Nitrogen – Plutonium – Zirconium

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Introduction

Investigations of the N-Pu-Zr system carried out at 1500°C by X-ray diffraction [1975Hol] showed that PuN and ZrN are soluble in the whole composition range. The properties of the (Pu,Zr)N solid solution, heat capacity (up to 1500°C), thermal conductivity and thermal expansion (up to 2500°C) were experimentally determined by [2005Bas] for ZrN and the solution $Pu_{0.25}Zr_{0.75}N$.

Binary Systems

The N-Zr system has been assessed by [1994Gri] which proposes for ZrN a sublimation point of 3410°C and a melting point of 3670°C under 6 MPa of nitrogen pressure, which is 700 K higher than the melting point estimated by [Mas2]. The N-Pu diagram is accepted from [Mas2] and has been assessed by [1989Wri]. The Pu-Zr diagram is accepted from the Calphad assessment of [1999Kur].

Solid Phases

The solid phases are presented in Table 1. The solid solution (Pu,Zr)N are prepared by mixing and compacting the powders under 100 MPa [2000Ara, 2003Min]. The discs, heated at 1400°C under an H_2-N_2 gas stream for homogenization are shown to obey the Vegard’s law.

Isothermal Sections

The isothermal section at 1500°C is given in Fig. 1. The diagram, mainly from [1975Hol], has been modified to be coherent with the accepted binaries. The position of the tie lines in the two-phase domain (Pu,Zr) liquid solution - (Pu,Zr)N solid solution confirms the well known fact that Zr has a stronger affinity for N than Pu.

Notes on Materials Properties and Applications

The solid solution of PuN having dissolved ZrN has been proposed as a potential fuel for transmutation use [2000Ara, 2003Min, 2005Str]. However, oxygen impurities deteriorate the irradiation behavior and has to be maintained below 0.2 mass% by adding small amount of carbon before the initial mixing.
Actinide mononitrides has been considered as an advanced fuel for fast reactors because of major thermal and neutronic properties [2005Ara]. Mononitrides are also candidates fuel material in the accelerator driven systems for minor actinides transmutation, being coupled with pyrotechnical treatment of spent nuclear fuel.

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
(αPu) < 125	*mP*16 $P2_1/m$ αPu	*a* = 618.3 *b* = 482.2 *c* = 1096.3 β = 101.97°	at 25°C [Mas2] dissolves ~1.5 at.% Zr at 115°C
(βPu) 215 - 125	*mC*34 *C*2/*m* βPu	*a* = 928.4 *b* = 1046.3 *c* = 785.9 β = 92.13°	[Mas2] dissolves ~7 at.% Zr at 280°C
(γPu) 320 - 215	*oF*8 *Fddd* γPu	*a* = 315.87 *b* = 576.82 *c* = 1016.2	[Mas2] dissolves ~3 at.% Zr at 280°C
(δPu) 463 - 320	*cF*4 $Fm\bar{3}m$ Cu	*a* = 463.71	[Mas2] dissolves up to 60 at.% Zr at 618°C [1999Kur]
(δ'Pu) 483 - 463	*tI*2 *I*4/*mmm* In	*a* = 332.61 *c* = 446.30	[Mas2] dissolves ~2 at.% Zr at 483°C
(αZr) < 1360	*hP*2 $P6_3/mmc$ Mg	*a* = 323.16 *c* = 514.75	at 25°C [Mas2] dissolves up to 13 at.% Pu at 618°C and 25 at.% N at 1985°C

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(εPu,βZr)	*cI*2 *Im*$\bar{3}$*m*		solid solution (εPu,βZr) [1995Oka, 1999Kur].
(εPu) 640 - 483	W	*a* = 363.43	The solubility of N in Pu is very small [1989Wri]
(βZr) 1855 - 863		*a* = 360.90	(βZr) dissolves ~5 at.% N at 1880°C
θ, Pu_4Zr < 345	*tP*80 *P*4/*ncc*	*a* = 1089.3 *c* = 1488.9	13 to 17 at.% Zr [1999Kur]
κ, $PuZr_3$ < 380	*hP*3 *P*6/*mmm* AlB_2	*a* = 505.5 *c* = 312.3	74 at.% Zr [Mas2]. May be metastable [1995Oka]
(Pu,Zr)N	*cF*8 *Fm*$\bar{3}$*m*		solid solution
PuN < 2830	NaCl	*a* = 490.5	[2003Min]
ZrN < 3410		*a* = 457.6	ZrN: 40 to 50 at.% N. Melts congruently at 3670°C, 6 MPa N_2 pressure [1994Gri]

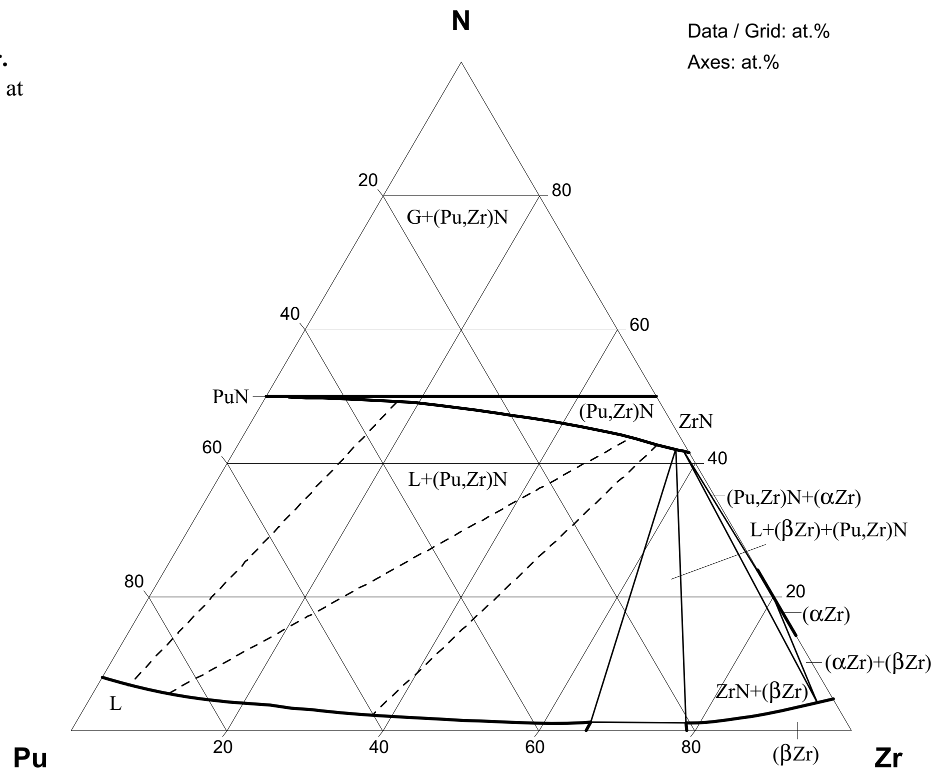

Fig. 1: N-Pu-Zr. Isothermal section at 1500°C