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Argonne National Laboratory

THORIUM-URANIUM-PLUTONIUM ALLOYS AS POTENTIAL FAST POWER-REACTOR FUELS

Part I. Thorium-Uranium-Plutonium Phase Diagram

by

B. Blumenthal, J. E. Sanecki,
and D. E. Busch

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ABSTRACT

The ternary Th-U-Pu system was investigated by means of metallography, room- and high-temperature X-ray diffraction, dilatometry, electrical resistance measurements, and differential thermal analysis.

The liquid miscibility gap is restricted to the Th-U side of the system. A eutectic trough connects the Th-U and Th-Pu sides of the diagram. The peritectic reaction $\alpha_{\text{Th}} + L \rightarrow C$ ($C = \text{Pu}_2\text{Th}_{1-x}$) of the Th-Pu binary at 615°C joins the eutectic trough in a ternary peritectic reaction $\alpha_{\text{Th}} + \epsilon_{\text{Pu}} + L \rightarrow C$ at 630°C . In the solid state, three 4-phase reactions occur involving α_{Th} and the phases on the uranium side of the U-Pu system: a class III reaction $\alpha_{\text{Th}} + \beta_{\text{U}} + \gamma_{\text{U}} \rightarrow \eta$ at 714°C , a class III reaction $\alpha_{\text{Th}} + \beta_{\text{U}} + \eta \rightarrow \zeta$ at 610°C , and a class II reaction $\alpha_{\text{Th}} + \beta_{\text{U}} \rightarrow \alpha_{\text{U}} + \zeta$ at 595°C .

Over a wide range of compositions the ternary alloys are in equilibrium with α_{Th} and the phases of the binary U-Pu system. The addition of uranium to the Th-Pu solid solution greatly lowers the solid solubility of plutonium in thorium. Alloys of potential use as fast reactor fuels are restricted to a relatively small range of compositions with no more than 10 a/o Pu and up to 25 a/o U.

The Th-U-Pu ternary system resembles other U-Pu systems to which a third element has been added, notably Mo, Ti, or Zr. In all four systems, the zeta phase forms by a peritectoid class III reaction, and the solubility of zeta for the third element is small. No such uniformity applies to the formation of the η phase in the four ternary systems.

I. METALLURGICAL AND REACTOR PHYSICS BACKGROUND

Work on the Th-U-Pu ternary alloys was initiated as a contribution to the development of plutonium-bearing fuels for fast power-breeder reactors. The development of the U-Mo and U-Pu-Fs alloys had reached an impasse because these alloys are subject to swelling when irradiated at

temperatures above 400°C. Uranium-plutonium-base metal fuels have attained high burnups by using strong cladding to restrain swelling. Kelman *et al.*,^{1,2} developed U-Pu-Zr and U-Pu-Ti alloys that attained burnups greater than 2.8×10^{21} and 2.5×10^{21} fiss/cm³,* respectively, at operating temperatures of 520 to 540°C. These results have considerably improved the outlook for metallic fuels.³

The combination of the isotropic properties of fcc thorium and the high melting temperatures of thorium-base alloys looked attractive, as they should make possible metallic fuels that have excellent thermal properties, are easily fabricated by rolling or injection casting, are compatible with sodium, and are reprocessable by pyrometallurgical methods.

Prior to the study of the Th-U-Pu ternary system, the work of Kittel *et al.*,⁴ had shown that the Th-U binary alloys with up to 25 w/o uranium behaved well under irradiation. Also, good irradiation results at temperatures to 450°C were obtained by Horak, Kittel, and Rhude⁵ with Th-Pu binary alloys that contained 5 and 10 w/o plutonium. Other investigations of the binary alloys were carried out at temperatures or burnup levels that were too low to be meaningful for the design of a fast power-breeder reactor fuel.⁶⁻¹⁰

Recently, Dickerman, Robinson, Stewart, and Blumenthal¹¹ studied sodium-bonded Th-20 w/o U fast-reactor-type fuel elements during transient meltdown experiments in the TREAT reactor. The investigators demonstrated that the high-melting thorium matrix constrained the uranium-phase during transient heating at temperatures several hundred degrees above the solidus temperature of the alloy. Thus, the relatively low solidus temperature of 1086°C is not necessarily objectionable. These observations should be applicable to the Th-U-Pu ternary alloys that have a U-Pu phase uniformly distributed in a high-melting thorium matrix.

The development of fuels for fast breeder reactors has been based almost exclusively on the U-238 → Pu-239 fuel cycle with little attention given to metallic thorium as a fertile material. Although thermal reactors have used the Th-232 → U-233 cycle, little interest in this cycle has been shown for fast reactor applications. Recent physics calculations by Okrent, Cohen, and Loewenstein¹² have shown that sodium-cooled fast breeder reactor cores which operate on the Th-232 → U-233 cycle tend to have more negative sodium void coefficients of reactivity than cores operating on the U-238 → Pu-239 cycle. Loewenstein has shown a significant advantage in sodium reactivity coefficient by replacing part of the U-Pu fuel with Th-U fuel. The resultant hybrid reactor core would have a central region of Th-U fuel enclosed by a larger region of U-Pu fuel; the core would have a reflector of natural or depleted uranium. The physical and metallurgical aspects of this approach have been described by Loewenstein and Blumenthal.¹³

*Burnup level is based on the effective density of the fuel-cladding combinations.

