Plutonium – Thorium – Uranium

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Introduction

Works on the Pu-Th-U system were initiated as a contribution to the development of plutonium-bearing fuels for fast power-breeder reactors. [1965Far] presented the 700 and 900°C sections of the ternary Pu-Th-U phase diagram that have been worked out by investigators at Argonne [1964Ric]. Phase boundaries between (αTh) and (βTh) were determined using mainly X-ray diffraction. [1968Blu] attempted to construct a series of isothermal sections as well as an isopleth at 10 at.% Pu. [1968Far, 1969Blu] reported about experiments with Pu-Th-U fuel alloys. Objectives of these experiments were to determine the restraint characteristics of the V-20 mass% Ti jacket, the relative swelling behavior of the fuels, and the maximum attainable burnup before jacket failure. Works on phase relations and structure are summarized in Table 1.

Binary Systems

The Th-U and Pu-Th phase diagrams are taken from [1985Pet2] and [1985Pet1], respectively. The thermodynamic optimization of the Pu-U phase diagram was carried out by [1991Lei] using a CALPHAD method. Since the results between data and calculation are satisfactory, the diagram proposed by [1991Lei] has been retained in this assessment. It is shown in the chapter "*Remarks on the Actinide Alloying Behavior*" in the present volume.

Solid Phases

No ternary phases are formed in the Pu-Th-U system. Crystal structures of unary and binary phases are presented in Table 2.

Invariant Equilibria

Some ternary reactions were found by [1968Blu] using complementary experimental investigations. In the solid state three four-phase reactions have been reported at 710, 614 and 595°C involving the (αTh) phase and the U rich Pu-U phases. More experimental investigations on the ternary reactions are needed since the high temperature phase (βTh) should be observed at the above temperatures. Consequently these reactions could not be accepted in the present evaluation. The absence of the crystalline phase (βTh) is certainly due to the shift of the nominal composition observed in the alloys after annealing at 900 and 700°C. This change of composition to higher Th content was detected in alloys containing more than 40 at.% Th.

Liquidus Surface

A liquidus surface was proposed by [1968Blu]. No ternary phase was detected. A ternary peritectic reaction was found involving the (αTh), (εPu) and Pu_7Th_3 phases at 630°C. This liquidus surface needs experimental amendments since normally the (βTh) should participate in these ternary reaction as indicated in the accepted binary Pu-Th.

Isothermal Sections

In the review of [1965Far], partial isothermal sections at 700 and 900°C were reported and taken from the experimental work of [1964Ric]. Later [1968Blu] investigated the ternary system and proposed isothermal sections. Discrepancies were observed along the binary edge Pu-Th since the (βTh) phase have not been detected by [1968Blu]. Disagreements have also been observed concerning the borders of the phase fields. Nevertheless, the schematic isothermal sections at 900 and 700°C were reproduced in Fig. 1 and Fig. 2, respectively, modified in agreement with the accepted binary systems. The Th rich region up to 50 at.% Pu was taken from [1964Ric] and reproduced as dashed lines. The borders of the phase fields inside the ternary

system have been indicated as tentative by dashed lines and some of them were taken from [1968Blu]. These tentative isothermal sections need further experimental investigations. As indicated by [1968Blu] the η phase certainly presents a small solubility range inside the ternary. Consequently the three-phase equilibria (αTh)+(βU)+η and (αTh)+η+(γU) proposed by [1968Blu] should not exist. This has been replaced by a small three-phase field (βU)+η+(γU) and a large three-phase field (αTh)+(βU)+(γU), with a very narrow two-phase field (βU)+(γU) in between.

Temperature – Composition Sections

The isopleth for Pu-Th-U system at 10 at.% Pu has been constructed by [1968Blu] and is presented in Fig. 3. Some modifications have been done concerning the binary edges to be in agreement with the accepted binary systems Pu-Th and Pu-U. [1968Blu] suggested the existence of the Pu-U binary phases η and ζ along the isopleth. The presence of these phases is certainly due to the segregation in the alloys since the existence of these phases is not reported at 10 at.% Pu in the binary phase diagram up to 400°C. Consequently the phase equilibria involving the ζ and η phases are not included in the accepted isopleth. Some additional phase equilibria were added at the Pu-Th side.

Notes on Materials Properties and Applications

The ternary Pu-Th-U alloys with 10 and 20 mass% U, and 10 mass% Pu are potentially useful fast reactor fuels.

