

Remarks on the Actinide Alloying Behavior

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Introduction

The actinide metals represent a peculiar group of elements and are constituents of very important materials systems, their dual use in civil and war applications very often generated strong emotional responses which will become more pronounced and controversial in future.

On the other side, from a more fundamental point of view, actinides are located at a crucial point of the Periodic Table, where peculiar properties may be noticed. Actinides, together with lanthanides, are the inner transition metals and form the *f*-block of the Periodic Table. Several characteristics of both families show more or less regular trends which have been widely studied by both experimental and theoretical methods, and often were used for extrapolation and prediction of the alloying behavior of such element combinations. Experimental investigations on actinide systems are indeed extremely difficult, as can be easily verified by examining the experimental papers, and therefore critical assessment of the available data and extrapolation, modelling and calculation techniques are important approaches for investigating constitutional properties of actinide-based alloys.

A few comments on the general alloying behavior of the actinides are reported in this introductory chapter, while more detailed information on selected ternary systems relevant to the nuclear materials technology is reported in the following contributions compiled by several authors of the MSI Team.

The overall information collected in this book, even in the relative scarcity of experimental results reported in the scientific literature, may be an important contribution not only to the development of nuclear materials but also to the science of materials constitution and physical chemistry in general, of this intriguing group of elements.

For the actinide systems we may suggest the Editors to go beyond the possibility of books: making the MSI research platform available for the coming renaissance in Europe of a peaceful nuclear research, including but not limited to phase diagrams.

While compiling this introductory chapter we have been continuously supported by Dr. Günter Effenberg, Dr. Svitlana Ilyenko and the staff at MSI. On this occasion we would like to thank them all for their hard work in planning, organizing and managing this multi-disciplinary, multi-national and multi-component adventure of a multi volume Landolt-Boernstein series.

1. Actinide Elements and Inter-Actinide Binary Systems

1.1 Actinide Elements

A summary of the constitutional properties of the actinide elements is given in Table 1, where crystal structure data (structural types, lattice parameters) and temperature range of stability relevant to the elemental phases are reported.

A different presentation of the same data is shown in Fig. 1, where the temperature ranges of stability of the different allotropic forms are shown as a function of the actinide atomic number. This figure (the history of which is reported in [2000Bor]) highlights the progressive structural changes we have as a function of the atomic number along the actinide series. It can also be underlined that this figure may be used as a first presentation of a group of inter-actinide binary systems: those formed by each element with the adjacent ones in the sequence.

A second interconnected diagram showing phase relations of the actinide metals at room temperature as a function of pressure is reported in Fig. 2. The figure is based mainly on Benedict [1987Ben] and updated with some data by Heathman [1998Hea].

In a comparison between the pressure behavior of actinides and lanthanides Benedict underlined the analogies between the right-hand part of Fig. 2 and the left-hand part of the corresponding inter-lanthanide graph. This comparison between the two diagrams is considered an illustration of the "shifted homologous

relationships" between the trans-plutonium actinides and the light rare earth metals, even if it is not always possible to establish a one-to-one relationship between specific metals of the two series.

In the figure the particular behavior of Cm may be observed: it shows transition temperatures much higher than the neighbouring elements.

It may be noted, both in Table 1 and in the figures, the peculiar complexity of the sequence in vicinity of Pu. This may be related to the trend illustrated in Fig. 3, where the periodic table has been re-arranged by Smith and Kmetko [1983Smi] in order to highlight the separation between elements with "localized" and "delocalized" electrons. This re-arranged periodic table shows the above-mentioned "shifted homologous relationships" qualitatively relating elements in different positions in the original periodic system. In particular borderline elements in this table are characterized by having their properties modified appreciably by small perturbations. Pu, in particular, has six allotropic structures and a seventh under pressure.

These structures are close to each other in energy, so minor changes in the surroundings conditions (temperature, pressure) may result in a change of structure and density. Some unusual crystal properties of Pu may be underlined: its room temperature form has a very low symmetry structure with 16 atoms in the unit cell. Among the other structures the face centred cubic phase (which may be stabilized and retained down to low temperature by alloying with small amounts of partner elements such as Al or Ga) has a very low density and an unusual negative thermal expansion coefficient.

Table 1: Crystal Structure Data for the Actinide Elements

Phase/ Temperature Range [°C]*	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(Ac) < 1051	<i>cF4</i> <i>Fm$\bar{3}m$</i> Cu	$a = 531.1$ $a = 567.0$	[Mas2] [V-C2]
(α Th) < 1360	<i>cF4</i> <i>Fm$\bar{3}m$</i> Cu	$a = 508.42$ $a = 508.61$	[Mas2] [V-C2]
(β Th) 1755 - 1360	<i>cI2</i> <i>Im$\bar{3}m$</i> W	$a = 411$	[Mas2, V-C2]
(α Pa) < 1170	<i>tI2</i> <i>I4/mmm</i> α Pa	$a = 394.0$ $c = 324.4$ $a = 392.1$ $c = 323.5$	[V-C2] [Mas2]
(β Pa) 1572 - 1170	<i>cI2</i> <i>Im$\bar{3}m$</i> W	$a = 381.0$	[Mas2]
(α U) < 668	<i>oC4</i> <i>Cmcm</i> α U	$a = 285.37$ $b = 586.95$ $c = 495.48$	[Mas2, V-C2]
(β U) 776 - 668	<i>tP30</i> <i>P4₂/mnm</i> β U	$a = 1075.9$ $c = 565.6$ $a = 1052$ $c = 557$	[Mas2] [V-C2]
(γ U) 1135 - 776	<i>cI2</i> <i>Im$\bar{3}m$</i> W	$a = 352.4$ $a = 353.2$	[Mas2] [V-C2]

Phase/ Temperature Range [°C]*	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(α Np) < 280	<i>oP8</i> <i>Pnma</i> α Np	$a = 666.3$ $b = 472.3$ $c = 488.7$	[Mas2, V-C2]
(β Np) 576 - 280	<i>tP4</i> <i>P42₁2</i> β Np	$a = 488.3$ $c = 338.9$ $a = 489.7$ $c = 338.8$	[Mas2] [V-C2]
(γ Np) 639 - 576	<i>cI2</i> <i>Im$\bar{3}m$</i> W	$a = 352$	[Mas2, V-C2]
(α Pu) < 125	<i>mP16</i> <i>P2₁/m</i> α Pu	$a = 618.3$ $b = 482.2$ $c = 1096.3$ $\beta = 101.97^\circ$	[Mas2, V-C2]
(β Pu) 215 - 125	<i>mC34</i> <i>C2/m</i> β Pu	$a = 928.4$ $b = 1046.3$ $c = 785.9$ $\beta = 92.13^\circ$ $a = 1183.0$ $b = 1044.9$ $c = 922.7$ $\beta = 138.65^\circ$	[Mas2] [V-C2]
(γ Pu) 320 - 215	<i>oF8</i> <i>Fddd</i> γ Pu	$a = 315.87$ $b = 576.82$ $c = 1016.2$	[Mas2, V-C2]
(δ Pu) 463 - 320	<i>cF4</i> <i>Fm$\bar{3}m$</i> Cu	$a = 463.71$ $a = 463.47$	[Mas2] [V-C2]
(δ' Pu) 483 - 463	<i>tI2</i> <i>I4/mmm</i> In	$a = 332.61$ $c = 446.30$ $a = 333.9$ $c = 444.6$	[Mas2] [V-C2]
(ϵ Pu) 640 - 483	<i>cI2</i> <i>Im$\bar{3}m$</i> W	$a = 363.43$ $a = 363.75$	[Mas2] [V-C2]
(α Am) < 769	<i>hP4</i> <i>P6₃/mmc</i> α La	$a = 346.81$ $c = 1124.1$ $a = 346.3$ $c = 1123.1$	[Mas2] [V-C2]
(β Am) 1077 - 769	<i>cF4</i> <i>Fm$\bar{3}m$</i> Cu	$a = 489.4$ $a = 465.6$	[Mas2] [V-C2]
(γ Am) 1176 - 1077	<i>cI2</i> <i>Im$\bar{3}m$</i> W	$a = ?$	[Mas2, V-C2]

