

Nitrogen – Plutonium – Uranium

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Introduction

Mixed plutonium-uranium mononitrides are universally recognized as advanced fuels for liquid metal cooled fast breeder reactors due to their thermal conductivity, ease of fabrication, complete dissolution in nitric acid, good compatibility with cladding and non-pyrophoric nature. The nitrides of uranium, plutonium and uranium-plutonium mixture may be even more attractive than the carbides from the point of view of higher mechanical strength and higher solubility of solid fission products. Thermodynamic properties and phase equilibria are of great importance to evaluate the fuel performance under normal and abnormal reactor conditions, but also in the fabrication process. The phase relations of the N-Pu-U have not been studied in detail and most studies have been confined to those on the solid solution between UN and PuN with Pu/(U+Pu) ratios of 0.15-0.20 from the technological interest for the possible fast reactor fuel materials. Structural studies on the system have been carried out by [1971Ten] and [1991Suz]. Experimental investigations have been carried out on $(\text{Pu}_{0.2}\text{U}_{0.8})\text{N}$ by [1963Ans]. [1987Mat1, 1987Mat2] have critically evaluated the thermodynamic properties of the PuN-UN subsystem. Numerous thermodynamic properties were calculated and measured, especially on vapor pressure of species [1971Ale, 1992Suz, 1993Oga, 1973Pot, 2001Kur]. Only calculated isothermal sections are available in the literature [1973Pot, 1975Hol, 1976Pot, 1980Udo, 1993Oga]. All the data are summarized in Table 1.

Binary Systems

The accepted phase diagram of the binary boundary system Pu-U is reported in the chapter “*Remarks on the Actinide Alloying Behavior*” in the present volume. It is based on the thermodynamic calculation by [1991Lei].

The N-U system has been taken from the thermodynamic assessments of [2000Che]. This assessment gives a consistent description of thermodynamic data and phase diagram data and therefore is accepted here. The binary system N-Pu has been taken from [Mas2] as assessed by [1989Wri].

Solid Phases

PuN and UN form a complete range of solid solutions [1971Ten] with the rock salt structure in the whole composition range. [1963Ans] first reported the lattice parameters of $(\text{Pu,U})\text{N}$ which widely varied following the heat treatment of the samples and reported a monotonous increase of the lattice parameter, obeying Vegard’s law with increasing Pu content. Values and composition dependence of the lattice parameter are not consistent with those measured by [1971Ten]. Consequently [1991Suz] carried out experiments in order to determine precisely the composition dependence of the lattice parameters of UN-PuN solid solutions. Results are in fairly agreement with those of [1971Ten], especially in the Pu rich composition. The solid solutions do not obey Vegard’s law [1971Ten, 1991Suz]. This deviation may be attributed to a change of the nature of electron population in the solid solution. Disagreements were observed concerning the position of the maximum which is at $(\text{U}_{0.28}\text{Pu}_{0.72})\text{N}$ in [1971Ten] and $(\text{U}_{0.1}\text{Pu}_{0.9})\text{N}$ in [1991Suz]. Further investigations are needed in order to determine precisely the location of this maximum value of the lattice parameter. Small discrepancies in the UN rich region is certainly due to the presence of a small amount of carbon in the UN samples.

As for UN and PuN, $(\text{Pu,U})\text{N}$ melting temperature strongly depends on the nitrogen pressure [1987Mat1, 1987Mat2].

Plutonium sesquinitride is an unstable compound and is reported to be stabilized in a $\text{UN}_{1.5}$ matrix by dissolution up to 15 mol% $\text{PuN}_{1.5}$ [1997Soo]. However, the thermodynamic properties of $\text{PuN}_{1.5}$ are not

available and its stabilization in solution with $\text{UN}_{1.5}$ at high temperatures, particularly in the absence of high nitrogen pressure, appears doubtful.

The crystallographic data for the N–Pu–U phases and their ranges of stability are summarized in Table 2.

Quasibinary Systems

Although the non stoichiometric region of the single phase $(\text{Pu},\text{U})\text{N}$ has not been well determined as a function of temperature, UN and PuN are considered to form a continuous solid solution in the temperature range from room temperature to 1650°C. [1987Mat1, 1987Mat2] compared their calculated partial pressures based on the ideal solution assumption with experimental results and concluded that the UN–PuN system behaves like an ideal solution.