They have attained high burnups by using strong cladding to restrain swelling. The combination of the isotropic properties of fcc thorium and the high melting temperatures of Th base alloys looked attractive, as they should make possible metallic fuels that have excellent thermal properties. They are easily fabricated by rolling or injection casting, are compatible with liquid sodium, and are reprocessable by pyrometallurgical methods [1968Blu]. The alloys compared favorably with other metal fuels in thermal cycling experiments. Only minor density and length changes were observed after 100 cycles in NaK between 450 and 800°C. The alloys are compatible with vanadium-base cladding materials up to 650°C, but not with stainless steel.

Alloys of the following compositions 80%Th-10%U(93.18% enriched)-10%Pu (94.96% ^{239}Pu, 4.56% ^{240}Pu, 0.48%^{241}Pu) and 70%Th-10.66%U(93.18% enriched)-9.34% U(normal)-10% Pu (94.96% ^{239}Pu, 4.56%^{240}Pu, 0.48%^{241}Pu) have been studied by [1968Blu]. Alloys were annealed at 850°C for 24 h, water quenched, reheated to 700°C for 1 h, furnace cooled. The intermediate inspection by neutron radiography after 2 at.% burnup showed that the alloys had an average elongation of 8%. The inspection after 5.6 at.% burnup showed that no additional elongation had taken place between 2 and 5.6% burnup. The total increase in volume at the end of the irradiation experiments was an average of 40%. Fuel swelling, measured after irradiation, was about 7.2% per atomic percent burnup. Fission-gas releases into the plenum were 72%.

Metallographic examination of the specimens before and after irradiation showed no significant change in microstructure. Lack of visible void formation in the ternary alloys suggested that interconnected microporosity, not readily resolved by optical microscopy, accounted for the high fission-gas release, in agreement with the behavior of other metal fuels.

References

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

Reference	Method/Experimental Technique	Temperature/Composition/Phase Range Studied
[1964Ric]	X-ray diffraction, metallography, microprobe analysis	700°C Th-up to 20 at.% U-up to 50 at.% Pu (αTh), (αTh)+(βTh), (βTh) (αTh)+(βU), (αTh)+(βU)+(γU) (αTh)+(γU), (αTh)+(γU)+L (αTh)+L, (αTh)+(βTh)+L, (βTh)+L 900°C Th-up to 20 at.% U-up to 40 at.% Pu (αTh), (αTh)+(βTh), (βTh) (αTh)+(γU), (αTh)+(γU)+L (αTh)+L, (αTh)+(βTh)+L, (βTh)+L
[1968Blu]	Room-temperature X-ray diffraction, metallography, high-temperature X-ray diffraction, electrical resistance, dilatometry, DTA	Th-20U-60Pu 700°C, 900°C

Table 2: Crystallographic Data of Solid Phase

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(εPu,γU)	*cI*2 $Im\bar{3}m$ W		continuous solid solution which exists between 1135 and 454°C [1991Lei]
(εPu) 640 - 483		a = 363.8	pure, 500°C, [1989Pet] dissolves 5.6 at.% Th at 605 ± 10°C [1985Pet1]
(γU) 1135 - 776		a = 352.4	pure, 805°C, [Mas2] dissolves 1.5 at.% Th at 1100°C [1985Pet2]
(δ'Pu) 483 - 463	*tI*2 *I*4/*mmm* In	a = 333.9 c = 444.6	pure, 477°C, [1989Pet] dissolves about 1.3 at.% U at 440°C [1991Lei]; dissolves about 1.4 at.% Th at 490°C [1985Pet1]; exists down to 437°C along the Pu-U binary [1991Lei] and down to 490°C along the Pu-Th binary [1985Pet1]
(δPu) 463 - 320	*cF*4 $Fm\bar{3}m$ Cu	a = 463.70	pure, 320°C, [1989Pet] dissolves about 1.6 at.% U at 318°C [1991Lei] and 2.6 at.% Th at 500°C [1985Pet1] exists up to 500°C along the Pu-Th binary [1985Pet1]
(γPu) 320 - 215	*oF*8 *Fddd* γPu	a = 315.87 b = 576.82 c = 1016.2	pure, 235°C, [1989Pet] dissolves about 1.6 at.% U at 278°C [1991Lei]; dissolves 1.2 at.% Th at 315°C [1985Pet1]
(βPu) 215 - 125	*mC*34 *C*2/*m* βPu	a = 928.4 b = 1046.3 c = 785.9 β = 92.13°C	pure, 190°C, [1989Pet] dissolves about 2.7 at.% U at 278°C [1991Lei] the solubility of Th is nearly absent [1985Pet1]
(αPu) < 125	*mP*16 $P2_1/m$ αPu	a = 618.3 b = 482.2 c = 1096.3 β = 101.79°C	pure, 21°C, [1989Pet], the solubilities of U and Th are nearly absent [1991Lei, 1985Pet1]
(βTh) 1755 - 1360	*cI*2 $Im\bar{3}m$ W	a = 411	pure, 1450°C [1985Pet1] dissolves 50 at.% Pu at 615°C [1985Pet1] and 12.2 at.% U at 1375°C [1985Pet2] exists up to 582°C along the Pu-Th binary [1985Pet1] and up to 1270°C along the Th-U binary [1985Pet2]