Phase/ Temperature Range [°C]*	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(δ Am) high pressure phase	<i>oC4</i> <i>Cmcm</i> α U	$a = 306.3$ $b = 596.8$ $c = 516.9$	at $p = 15.2$ GPa [Mas2, V-C2]
(Am) high pressure phase	<i>mP4</i> <i>P2₁/m</i> Am	$a = 302.5$ $b = 1188.7$ $c = 283.0$ $\beta = 106.11^\circ$	at $p > 12.5$ GPa [V-C2]
(α Cm) < 1277	<i>hP4</i> <i>P6₃/mmc</i> α La	$a = 349.6$ $c = 1133.1$ $a = 350.2$ $c = 1132$	[Mas2] [V-C2]
(β Cm) 1345 - 1277	<i>cF4</i> <i>Fm$\bar{3}m$</i> Cu	$a = 503.9$	[V-C2]
(Cm) high pressure phase	<i>oC4</i> <i>Cmcm</i> α U	$a = 243.6$ $b = 581.0$ $c = 451.5$	at $p = 45.5$ GPa [V-C2]
(α Bk) < 977	<i>hP4</i> <i>P6₃/mmc</i> α La	$a = 341.6$ $c = 1106.9$	[Mas2]
(β Bk) 1050 - 977	<i>cF4</i> <i>Fm$\bar{3}m$</i> Cu	$a = 499.7$	[Mas2]
(α Cf) < 590	<i>hP4</i> <i>P6₃/mmc</i> α La	$a = 339$ $c = 1101.5$	[Mas2]
(β Cf) 900 - 590	<i>cF4</i> <i>Fm$\bar{3}m$</i> Cu	$a = ?$	[Mas2]
(Cf) high pressure phase	<i>oC4</i> <i>Cmcm</i> α U	$a = 231.3$ $b = 552.6$ $c = 447.2$	at $p = 46.6$ GPa [V-C2]
(α Es) < ?	<i>hP4</i> <i>P6₃/mmc</i> α La	$a = ?$ $c = ?$	[Mas2]
(β Es) 860 - ?	<i>cF4</i> <i>Fm$\bar{3}m$</i> Cu	$a = ?$	[Mas2]

* Melting point in bold

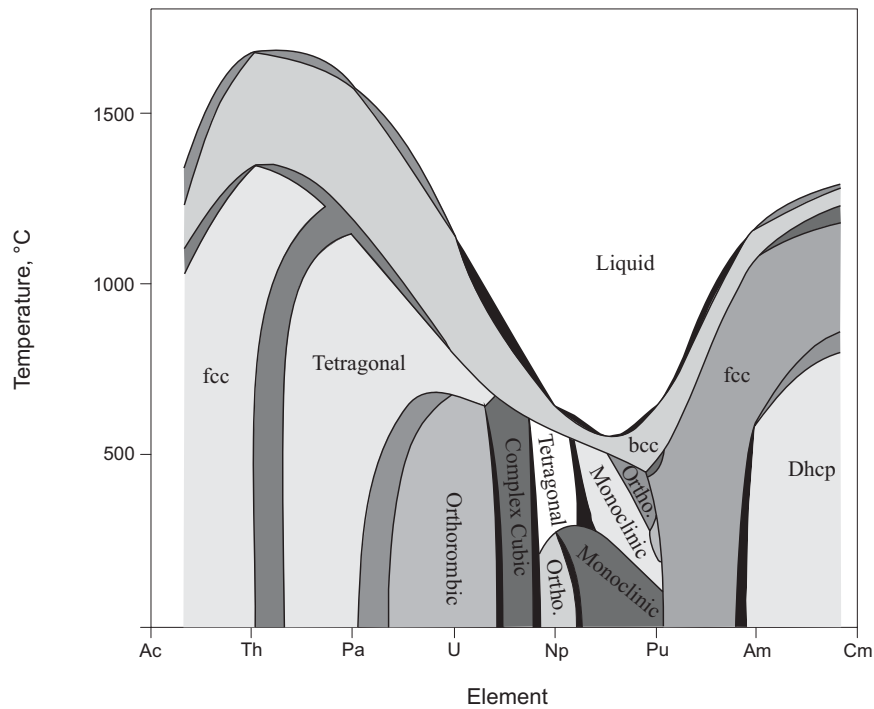


Fig. 1: Interconnected phase diagram of the binary An-An' systems formed by consecutive elements in the actinide series. Stability ranges of the different crystal structures are shown as a function of temperature. Among two-phase fields the black ones have been experimentally determined the others have been predicted. The formation of several low-symmetry structures and the overall destabilisation of the solid phases may be observed in the central part of the diagram, especially between Np and Pu.

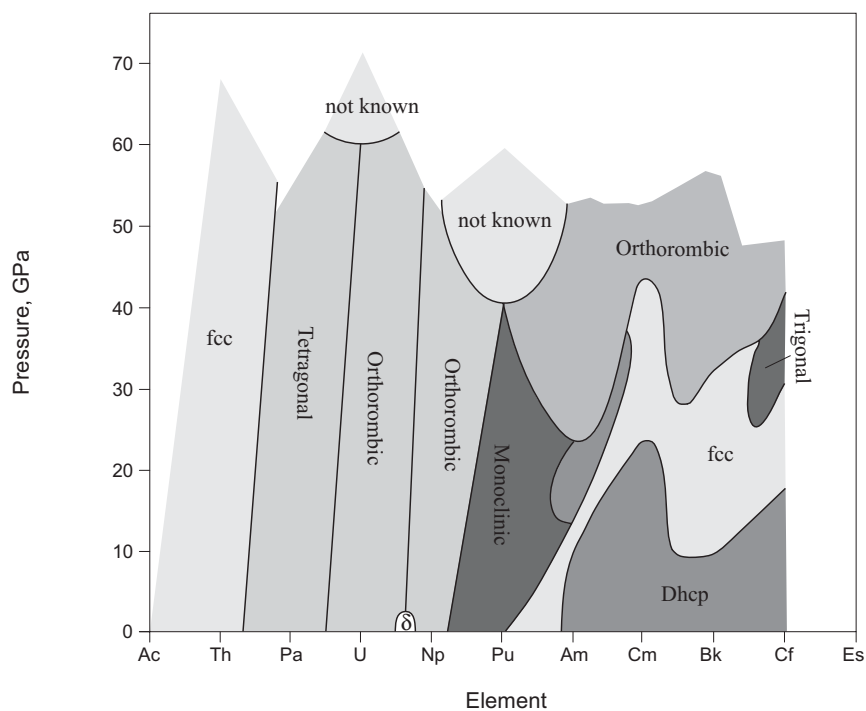


Fig. 2: Interconnected phase diagram of the binary An-An' systems formed by consecutive elements in the actinide series. Stability ranges of the different crystal structures are shown as a function of pressure.

4f	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
5f	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
3d	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn				
4d	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd				
5d	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg				

Fig. 3: Modified periodic table of the *f* and *d* series according to Smith and Kmetko [1983Smi]. Elements in the upper right part are characterised by having localised *f* or *d* electrons and became magnetic at low temperature. Elements in the lower left part are characterised by having itinerant *f* or *d* electrons and became superconductor at low temperature. Border line elements, such as Ce, Np, Pu, Mn, Fe, etc., have their properties modified appreciably by small perturbations: for example they show a large number of allotropic structures which can be alternately stabilised by temperature and/or pressure variations.

1.2 Inter – Actinide Binary Systems

The sequence of the binary diagrams (interconnected diagram) between adjacent actinide elements has been shown in Fig. 1. This well-known diagram has been frequently used to highlight general trends inside the actinide series. It may be noted that, due to the high number of allotropic forms assumed by Pu, the graph became particularly complex in vicinity of this element.

Only a few binary inter-actinide phase diagrams have been investigated. The available information reported in literature is here briefly summarized. The systems are sorted according to the atomic number of the component elements. Crystal structure data have been summarized in Table 2.