Invariant Equilibria

[1980Udo] carried out thermodynamic calculations and proposed the existence of a ternary four-phase equilibrium $\beta\text{U}_2\text{N}_3 + (\text{Pu},\text{U})\text{N} + \text{N}_2 \rightleftharpoons \alpha\text{U}_2\text{N}_3$ at about $1250 \pm 100^\circ\text{C}$. Since the $\alpha\text{U}_2\text{N}_3$ appears at much lower temperature in the binary 1135°C, the crystallization of this phase inside the ternary at a temperature of $1250 \pm 100^\circ\text{C}$ is certainly improbable. Consequently this reaction has not been retained here and the schematic reaction scheme proposed by [1980Udo] has not been reported here. Further experimental investigations and thermodynamic calculations are needed.

Isothermal Sections

Isothermal sections were only estimated from thermodynamic calculations [1973Pot, 1975Hol, 1976Pot, 1980Udo, 1993Oga]. [1973Pot, 1980Udo] suggested that the solubility of Pu in $\alpha\text{U}_2\text{N}_3$ is up to the ratio $\text{Pu}/(\text{Pu}+\text{U}) = 0.15$ at around 1000°C. Since only one experimental data of solubility is available in literature for $\alpha\text{U}_2\text{N}_3$, [1973Pot] shows two different version of the isothermal section at 800°C. According to [1973Pot] a decision can not be made. Later [1980Udo] calculated isothermal sections at 795, 805, 960 and 1135°C taking into account the experimental results of the solubility range of $\alpha\text{U}_2\text{N}_3$. According to the accepted binary N–U phase diagram, only the low temperature phase $\alpha\text{U}_2\text{N}_3$ exists at this temperature. Consequently the phase equilibria involving the $\beta\text{U}_2\text{N}_3$ phase could not be retained in the calculated isothermal sections at 800°C and 805°C proposed respectively by [1973Pot] and [1980Udo]. [1980Udo] expected that at $1250 \pm 100^\circ\text{C}$ a four-phase reaction would occur: $\beta(\text{Pu},\text{U})_2\text{N}_{3-y} + \text{N}_2 + (\text{Pu},\text{U})\text{N} \rightleftharpoons (\text{Pu},\text{U})_2\text{N}_{3+x}$. According to the binary phase diagram N–U it is improbable that the $\alpha(\text{Pu},\text{U})_2\text{N}_{3+x}$ could exist in this temperature range. Consequently, modifications have been made on the isothermal section at $1250 \pm 100^\circ\text{C}$ presented by [1980Udo]. The accepted calculated isothermal sections are reported in Figs. 1 to 4. Some modifications have been made according to the binary systems. The liquid phase along the Pu–U and N–U system present a solubility range at 795°C and has been taken into account in the drawing at 795°C. The solubility of $\alpha\text{U}_2\text{N}_3$ has been suppressed and the (γU) phase has been added at 1135°C since this temperature is identical to the melting temperature of this phases. Moreover the nitrogen rich part of the Pu–N phase diagram is not established, specially the phase equilibria between PuN and N and as well as the limit solubility of PuN on the nitrogen rich side. All these slight modifications are indicated as dashed lines in the figures. [1993Oga] predicted isothermal phase boundaries between the mixed mononitrides and liquid alloys at 1727°C from modeling of the free Gibbs energies of mixed nitrides $(\text{Pu},\text{U})\text{N}$ using a sublattice formalism. An increase of the N_2 pressure leads to an enrichment in Pu of the nitride and in U of the metal liquid. [1975Hol] calculated invariant points of the three-phase equilibria for various nitrogen pressure in the nitrogen rich part of the phase diagrams. $\alpha\text{U}_2\text{N}_3$ and $\beta\text{U}_2\text{N}_3$ coexist at 1000°C and 1 bar N_2 . At 0.1 bar N_2 , only $\beta\text{U}_2\text{N}_3$ occurs.

More systematic experimental work is necessary.