Phase/ Temperature Range [°C]	Pearson Symbol/ Space Group/ Prototype	Lattice Parameters [pm]	Comments/References
(αTh) < 1360	*cF*4 $Fm\bar{3}m$ Cu	*a* = 508.45	pure, 25°C [1985Pet1] dissolves 48 at.% Pu at 582°C [1985Pet1] and 6.8 at.% U at 1270°C [1985Pet2]
(βU) 776 - 668	*tP*30 $P4_2/mnm$ βU	*a* = 1075.9 *c* = 565.6	pure, 720°C, [1989Pet] dissolves about 24 at.% Pu at 702°C [1991Lei] the solubility of Th is very small [1985Pet2] exists down to 557°C along the Pu-U binary [1991Lei]
(αU) < 668	*oC*4 *Cmcm* αU	*a* = 285.37 *b* = 586.95 *c* = 495.48	pure, at 25°C [1989Pet] dissolves about 11 at.% Pu at 557°C [1991Lei] the solubility of Th is very small [1985Pet2]
Pu_7Th_3 < 615	*o**	*a* = 622 *b* = 1162 *c* = 709	30 at.% Th [1985Pet1]
η, PuU 702 - 278	*tP*52	 *a* = 1057 *c* = 1076	~4 to ~78 at.% U at 25 at.% U [1969Lea]
ζ, PuU ≲ 628	*cP*58	 *a* = 1069.2 *a* = 1065.1 *a* = 1066.4	~26.4 to ~77 at.% U at 25°C, 35 at.% U [1969Lea] at 25°C, 70 at.% U [1969Lea] at 25°C, 50 at.% U [V-C2]

Table 3: Investigations of the Pu-Th-U Materials Properties

Reference	Method/Experimental Technique	Type of Property
[1969Blu]	Optical microscopy, measurements of density, neutron radiography	Swelling after irradiation