Table 2: Crystal Structure Data for the Inter-Actinide Binary Systems

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments
Th-U			
(α Th) < 1360	<i>cF4</i> <i>Fm$\bar{3}m$</i> Cu	$a = 508.4$ to 508.7 $a = 514.3$ to 514.7 $a = 508.1$ $a = 514.3$ $a = 508.1$ $a = 513.8$ $a = 516.5$ $a = 513.5$ $a = 516.0$ $a = 515.4$ $a = 515.4$	at $x(\text{U}) = 0$, room T at $x(\text{U}) = 0$, $T = 950^\circ\text{C}$ at $x(\text{U}) = 1.0$ (saturation limit), room T at $x(\text{U}) = 1.0$, $T = 950^\circ\text{C}$ at $x(\text{U}) = 2.0$, room T at $x(\text{U}) = 2.0$, $T = 950^\circ\text{C}$ at $x(\text{U}) = 2.0$, $T = 1250^\circ\text{C}$ at $x(\text{U}) = 5.0$, $T = 950^\circ\text{C}$ at $x(\text{U}) = 5.0$, $T = 1250^\circ\text{C}$ at $x(\text{U}) = 8.0$, room T at $x(\text{U}) = \sim 10.0$, $T = 1250^\circ\text{C}$ [1975Fer]
Th-Pu			
(α Th) < 1360	<i>cF4</i> <i>Fm$\bar{3}m$</i> Cu	$a = 508.5$ $a = 505.5$ $a = 501.3$ $a = 497.0$ $a = 496.3$	at $x(\text{Pu}) = 0$, $d_x = 11.72 \text{ g}\cdot\text{cm}^{-3}$ at $x(\text{Pu}) = 0.1$, $d_x = 11.98 \text{ g}\cdot\text{cm}^{-3}$ at $x(\text{Pu}) = 0.25$, $d_x = 12.36 \text{ g}\cdot\text{cm}^{-3}$ at $x(\text{Pu}) = 0.40$ at $x(\text{Pu}) = 0.43$, $d_x = 12.84 \text{ g}\cdot\text{cm}^{-3}$ [1975Fer]
ζ , Th ₃ Pu ₇ < 615	<i>o*20</i>	$a = 622$ $b = 1162$ $c = 709$	$d_x = 15.35 \text{ g}\cdot\text{cm}^{-3}$; $d_{\text{exp}} = 15.39 \text{ g}\cdot\text{cm}^{-3}$ [1968Mar]
U-Np			
(α U) < 668	<i>oC4</i> <i>Cmcm</i> α U	$a = 283.29$ $b = 586.04$ $c = 493.47$	at $x(\text{U}) = 0.968$ [V-C2]
(α Np) < 280	<i>oP8</i> <i>Pnma</i> α Np	$a = 669.4$ $b = 473.3$ $c = 491.2$	at $x(\text{U}) = 0.15$ [V-C2]
(β Np) 612 - 185	<i>tP4</i> <i>P42₁2</i> β Np	$a = 495.0$ $c = 338.6$	at $x(\text{U}) = 0.15$, $T = 400^\circ\text{C}$ [V-C2]
δ , U _x Np _{1-x} < 668	<i>cP58</i> (?)	$a = 1055$ $a = 1063$	at $x = 0.25$ at $x = 0.50$ [1959Mar]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments
U-Pu			
(α U) < 668	<i>oC4</i> <i>Cmcm</i> α U	$a = 286.24$ $b = 585.61$ $c = 496.27$	at $x(\text{U}) = 0.85$ [V-C2]
$\alpha\text{U}_x\text{Pu}_{1-x}$ 1135 - 480	<i>cI2</i> <i>Im\bar{3}m</i> W	$a = 363.6$ $a = 361.2$ $a = 353$	at $x = 0$ at $x = 0.08$ at $x = 1$
(β Pu) 278 - 121	<i>mC34</i> <i>C2/m</i> β Pu	$a = 1181.8$ $b = 1041.8$ $c = 921.5$ $\beta = 138.68^\circ$ $a = 1190.3$ $b = 1043.9$ $c = 926.4$ $\beta = 138.85^\circ$ $a = 1196.9$ $b = 1044.4$ $c = 930.2$ $\beta = 139.03^\circ$	at $x(\text{U}) = 0.02$, $T = 83^\circ\text{C}$ at $x(\text{U}) = 0.02$, $T = 186^\circ\text{C}$ at $x(\text{U}) = 0.02$, $T = 252^\circ\text{C}$
η , $\text{U}_x\text{Pu}_{1-x}$ 702 - 278	<i>tP52</i>	$a = 1057$ $c = 1076$	$0.04 < x < 0.70$ at $x = 0.25$, $T = 500^\circ\text{C}$
ζ , $\text{U}_x\text{Pu}_{1-x}$ < 590	<i>cP58</i> <i>hR58</i> <i>R\bar{3}m</i>	$a = 1069.2$ $a = 1066.4$ $a = 1065.1$ $a = 1507.64$ $c = 1859.26$	$0.25 < x < 0.77$ at $x = 0.35$, $T = 25^\circ\text{C}$ at $x = 0.50$, $T = 25^\circ\text{C}$ at $x = 0.70$, $T = 25^\circ\text{C}$ rhombohedral settings [1996Law]: $a = b = c = 1068.53$ $\alpha = \beta = \gamma = 89.736^\circ$
Np-Pu			
(α Pu) < 300	<i>mP16</i> <i>P2_1/m</i> α Pu	$a = 612$ $b = 480$ $c = 1095$ $\beta = 101.74^\circ$	$0 < x(\text{Np}) < 0.96$ at $x(\text{Np}) = 0.565$ [V-C2]
η , $\text{Np}_x\text{Pu}_{1-x}$ 508 - 288	<i>o**</i>	$a = 1086$ $b = 1067$ $c = 1043$	$0.03 < x < 0.49$ Uncertain parameters. Structure tentatively related to a $3 \times 3 \times 3$ bcc superstructure [1985She1].
Pu-Am			
$\delta\text{Pu}_x\beta\text{Am}_{1-x}$ < 1077	<i>cF4</i> <i>Fm\bar{3}m</i> Cu	$a = 479.4$	$0 < x < 1$ at $x = 0.50$ [V-C2]

Ac-An

No experimental data are available on these phase diagrams. Ac-Th phase equilibria reported in Fig. 1 have been drawn by assuming complete mutual solubility between Ac and Th in both fcc and bcc structures. This also in analogy with the known La-Th system.

Th-U

The Th-U phase diagram is shown in Fig. 4 according to the critical assessment by [1985Pet2]. Phase equilibria have been determined by a variety of techniques including DTA and, above the monotectic temperature, chemical analysis of equilibrated samples.

No intermediate phases are present in this system. It is characterized by small solid solution in α - and β Th and very small solid solution in the different forms of U. A miscibility gap appears in the liquid phase.

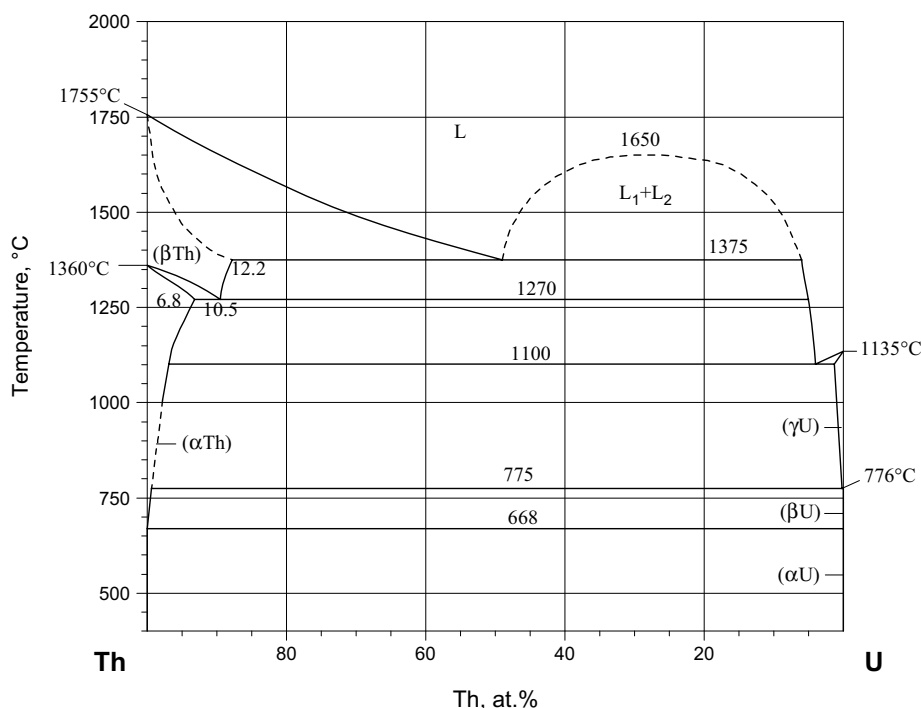


Fig. 4: Phase diagram of the Th-U system

Th-Np

No experimental data are available on this phase diagram. An early Calphad prediction of this system has been performed by Chan *et al.* [1980Cha].

