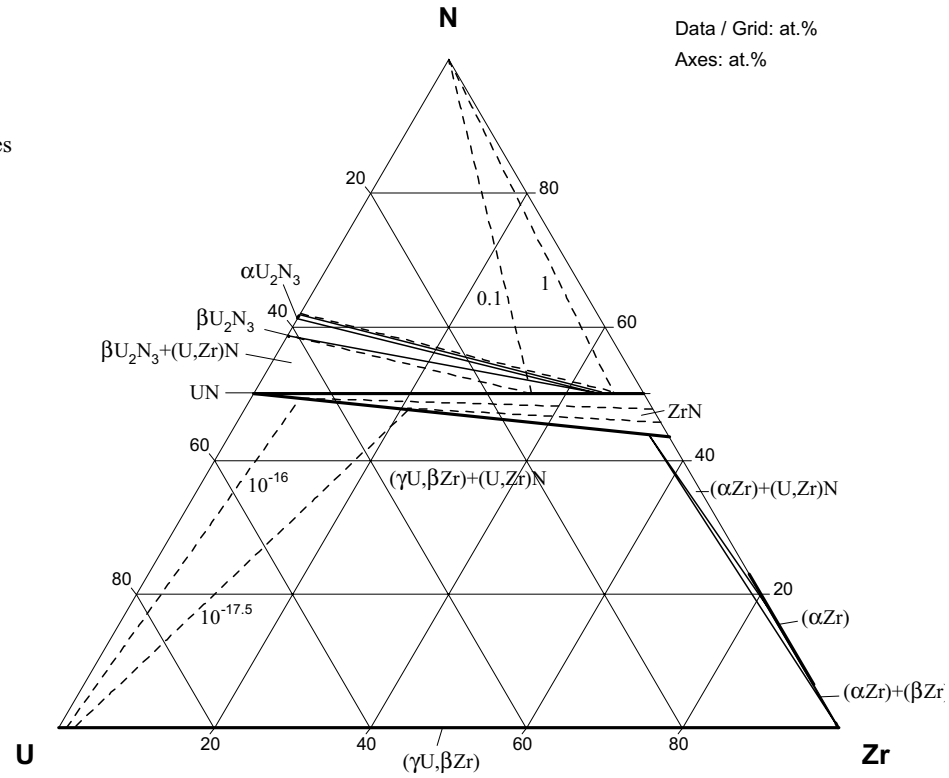


**Fig. 2: N-U-Zr.** Phase equilibria at 1000°C showing some isobaric curves (dashed lines - pressures in bar)