Thermodynamics

There are only two sets of vapor measurements [1971Ale, 1992Suz] on the mixed nitrides, which contradict each other on some crucial points. [1971Ale] showed that the vaporization behavior of (Pu,U)N was governed by the preferential loss of PuN as elemental plutonium and molecular nitrogen. It stipulated that the vapor pressure of Pu(g) over (U_{0.8}Pu_{0.2})N was nearly 20% of that over PuN, indicating that (U_{0.8}Pu_{0.2})N is a nearly ideal solution of UN and PuN. [1993Oga] predicts by calculation that U(g) pressure is significantly suppressed with a small addition of PuN to UN. The behavior observed by [1971Ale] agrees with this prediction. [1993Oga] found also that the apparent temperature dependence of U(g) pressure over the mixed nitrides is larger than that over the pure uranium nitride. On contrary to this prediction, [1992Suz] found that the temperature dependences of U(g) pressures of (U_{0.8}Pu_{0.2})N and (U_{0.65}Pu_{0.35})N do not differ appreciably from that of UN. Possible causes of the discrepancy may be the carbon contamination occurring in the carbothermic reduction process used for the sample preparation done by [1992Suz]. Thus the question of impurity effects remains open. [1971Ale] suggested the existence of a steady state of the weight loss rate of (U_{0.8}Pu_{0.2})N. Due to high vapor pressure of U(g), the condensate is consisted of Pu, U, PuN after vaporization of (U_{0.4}Pu_{0.6})N and (U_{0.2}Pu_{0.8})N [1987Mat1, 1987Mat2]. The Pu pressures and total pressures above the congruently vaporizing U_{0.8}Pu_{0.2} mononitride calculated by [1973Pot] are in good agreement with the measured values of [1971Ale]. The vapor pressure of U(g), Pu(g), N₂(g), PuN(g) and UN(g) over liquid (Pu,U)N and U(g), Pu(g), N₂(g) and PuN(g) over solid (Pu,U)N were calculated by [1987Mat1, 1987Mat2]. [1987Mat1, 1987Mat2] concluded that (U_{0.8}Pu_{0.2})N is effectively a nearly ideal solution of UN and PuN up to 2127°C. Experimental data on vapor pressure measurements are indicated on Table 3.

The high temperature enthalpy and heat capacity of (U_{0.8}Pu_{0.2})N have been measured by [1971Ale] from room temperature to 1527°C. These measurements seem to be unreliable from the point of view of an ideal solution model, since the heat capacity of mixed nitrides is given lower than those of UN and PuN. This assumption is in contradiction with the vapor pressure measurements of [1971Ale] who concluded that (U_{0.8}Pu_{0.2})N has an ideal solution behavior. [2001Kur] calculated the heat capacity of (U_{0.8}Pu_{0.2})N as the sum of the contribution of lattice vibration and dilatation in the temperature range 27–2227°C. Results show a slight difference with experimental data leading to the fact that other contributions have to be considered in the calculation as for example the Frenkel defect effect.

There has been no reports on the enthalpy of formation for (Pu,U)N. The enthalpy of formation for (U_{0.8}Pu_{0.2})N was estimated by [1987Mat1, 1987Mat2] to be $-296.5 \text{ kJ}\cdot\text{mol}^{-1}$ on the basis of an ideal solid solution model from the enthalpy of solution of UN and PuN at 27°C.

Notes on Materials Properties and Applications

[1992Ara] found that the thermal conductivity of (U_{0.8}Pu_{0.2})N system decreases with increase in porosity and the temperature dependence does not change with porosity. Results agreed fairly well with those of [1970Ale, 1971Ale] but gave slightly higher values than those of [1967Pas] over the temperature range investigated. Moreover addition of Pu in (Pu,U)N pellets decreases the thermal conductivity except for the case of PuN indicating a little higher thermal conductivity than the PuN rich (Pu,U)N solid solutions below 727°C. [1992Ara] also noticed that the decreasing rate of thermal conductivity with Pu content is prominent in the UN rich region. The Pu content dependence of thermal conductivity of [1992Ara] agrees well with results of [1991Gan] for pellets of (U_{0.8}Pu_{0.2})N. The big differences observed for the (U_{0.45}Pu_{0.55})N between [1992Ara] and [1991Gan] is not clear for the moment. Further experiments are needed. [2001Kur] calculated the thermal conductivity of (Pu_{0.2}U_{0.8})N using Green-Kubo relations in the temperature range 27–1727°C. These calculated results from Monte-Carlo simulation are systematically lower than the experimental data [1970Ale, 1971Ale, 1992Ara, 1967Pas].