Th-Pu

The Th-Pu phase diagram has been assessed by [1985Pet1] and it is shown in Fig. 5. It has been studied in the entire composition range by metallography, X-ray diffraction, thermal analysis, dilatometry.

It is characterized by the formation of an intermediate compound which has a peritectic decomposition at 615°C. Large solubility regions are given by Pu in α - and β Th while solubility of Th in the different Pu phases ranges from 0 (in α - and β Pu) to 2.6 and 5.6 at.% Th in δ - and ϵ Pu, respectively.

One binary phase is known for this system: it was previously reported as $\text{Pu}_{13}\text{Th}_6$ homogeneous around 67-70 at.% Pu and orthorhombic ($a = 982$, $b = 816.4$, $c = 668.1$). In agreement with [1985Pet1], however, it is indicated as Pu_7Th_3 in Table 2.

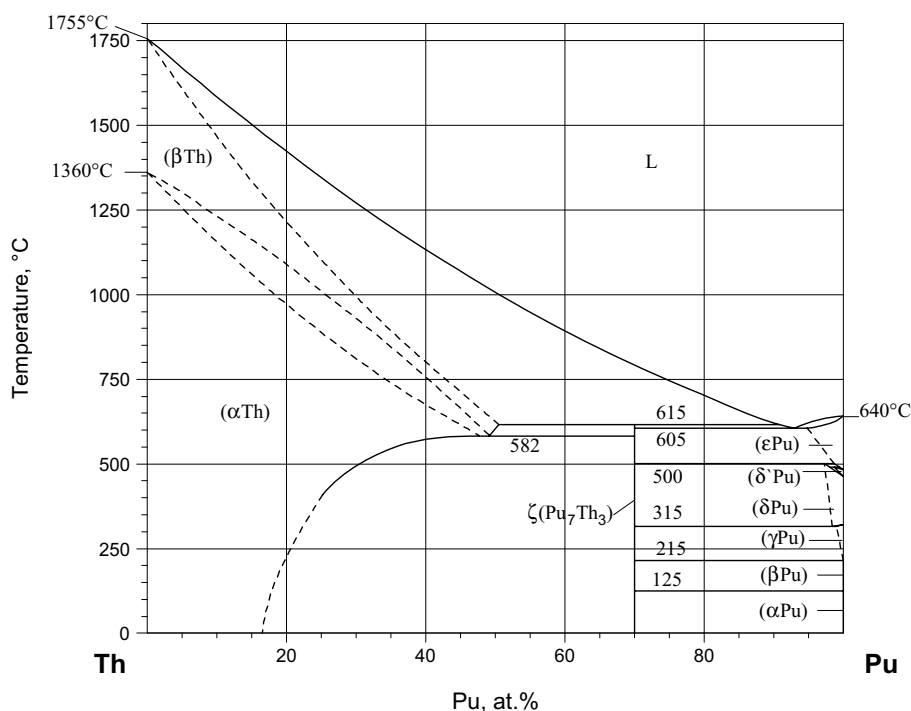


Fig. 5: Phase diagram of the Th-Pu system

Pa-An

No experimental data are available on these phase diagrams. Th-Pa and Pa-U phase diagrams reported in Fig. 1 have been drawn by assuming the simplest combination of equilibria compatible with the elemental phases. In particular, large solid solutions and no intermediate compounds have been predicted.

U-Np

A critical assessment of the U-Np system has been presented by [1985She2], based on the experimental work of [1959Mar]. Figure 6 shows the phase diagram as reported by [1985She2]. The fcc solid solution and its equilibria with liquid are in agreement with a calculation performed by [1993Oga] on the basis of the Brewer valence bond model. It is also in fair agreement with the phase equilibria schematically reported in Fig. 1.

As for the solid state equilibria, further experimental investigation could be useful, considering the shape of the reported phase boundaries, sometime not well defined and eventually unlikely.

Only one intermediate δ phase is reported in this system (see Table 2), characterized by a large solubility range.

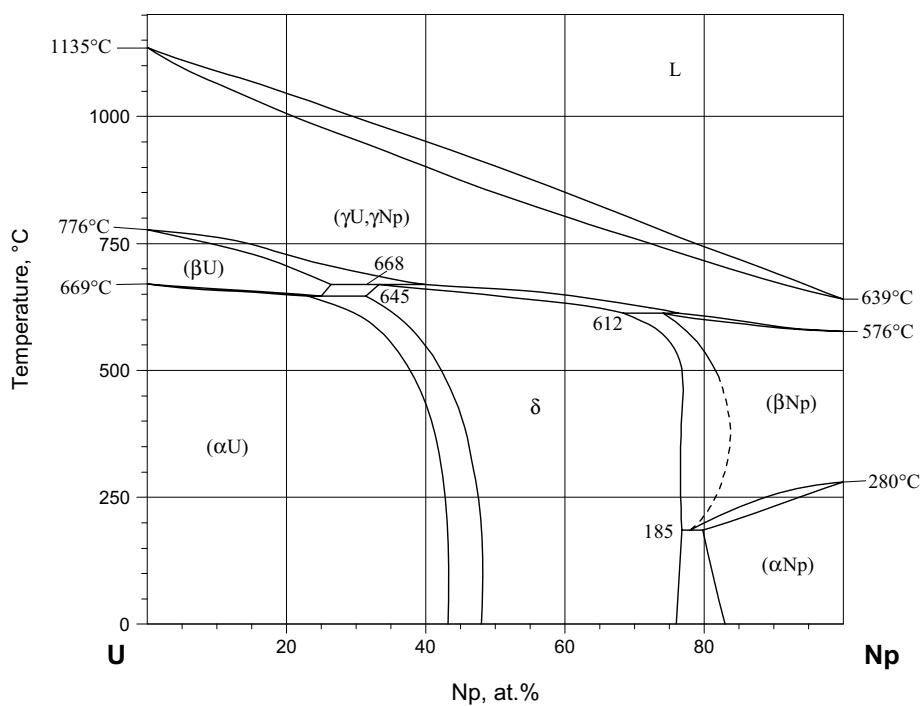


Fig. 6: Phase diagram of the U-Np system

U-Pu

The U-Pu phase diagram was assessed by [1989Pet] on the basis of several experimental data. This diagram was criticized by [1992Oka] considering several thermodynamically unlike features. The diagram reported in Fig. 7 was proposed by [1996Oka], based on the assessment of [1989Pet], new experimental results by [1994Oka] and thermodynamic modelling by [1991Lei].

The bcc solid solution and its equilibria with liquid are in fair agreement also with a calculation performed by [1993Oga] on the basis of the Brewer valence bond model. The crystal structure of the ζ phase was determined by [1996Law].

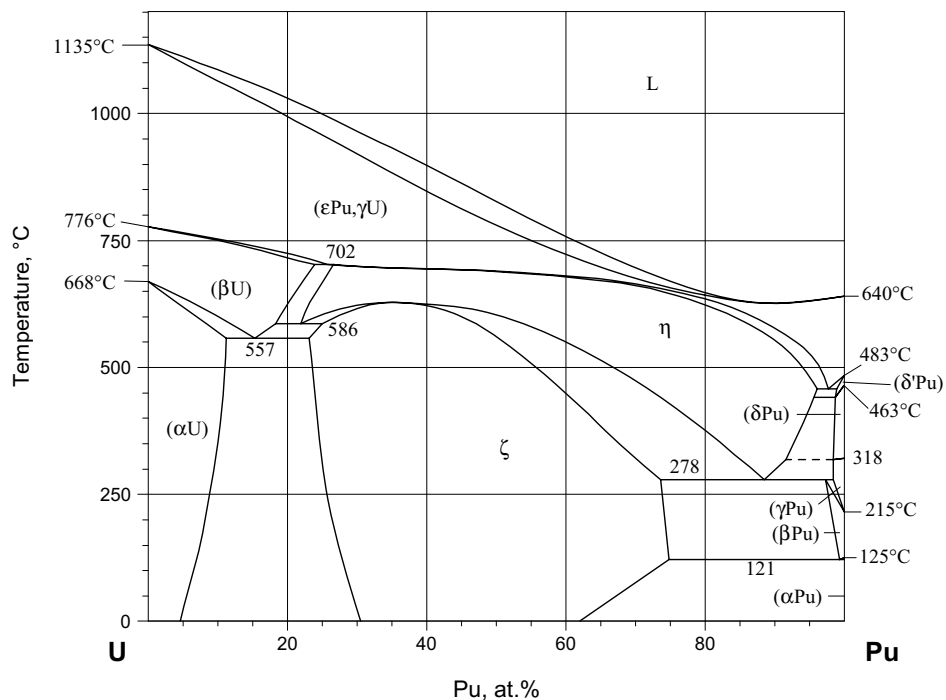


Fig. 7: Phase diagram of the U-Pu system

U-Am

No experimental information is available in literature. In Fig. 8 it is reported the predicted phase diagram calculated by [1993Oga] using interaction parameters obtained on the basis of the Brewer valence bond model.