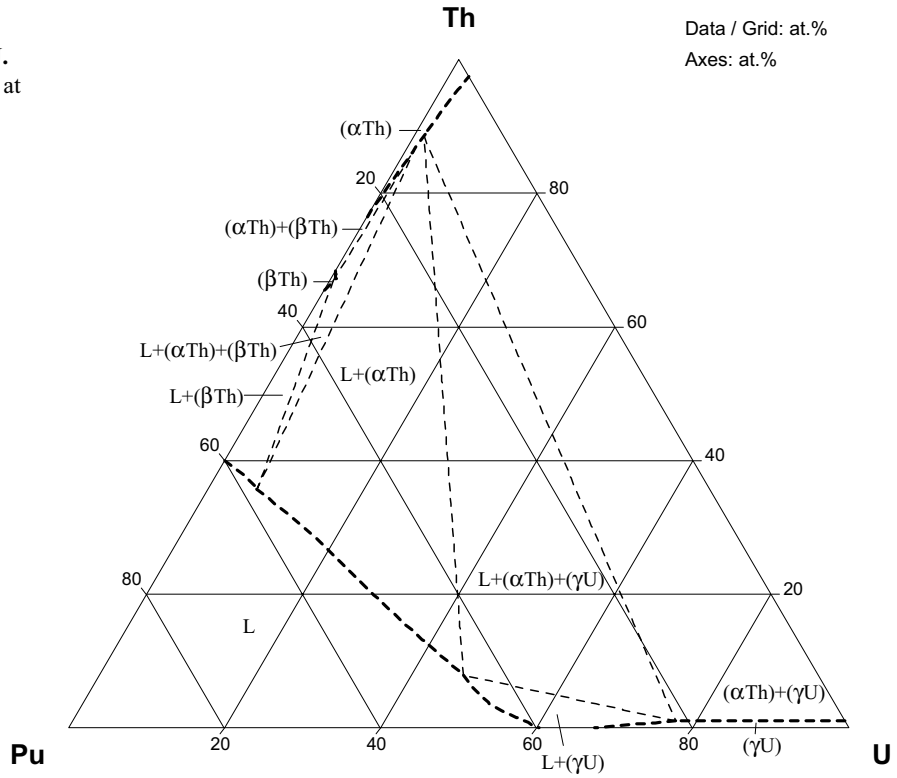

Fig. 1: Pu-Th-U. Isothermal section at 900°C

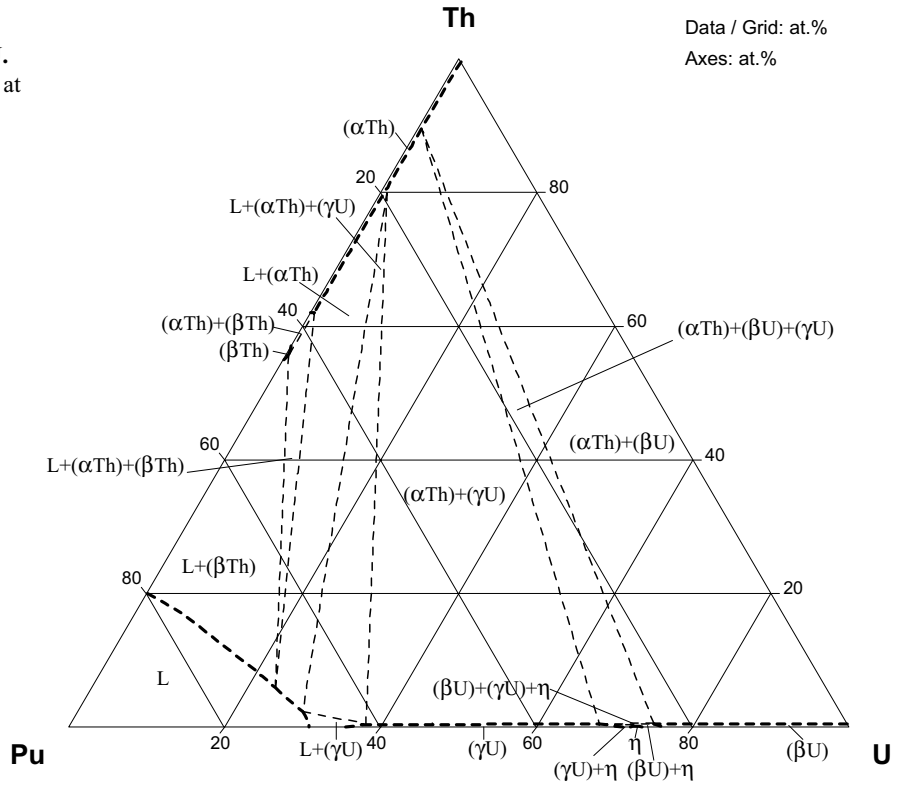

Fig. 2: Pu-Th-U. Isothermal section at 700°C

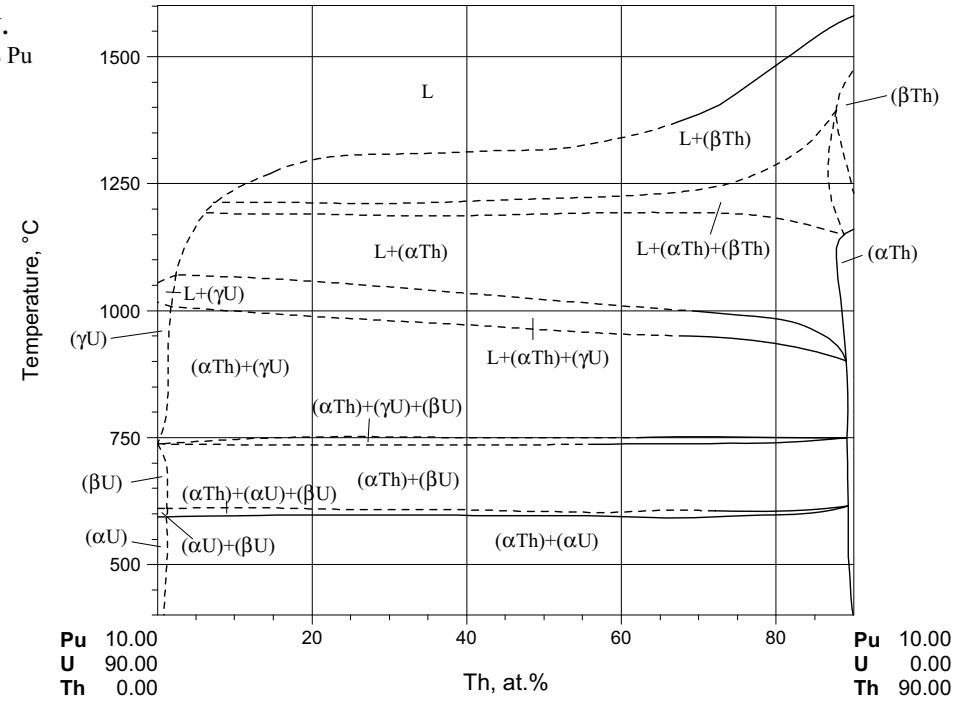

Fig. 3: Pu-Th-U.
Isopleth at 10 at.% Pu