[1969Par] demonstrated that the mixed nitrides have extremely good irradiation resistance and a potential for burnups with appropriate fuel element design. Data are summarized in Table 4.

Miscellaneous

[1974Ten] have conducted sintering experiments of $(\text{Pu}_x\text{U}_{1-x})\text{N}$ as a function of temperature and nitrogen pressure. They found reducing the nitrogen pressure caused an enhancement in sintering. After diffusion in the solid state of PuN-UN mixture, the solid solution obtained can be sintered to 90% of theoretical density [1963Ans].

At a pressure of $0.1 \cdot 10^{-8}$ bar, [2001Kur] have performed a molecular dynamics study and evaluated the thermal expansion and the compressibility coefficients of $(\text{U}_{0.8}\text{Pu}_{0.2})\text{N}$.

The most common method for the preparation of mixed nitride fuels is the carbothermic reduction of $\text{UO}_2 + \text{PuO}_2 + \text{C}$ mixture in a nitrogen atmosphere. Phase diagram N-Pu-U of the nitride fuels, in the composition range of interest for fuel manufacture, have been extensively calculated with carbon and oxygen impurities [1973Pot, 1976Pot, 1993Oga, 1997Soo, 1999Aga]. Considering calculation based on ideal solution behavior, it was found that the oxygen impurity of the nitride fuel affects plutonium partial pressure [1999Aga]. [1998Jai] have commented on the paper of [1997Soo] that they have wrongly inferred the presence of a phase $\text{UN}_{1.5}$.

Carbon and oxygen contents ranging from 400-6000 ppm and 2000-9000 ppm, respectively do not significantly affect the melting behavior of $(\text{Pu,U})\text{N}$ fuels [1968Web].

[1992Bar] have conducted kinetic experiments on the mechanism of sintering of $(\text{Pu}_x\text{U}_{1-x})\text{N}$. It was found that the rate of reaction follows an Arrhenius law as a function of temperature. The apparent activation energy for the $(\text{Pu,U})\text{N}$ synthesis is lower than the value of the UN formation. This can be explained by the higher ionic character of PuN which enhances probably the transformation of PuO_2 in PuN. The apparent activation energy ($66 \text{ kJ} \cdot \text{mol}^{-1}$) is lower under N_2 -6% H_2 than the one ($244 \text{ kJ} \cdot \text{mol}^{-1}$) observed with pure N_2 and the kinetic parameter is independent on the gas flow rate.

It was found that the nitride Pu-U mixtures are generally more reactive than the Pu-U oxides mixtures [1975Bie].

[1965Far, 1966Far, 1968Far1, 1968Far2, 1969Fac, 1969Far, 1970Bar] undertook a review of mechanical properties, method of fabrication and irradiation influence on mixed plutonium-uranium nitrides.

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

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1963Ans]	Metallography X-ray powder diffraction, chemical analysis	900°C/ (Pu _x U _{1-x})N
[1971Ale]	Oelsen calorimeter, massspectrometry	27 - 2127°C / (Pu,U)N
[1971Ten]	X-ray measurements, chemical analysis	1400 - 1800°C for 325 minutes / (Pu _x U _{1-x})N
[1991Suz]	X-ray diffraction	1752°C/ (Pu _x U _{1-x})N
[1992Suz]	Knudsen effusion mass spectrometry, X-ray diffraction	1477 - 1727°C / (Pu _x U _{1-x})N