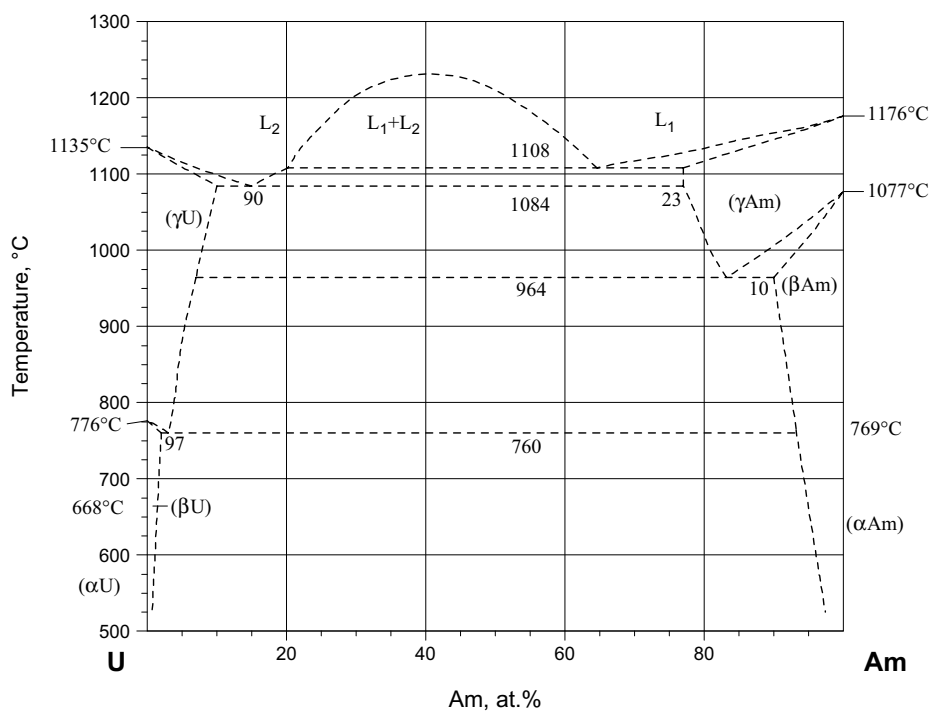


Fig. 8: Predicted phase diagram of the U-Am system (α U and α Am have been omitted in the calculation)

Np-Pu

A critical assessment of the very complex Np-Pu system has been presented by [1985She1], based on the experimental work of [1961Mar].

Lattice parameters of the high temperature solid solution based on β Pu have been reported by [1961Mar]. The cell, however, has been described as orthorhombic instead of monoclinic. For the $c/2$ -(γ Np, ϵ Pu) solid solution $a = 356.5$ was reported for 550°C and $x(\text{Pu}) = 0.5$.

The phase diagram is shown in Fig. 9, in agreement with the assessment of [1985She1]. The bcc solid solution and its equilibria with liquid are in agreement with a calculation performed by [1993Oga] on the basis of the Brewer valence bond model.

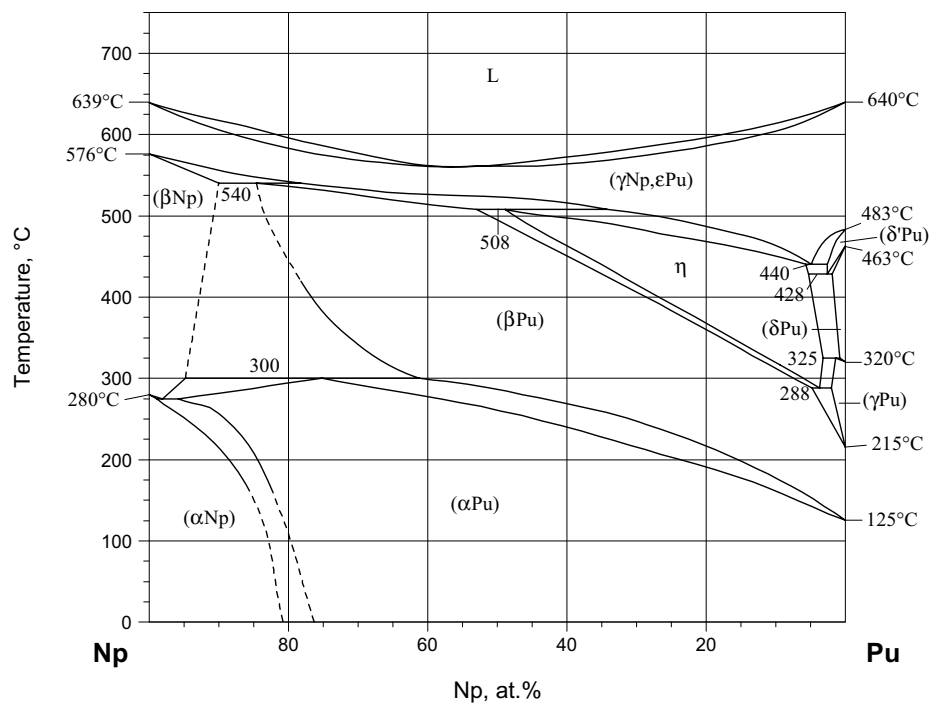


Fig. 9: Phase diagram of the Np-Pu system

Np-Am

A DTA investigation was carried out on a few alloys by [1992Gib]. Measurements on a $\text{Np}_{0.54}\text{Am}_{0.46}$ sample suggested some degree of mutual solubility although terminal solid phases, one Np rich and one Am rich, were found to coexist.

The phase diagram reported in Fig. 10 was calculated by [1993Oga] using regular interaction parameters obtained on the basis of the Brewer valence bond model. Low temperature phases αAm and βNp were not considered. Barely noticeable liquid miscibility gap was suggested. The model predicts greater solubility of Np in Am than *vice-versa*. This seems to be in agreement with the DTA data by [1992Gib].

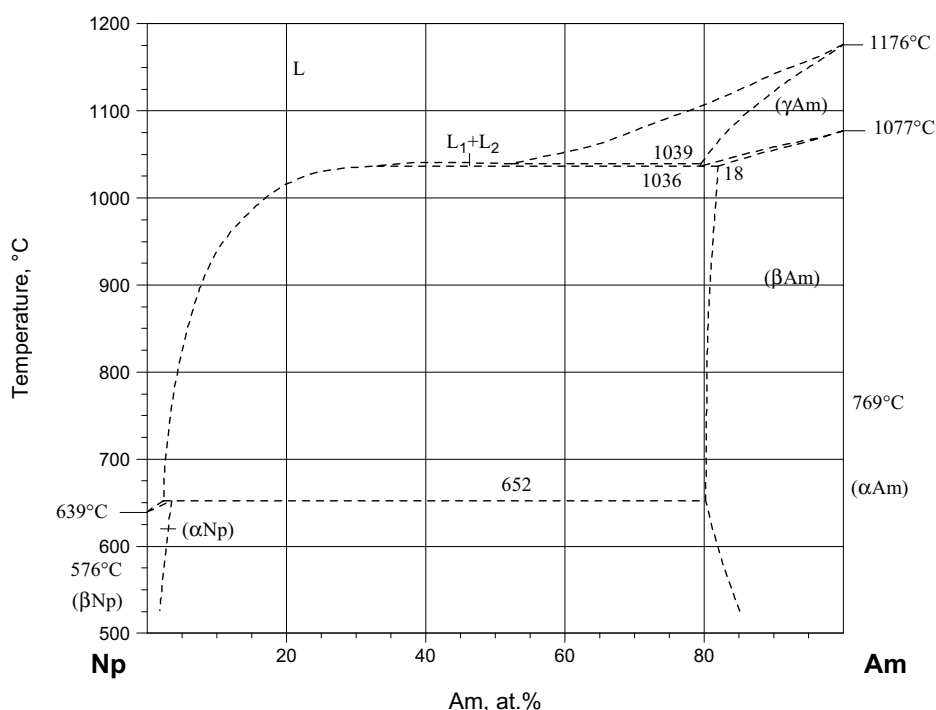


Fig. 10: Predicted phase diagram of the Np-Am system (βNp and αAm have been omitted in the calculation)

Pu-Am

An experimental investigation of the Pu-Am phase diagram was carried out by [1990Shu] by DTA, microscopy, high temperature X-ray analysis, density measurements. The obtained phase diagram, reported in [Eff1], is characterized by continuous ranges of solid solutions (ϵ Pu, γ Am) bcc and (δ Pu, β Am) fcc. The fcc structure is stable to room temperature between 6.2 and 80 at.% Am. Okamoto [1999Oka2] presented a phase diagram in good qualitative agreement with the previous one, which was obtained combining the liquid + (γ Am, ϵ Pu) and (γ Am, ϵ Pu) + (β Am, δ Pu) two-phase fields calculated by [1993Oga] with the boundaries of the low temperature phases (α Am, γ Pu, β Pu, α Pu) previously proposed by Ellinger [1966Ell]. Okamoto tentatively added a small δ' Pu field, which possibly corresponds to the (η Pu) field shown by Ellinger.

The phase diagram reported in Fig. 11 is mainly based on [1990Shu], slightly modified by smoothing the original curves.

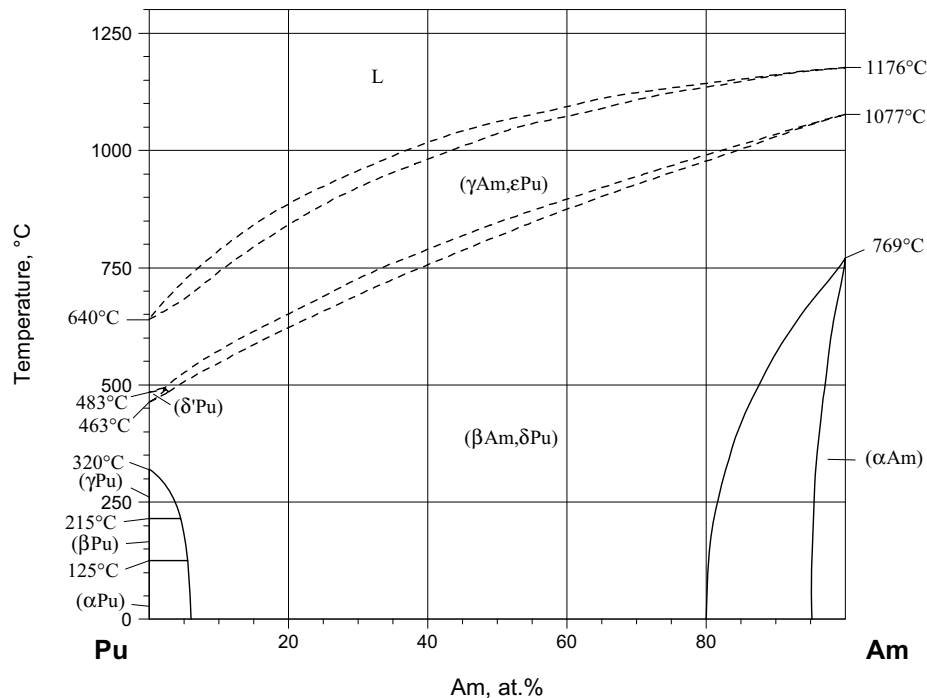


Fig. 11: Phase diagram of the Pu-Am system

Pu-Cm

The phase diagram has been studied by [1995Shu], by using DTA, high temperature X-ray diffraction and microstructural analysis. The phase diagram with experimental points has been reported in [Eff1] and in a slightly smoothed version by [2000Oka]. This is shown in Fig. 12.

The (β Cm) solid solution tends to remain in a metastable state down to room temperature. As a consequence it is difficult to equilibrate the (α Cm) solution. The (α' Cm) region, probably metastable, corresponds to a faulted fcc phase differing from dhcp (α Cm) in the ordering of the close-packed layers.

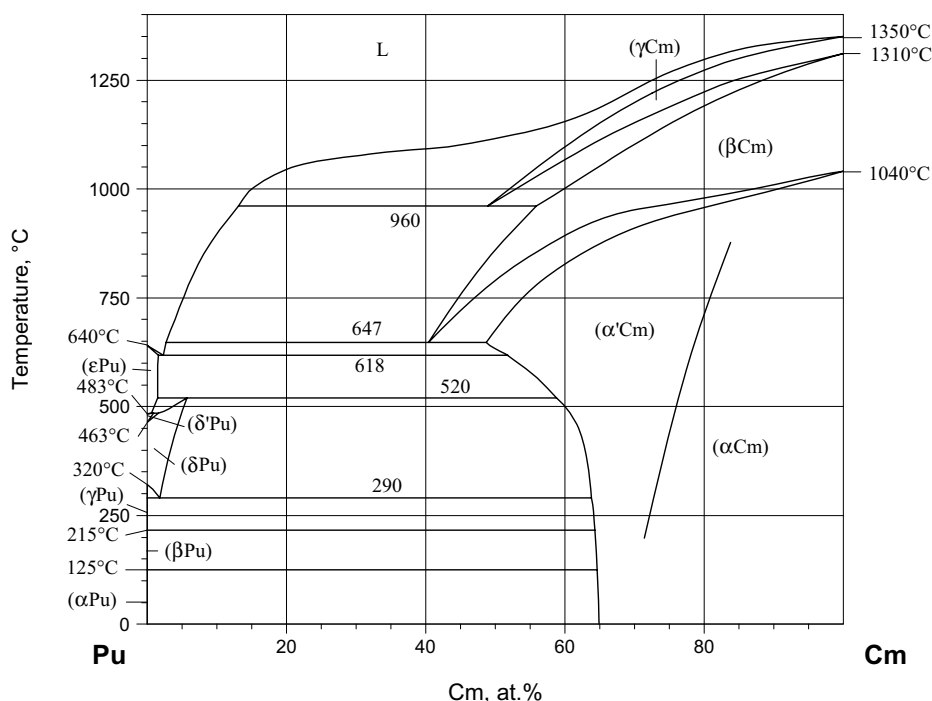


Fig. 12: Phase diagram of the Pu-Cm system

Cm-Bk

Cm-Bk alloys were studied by [1998Hea], by X-ray diffraction up to 53 GPa to probe their structural behavior under pressure. Two Bk-Cm alloys containing 70 and 46 at.% Cm were investigated. These studies resulted in the determination of the transition pressure reported in Fig. 2.

2. General Alloying Behavior of the Actinides

2.1. Notes about the Systems An-Me

For only a few actinides binary phase diagrams with several partner elements are available in literature. Main characteristics of the binary equilibria formed by Th, U and Pu, have been summarized and schematically shown in Fig. 13a, 13b, and 13c, respectively. In these figures the partner elements are represented by their position in the Periodic Table and in the various corresponding “boxes” of the Table a few symbols have been inserted in order to show the characteristic features of the alloying behavior (solubility or miscibility gaps in the solid and/or liquid state, formation of intermediate phases in the solid state, *etc.*).

Solubility in the Liquid State

As for Th-Me systems complete liquid solubility is shown for all partner elements except for a small miscibility gap with O and extended gaps with Eu and Yb.

As for U, miscibility gaps in the liquid state have been observed with rare earth and actinide elements, and with Zn and 11th group elements.

Similar behavior is shown by Pu: miscibility gaps are present in the systems with oxygen, lanthanides, actinides, Mg, Ag, Cd.

Solubility in the Solid State

More or less extended solid solutions are observed with most of the partner elements. In a few cases complete solid solutions are observed at least for one of the actinide solid phases.

For Th complete solid solutions are present only with Zr and rare earths (in particular with La complete solid solution is present in both fcc and bcc structures).

Complete solid solutions are formed by U only with Ti, Zr, Hf and Nb, while Pu shows complete solid solutions with Sc and Zr.