Table 2: Crystallographic Data of Solid Phases

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(εPu, γU)	<i>cI2</i> <i>Im$\bar{3}m$</i> W		continuous solid solution which exists between 1135 and 454°C [1991Lei]
(εPu) 640 - 483		$a = 363.8$	pure, 500°C, [1989Pet]
(γU) 1135 - 776		$a = 352.4$	pure, 805°C, [Mas2]
(δ'Pu) 483 - 463	<i>tI2</i> <i>I4/mmm</i> In	$a = 333.9$ $c = 444.6$	pure, 477°C, [1989Pet] dissolves about 1.3 at.% U at 440°C [1991Lei]; exists down to 437°C in the Pu-U binary [1991Lei]
(δPu) 463 - 320	<i>cF4</i> <i>Fm$\bar{3}m$</i> Cu	$a = 463.70$	pure, 320°C, [1989Pet] dissolves about 1.6 at.% U at 318°C [1991Lei]
(γPu) 320 - 215	<i>oF8</i> <i>Fddd</i> γPu	$a = 315.87$ $b = 576.82$ $c = 1016.2$	pure, 235°C, [1989Pet] dissolves about 1.6 at.% U at 278°C [1991Lei];
(βPu) 215 - 125	<i>mC34</i> <i>C2/m</i> βPu	$a = 928.4$ $b = 1046.3$ $c = 785.9$ $\beta = 92.13^\circ$	pure, 190°C, [1989Pet] dissolves about 2.7 at.% U at 278°C [1991Lei]
(αPu) < 125	<i>mP16</i> <i>P2₁/m</i> αPu	$a = 618.3$ $b = 482.2$ $c = 1096.3$ $\beta = 101.79^\circ$	pure, 21°C, [1989Pet] the solubility of U is nearly absent [1991Lei]
(βU) 776 - 668	<i>tP30</i> <i>P4₂/mnm</i> βU	$a = 1075.9$ $c = 565.6$	pure, 720°C, [1989Pet] dissolves about 24 at.% Pu at 702°C [1991Lei] exists down to 557°C along the Pu-U binary [1991Lei]
(αU) < 668	<i>oC4</i> <i>Cmcm</i> αU	$a = 285.37$ $b = 586.95$ $c = 495.48$	pure, at 25°C [1989Pet] dissolves about 11 at.% Pu at 557°C [1991Lei]
(U _x Pu _{1-x})N	<i>cF8</i> <i>Fm$\bar{3}m$</i> NaCl	$a = 488.918$ to 490.386	$0 \leq x \leq 1$ [1971Ten]
UN < 2789		$a = 488.87$	UN melts congruently at 2835°C at 2.5 MPa N ₂ [2000Che], lattice parameters from [V-C2]
PuN < 2830		$a = 490.5$	[2003Min]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
$\beta\text{U}_2\text{N}_3$ 1349 - 955	$hP5$ $P\bar{3}m1$ La_2O_3	$a = 370.0$ $c = 582.5$	58.7 at.% N [2000Che] [V-C2]
$\alpha\text{U}_2\text{N}_3$ < 1135	$cI80$ $Ia\bar{3}$ Mn_2O_3	$a = 1068.2$	60 to 64 at.% N. Gradually change to CaF_2 type with increasing N content [2000Che], lattice parameters from [V-C2]
η , PuU 702 - 278	$tP52$	$a = 1057$ $c = 1076$	~4 to ~78 at.% U at 25 at.% U [1969Lea]
ξ , PuU ≤ 628	t^{**}	$a = 1069.2$ $a = 1065.1$	~26.4 to ~77 at.% U at 25°C, 35 at.% U [1969Lea] at 25°C, 70 at.% U [1969Lea] $c/a \approx 1$

Table 3: Vapor Pressure Measurements

Phase(s)	Temperature [°C]	Pressure [bar]	Comments
$\text{N}_2(\text{g})$	1127 to 2127	$p_{\text{N}_2(\text{g})} = 3 \cdot 10^{-11}$ to $5.5 \cdot 10^{-5}$	Over $(\text{U}_{0.8}\text{Pu}_{0.2})\text{N}$ [1971Ale]
$\text{Pu}(\text{g})$	1127 to 2127	$p_{\text{Pu}(\text{g})} = 2 \cdot 10^{-10}$ to $3.1 \cdot 10^{-4}$	Over $(\text{U}_{0.8}\text{Pu}_{0.2})\text{N}$ [1971Ale]
$\text{U}(\text{g})$	1127 to 2127	$p_{\text{U}(\text{g})} = 1 \cdot 10^{-14}$ to $8.1 \cdot 10^{-6}$	Over $(\text{U}_{0.8}\text{Pu}_{0.2})\text{N}$ [1971Ale]
$\text{U}(\text{g})$	1520 - 1640	$\log p_{\text{U}(\text{g})} = -(26.4 \pm 0.9) \cdot 10^{-2} / T$	Over 0.8UN-0.2PuN [1992Suz]
$\text{Pu}(\text{g})$	1380 - 1660	$\log p_{\text{Pu}(\text{g})} = -(20.5 \pm 0.2) \cdot 10^{-2} / T$	Over 0.8UN-0.2PuN [1992Suz]
$\text{U}(\text{g})$	1540 - 1560	$\log p_{\text{U}(\text{g})} = -26.9 \cdot 10^{-2} / T$	Over 0.65UN-0.35PuN [1992Suz]
$\text{Pu}(\text{g})$	1320 - 1560	$\log p_{\text{Pu}(\text{g})} = -(19.6 \pm 0.2) \cdot 10^{-2} / T$	Over 0.65UN-0.35PuN [1992Suz]
$\text{Pu}(\text{g})$	1280 - 1500	$\log p_{\text{Pu}(\text{g})} = -(22.0 \pm 0.2) \cdot 10^{-2} / T$	Over 0.4UN-0.6PuN [1992Suz]
$\text{Pu}(\text{g})$	1280 - 1500	$\log p_{\text{Pu}(\text{g})} = -(21.1 \pm 0.2) \cdot 10^{-2} / T$	Over 0.2UN-0.8PuN [1992Suz]