Compound Formation

The binary systems in which we have the formation of intermediate phases form, in the Periodic Table, a nearly well defined pattern, which is similar for the different actinides and shows close analogies also with the corresponding pattern of the lanthanides and, more generally, with those of the elements of the first groups of the Periodic Table.

As a general rule compound formation is found with partner elements on the right of the Periodic Table, typically from the 7th group on. The elements on the left (with some exceptions for the lightest ones: Be, Mg, *etc.*) do not form any intermediate phases; their binary phase diagrams with An are generally of the simple eutectic or monotectic type. For selected actinides however, the formation by solid state reaction of low temperature phases has also been observed.

As an exceptions to this general behavior the compounds formed by U with Ti, Zr and Mo, and by Pu with Sc, Zr and Hf may be mentioned. These phases are generally formed by solid state reaction and are stable only at relatively low temperature.

Considering the general validity of this subdivision, it may be assumed that it is also applicable to the heavy transplutonium actinides. For Am, the data available, even though approximate and incomplete, are in agreement with the mentioned general behavior. An overview of the Am alloying behavior has been recently published [2001Fer].

Th															
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
== 2															
	== 1											== 3	== 2	== 2	<> 1
== 1	== 2											== 7	== 4	== 4	== 5
		== ==	== 0	== 0	== 0	== 3	== 5	== 5	== 7	== 4	== 4	== 4	== 6	== 3	== 5
		== ==	== ==	== 0	== 0		== 4	== 7	== 7	== 3	== 6	== 4	== 4	== 3	== 4
	0	== ==	== 0	== 0	== 0	== 1	== 3	== 6	== 8	== 6	== 4	== 5	== 4	== 6	
Ln	== ==	== ==	== ==	== ==	== ==	== ==	<> 0	== ==	== ==	== ==	== ==	== ==	== 0	<> 0	== 0
	An	Th		<>		== 1									

Fig. 13a: Systematics of the binary alloying behavior of Thorium. Data relevant to the Th-X system are reported at the cell of the element X in the periodic tables.
Legend:
Empty cell: no information.
Upper part: liquid state behavior; == complete solubility; <> miscibility gap.
Lower part: solid state behavior; == complete solubility (at least in a temperature range);
<> miscibility gap; the number of known intermediate compounds or phases is also reported.

U															
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
<div>== 1</div>															
<div>0</div>	<div>◇ 1</div>											<div>== 3</div>	<div>== 3</div>	<div>== 3?</div>	<div>== 6?</div>
<div>== 0</div>	<div>◇ 0</div>											<div>== 3</div>	<div>== 7</div>	<div>== 3</div>	<div>== 6</div>
		<div>◇ 0</div>	<div>== 1</div>	<div>== 0</div>	<div>== 0</div>	<div>== 2</div>	<div>== 2</div>	<div>== 6</div>	<div>== 7</div>	<div>◇ 1</div>	<div>◇ 2</div>	<div>== 5?</div>	<div>== 7</div>	<div>== 3</div>	<div>== 6</div>
		<div>◇ 0</div>	<div>== 1</div>	<div>== 0</div>	<div>== 1</div>		<div>== 5</div>	<div>== 4</div>	<div>== 5</div>	<div>◇ 0</div>	<div>== 1</div>	<div>== 5?</div>	<div>== 5</div>	<div>== 4</div>	<div>== 10</div>
			<div>== 0</div>	<div>== 0</div>	<div>== 0</div>	<div>== 2</div>	<div>== 4</div>	<div>== 5</div>	<div>== 4</div>	<div>◇ 2</div>	<div>== 4</div>	<div>== 1</div>	<div>◇ 2</div>	<div>◇ 3</div>	

Ln	<div>◇ 0</div>	<div>◇ 0</div>	<div>◇ 0</div>		<div>◇ 0</div>	<div>◇ 0</div>								<div>◇ 0</div>	
An	<div>◇</div>		U	0	2	<div>◇ 0</div>									

Fig. 13b: Systematics of the binary alloying behavior of Uranium. Data relevant to the U-X system are reported at the cell of the element X in the periodic tables. See caption of Fig 13a for the legend.

Pu															
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
== 2															
== 0	== 1											== 5	== 4	== 1	◇ 4
== 0	◇ 3											== 5	== 5	== 1	3
0	== 0	== =1=	== 0	== 0	== 0	== 1	== 2	== 6	== 6	== 4	== 6	== 12	== 3?	== 1	4
	0	== 0	== 1	== 0	== 0		== 5	== 8	== 4	◇ 2	◇ 4	== 5	== 7	== 5	2
	0	◇ 0	== 2	== 0	== 0	== 1	== 4	== 4	== 8	== 8	== 2	== 2	== 6	== 3	
Ln	◇ 0	◇ 0	◇ 0			◇ 0	◇ 0	◇ 0	◇ 0	◇ 0	◇ 0		0	◇ 0	0
An	◇ =1=			=2=	==	Pu	◇ 0								

Fig. 13c: Systematics of the binary alloying behavior of Plutonium. Data relevant to the Pu-X system are reported at the cell of the element X in the periodic tables. See caption of Fig. 13a for the legend. For a few partner elements both intermediate compounds and complete solid solutions are observed.

2.2. Stabilization of the U and Pu Elementary Structures

Another important feature in the alloying behavior of the actinides is the effect of alloying elements on the stability of the different actinide elementary structures. Particular interest has been devoted to U and Pu, also because of their relevance in nuclear technology and the high number of polymorphic forms of these elements.

Uranium

The (γ U) phase (*c*/2-*W* type structure) generates continuous solid solutions with the elements having the same structure, and in particular with Ti, Zr, Hf, Nb, at least in a limited high temperature range. With other early-transition elements the gamma field is also stabilized. The solubility of partner elements in (β U) is generally lower than in (γ U).

[2002Bla] studied the phase stabilization of the light actinide phases in binary alloys. They proposed a quantitative evaluation of the stabilization of a selected phase with respect to the other phases stable at lower temperature by considering the initial slope dT/dc of the two-phase boundary between the two phases (β to α transus).

According to this definition the β stabilizing elements are placed in the central part of the *d*-block. They are Cr and Mn, Mo to Rh, Re to Pt in first, second and third transition series, respectively.

It may be observed that with *s*-block metals and early transition elements (groups 1 to 6), no intermediate compounds are formed or they are stable only at relatively low temperature and decompose before melting. With the elements from group 7 to 10 an increasing number of compounds are formed and, in particular with elements from Mn to Ni, U rich compounds (typically U_6Mn type) appear which compete with the stability of the β - and γ based solid solutions.

Plutonium and the “Saga” of Ga-Pu System

Among topics related to the stabilization of the actinide allotropic phases the question related to the stability of the fcc (δ Pu) is particularly important. (δ Pu) is malleable and easily shaped, and it is important because of its uses (in nuclear weapons, *etc.*).

This phase may be retained (either in stable or metastable conditions) down to room temperature by the addition of gallium or aluminium. Of particular interest is therefore the Ga-Pu system. The question of the stabilization of delta plutonium and the related investigation of this phase diagram has been the subject of an intense research activity carried out, during the cold war, separately by two teams (the Anglo-American one and that from the Soviet Union) with the production of two different versions, reported in Fig. 14a and 14b, respectively, which only recently came to an agreement.

The two versions, in a way, may now be reconciled: the diagram shown in Fig. 14a represents the metastable conditions and it is adequate for practical applications; the equilibrium diagram of Fig. 14b shows the eutectoid decomposition of the (δ Pu) phase, which however, due to very slow diffusion processes, cannot be directly observed. It was only through long-term annealing treatments (several thousands of hours at 130°C, or at 150°C) with pre-treated (preconditioned) samples subjected to high pressure or compressive plastic deformation, that it was finally possible to deduce (to extrapolate from a slightly higher temperature) the equilibrium phase boundaries and confirm the diagram of Fig. 14b.

As a final comment to this point we may remark that, as observed by Hecker and Timofeeva [2000Hec], the situation in Pu alloys (especially Ga-Pu, Al-Pu) is similar to that in steel where for the C-Fe system two diagrams (stable with graphite and metastable with Fe_3C) must be considered.

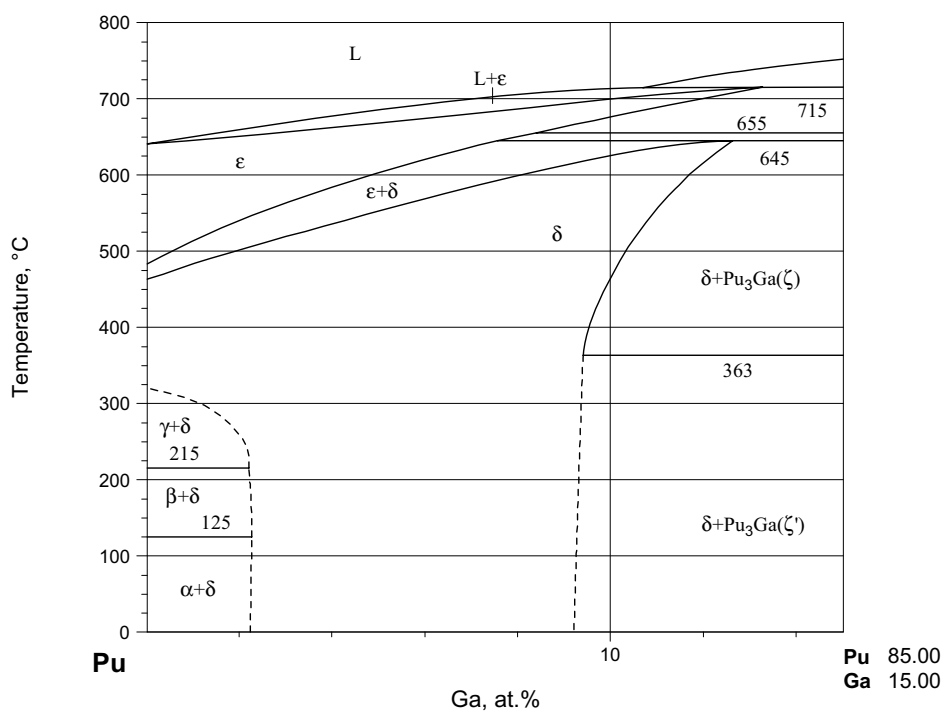


Fig. 14a: Metastable phase diagram of the Ga-Pu system

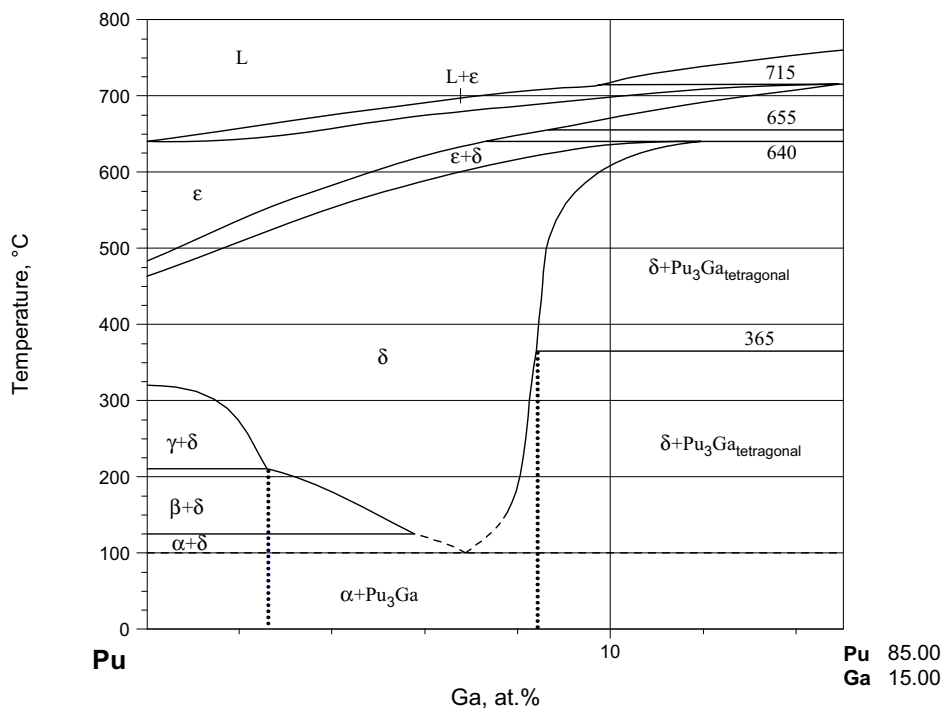


Fig. 14b: Equilibrium phase diagram of the Ga-Pu system

2.3. Notes about the Systems An'-An''-Me

For the ternary alloy systems formed by two actinides with a third element the lack of experimental data available in literature is particularly evident. A short list of these systems is reported in Table 3 with a synopsis of the experimental investigations performed.

No data have been found in literature about experimental investigations on phase equilibria in ternary inter-actinide systems An'-An''-An'''.

Table 3: Notes on Experimental Studies on Phase Equilibria in An'-An''-X Ternary Systems Mainly Based on [TA], [Eff1, Eff2, Eff3, Eff4, Eff5, Eff6, Eff7] and [Vil3]

An'-An'' Elements	-X element	Experimental Information
Th-U	-Al	Partial liquidus projection. Solubility of U in ThAl ₃
	-As	Solid solubility of Th ₃ As ₄
	-B	Partial isothermal section at 800°C (range UB ₂ -Th-U). Solid solubility of (Th _{1-x} U _x)B ₄
	-Be	Complete solid solubility of (Th _{1-x} U _x)Be ₁₃
	-Bi	Partial isothermal section at 1000°C (80-100 at.% Bi)
	-C	Several partial isothermal sections Temperature-composition section ThC ₂ -UC ₂ Complete solid solubility of (Th _{1-x} U _x)C
	-Fe	Partial liquidus projection (range UFe ₂ -Th-U) Partial isothermal section (range UFe ₂ -Th-U) Ternary compound UFe ₂ Th ₂ (no structure data available)
	-Mn	Partial liquidus projection (range UMn ₂ -Th-U)
	-Ni	Partial liquidus projection (range 0-60 at.% Ni)
	-P	Complete solid solubility of (Th _{1-x} U _x) ₃ P ₄
	-Pd	Partial liquidus projection and isothermal section (Pd rich corner) Complete solid solubility of (Th _{1-x} U _x)Pd ₄
	-Re	Solubility of U in ThRe ₂ (MgZn ₂ type) and solubility of Th in URe ₂ (URe ₂ type)
	-S	Complete solid solubility of (Th _{1-x} U _x)S (NaCl type) U ₂ ThS ₅ (U ₃ S ₅ derivative) ternary compound (or solid solution?)
	-Sb	Complete solid solubility of (Th _{1-x} U _x)Sb ₂ (Cu ₂ Sb type)
	-Se	Complete solid solubility of (Th _{1-x} U _x)Se (NaCl type)
	-Te	Solubility of U in ThTe (CsCl type) and solubility of Th in UTe (NaCl type)
	-Zr	Complete liquidus and solidus projections Several isothermal sections
Th-Pu	-C	Partial isothermal sections at 1100, 1300, 1600°C Temperature-composition section (ThC ₂ -PuC ₂)
	-N	Partial isothermal sections. Isothermal section at 1500 (computed) Complete solid solubility of (Th _{1-x} Pu _x)N

An'-An" Elements	-X element	Experimental Information
U-Np	-O	Partial isothermal section at 1000°C Complete solid solubility of $(U_{1-x}Np_x)O_2$
	-Pt	Solubility of Np in UPt_3 (SnNi ₃ and TaPd ₃ type)
	-Zr	Partial isothermal sections at 520, 595 and 700°C
U-Pu	-C	Liquidus projection Several isothermal sections Several temperature-composition sections (UC_2 - PuC_2 , etc.)
	-Mo	Full phase diagram in the range 35-100 at.% U Partial liquidus projection Partial isothermal sections at different T Solid solubility of $(U_{1-x}Pu_x)_4Mo$ (W type) $0 < x < 0.22$ (metastable?).
	-N	Complete solid solubility of $(U_{1-x}Pu_x)N$ (NaCl type) Isothermal section at 1000 (computed)
	-Pt	Solubility of Pu in UPt_3 (SnNi ₃ type)
	-S	Solid solubility of Pu in U_3S_5
	-Sn	Complete solid solubility of $(U_{1-x}Pu_x)Sn_3$ (AuCu ₃ type)
	-Zr	Liquidus and solidus projections Several isothermal sections at different T Zr migration in alloys exposed to a thermal gradient
Np-Pu	-B	Complete solid solubility of $(Np_{1-x}Pu_x)B_2$ (AlB ₂ type)

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