Table 4: Investigations of the N-Pu-U Materials Properties

Reference	Method/Experimental Technique	Type of Property
[1967Pas]	Transient methods	Thermal conductivity
[1971Ale]	Laser pulse method	Thermal conductivity, thermal expansion, Transport rate
[1991Gan]	Transient heat flow method	Thermal conductivity
[1992Ara]	Laser flash method	Thermal conductivity

Fig. 1: N-Pu-U.
Calculated isothermal
section at 795°C

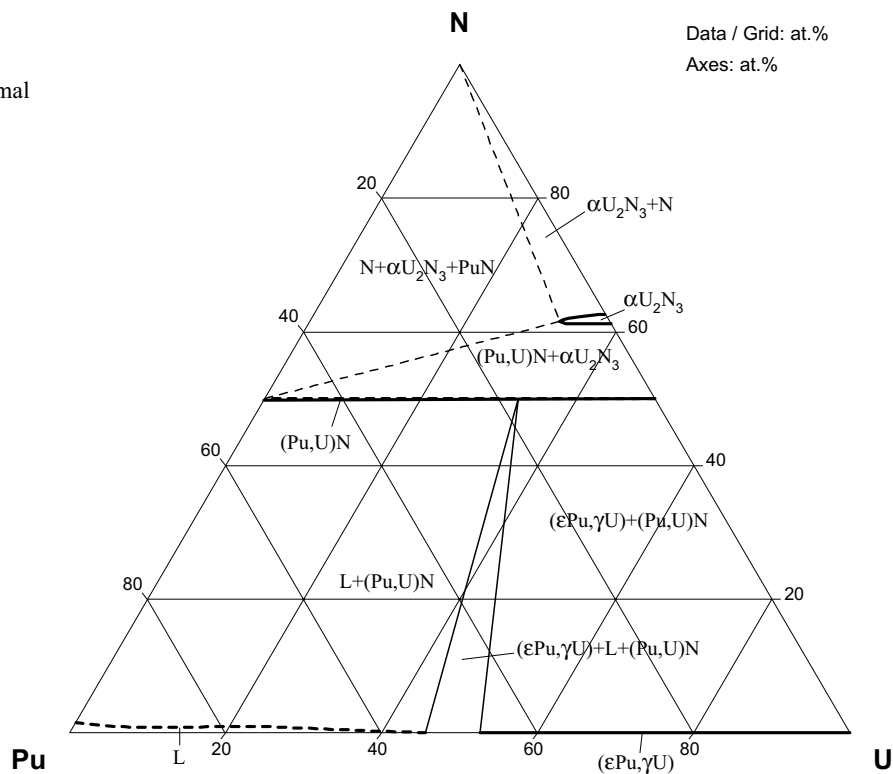


Fig. 2: N-Pu-U.
Calculated isothermal
section at 1135°C

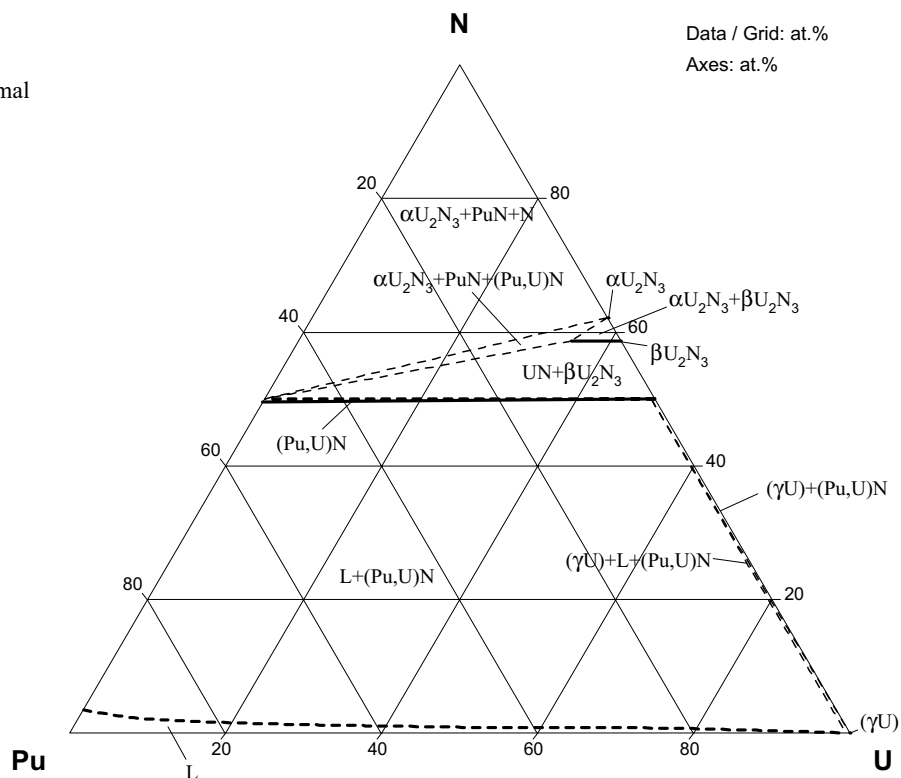


Fig. 3: N-Pu-U.
Calculated isothermal
section
at $1250 \pm 100^\circ\text{C}$

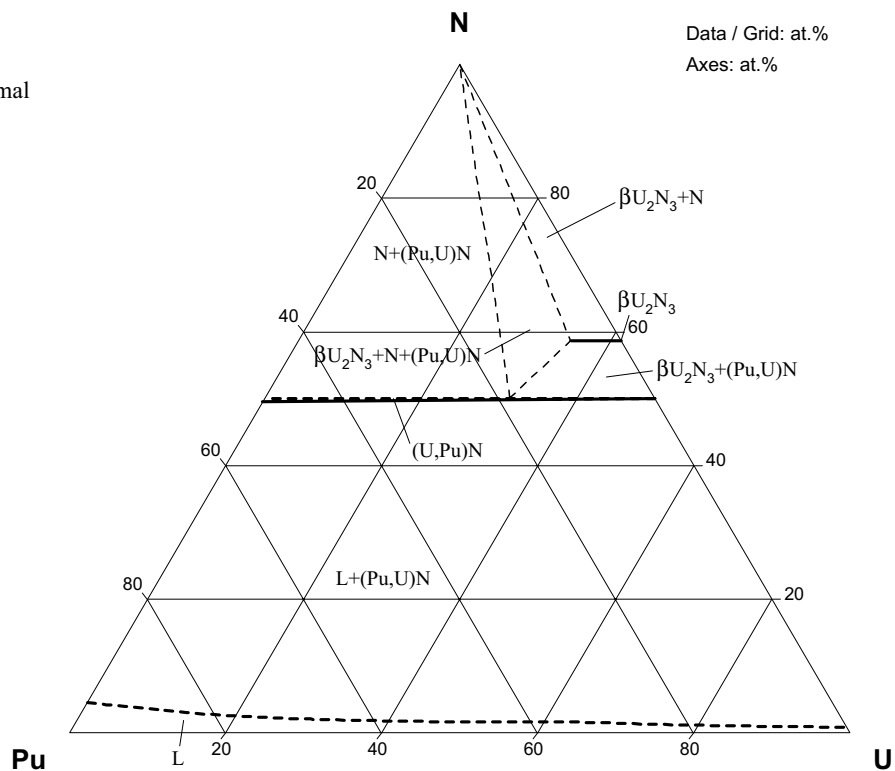


Fig. 4: N-Pu-U.
Calculated isothermal
section at 1355°C