Combinations of the Th-232 $\rightarrow$ U-233 and U-238 $\rightarrow$ Pu-239 fuel cycles occur when Th-232 is alloyed with either U-235 or Pu-239. The evaluation and subsequent utilization of these more complex systems requires a knowledge of the phase diagram and properties of the Th-U-Pu ternary alloys.

The literature contained no information on the Th-U-Pu ternary alloys at the time this work was started (1961). Therefore, a decision was made to investigate the Th-U-Pu ternary system in order to select the most promising alloys, and then to determine their pertinent properties. Although the investigation is by no means complete, it is possible to show the salient features of the ternary system and to determine the alloy compositions that have the greatest potential for future applicability to fast reactor technology. This report will discuss the ternary phase diagram and related work on the binary boundary systems. Properties pertinent to reactor application will be described in a second report.

II. INTRODUCTION TO PHASE-DIAGRAM WORK

A. Binary Boundary Systems

1. Thorium-Uranium System. The phase diagram of the Th-U system, shown in Fig. 1, is based on the early results of Carlson¹⁴ and the investigation by Bentle.¹⁵ Considerable differences exist between the solid-solubility data of Bentle for uranium in thorium and the data of other investigators.¹⁶⁻¹⁸ After Elliot reviewed the system,¹⁹ Carlson's and Bentle's version of the diagram was considered sufficient for the purposes of this investigation.

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Fig. 1. Thorium-Uranium Phase Diagram (O. N. Carlson and G. G. Bentle)

The melting point of pure thorium was redetermined by Kato²⁰ as 1725°C. The best value for the $\beta \rightleftharpoons \alpha$ transformation temperature is 1365°C, as determined by Bentle.¹⁵ The transformation points for uranium are those reported by Blumenthal.²¹

2. Uranium-Plutonium System. The U-Pu phase diagram shown in Fig. 2 is based on the diagram by Ellinger, Elliott, and Cramer.²² On the uranium side the solubility limits of plutonium in uranium were modified to conform with the results of Berndt.²³ Recent differential thermal analysis (DTA) data by Blumenthal place the peritectoid formation of the η phase by $\beta_U + \gamma_U \rightleftharpoons \eta$ at 710°C, which is in agreement with earlier

DTA results of Wittenberg and Etter.^{24*} The absence of a thermal arrest at 560°C in an alloy with 25 a/o plutonium restricts the width of the $\alpha_U + \zeta$ field, which also agrees with results obtained by Wittenberg and Etter. The plutonium end of the diagram given by Elliott and Larson²⁵ has limited bearing on the present investigation.

Fig. 2

Uranium-Plutonium Phase Diagram (F. H. Ellinger, R. O. Elliott, and E. M. Cramer, Los Alamos; including data by A. F. Berndt)

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3. Thorium-Plutonium System. Two versions of the Th-Pu phase diagram exist. The diagram of Poole, Williamson, and Marples²⁶ is more detailed and agrees with the one by Schonfeld.²⁷ The diagram, shown in Fig. 3, is based on the results of both investigators. The only intermediate

phase in the system is formed peritectically and is orthorhombic. According to Poole and co-workers, this intermediate phase has the composition $Pu_{13}Th_6$, whereas Schonfeld and co-workers describe the phase as Pu_2Th . Both groups of investigators report that the maximum solubility of plutonium in α -Th is about 48.5 a/o, which was confirmed by Portnoff and Calais.²⁸ The latter authors describe the intermediate phase as being close to Pu_7Th_3 , which is equivalent to thorium-deficient Pu_2Th or Pu_2Th_{1-x} , where $x \approx 1/6$.

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Fig. 3. US-UK Thorium-Plutonium Phase Diagram with Arbitrary High-temperature Extrapolation

whereupon β_{Th} eutectoidially transforms to Pu_2Th and α_{Th} . Bochvar reports that the maximum solid solubility of plutonium in thorium is 33 a/o.

Bochvar *et al.*,²⁹ give a diagram (Fig. 4) wherein the β_{Th} phase field is stable down to 600°C,

*The minor change from 705°C, as reported by Schonfeld, is made because the peritectoid formation of the η phase in the ternary system occurs just a few degrees above that in the binary system. The proper classification of this four-phase reaction is aided by the information that the reaction in the ternary system occurs above and not below the reaction temperature in the binary system.

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Fig. 4. Thorium-Plutonium Phase Diagram. (A. A. Bochvar et al.)

Our early experiments supported the higher solubility of plutonium in α -thorium of about 48 a/o. Later X-ray diffraction data on quenched high-purity alloys offered contradictory evidence. A search for the β -thorium phase was made by means of high-temperature X-ray diffraction by Marples³⁰ and by Blumenthal. Supplementary dilatometric, electrical resistance, and DTA measurements were made by the authors. No evidence was detected for the stability of the β_{Th} phase at temperatures up to 800°C. A detailed description of these experiments will be given below. Thus, it is concluded that the US-UK diagram is valid and serves as the third boundary diagram of the ternary Th-U-Pu system.

For the purpose of constructing a schematic of the ternary system, the phase diagram by Poole was extrapolated to higher temperatures (see Fig. 3). We assumed that the α_{Th} phase was formed from β_{Th} and the liquid by a peritectic reaction at 1400°C. No experiments were made to confirm this extrapolation.

B. Investigation of the Ternary System

The review of the binary boundary systems suggested that the ternary solid solubility of uranium and plutonium in thorium would be limited to a narrow composition range. Therefore, the effect of small amounts of uranium on the solid solubility of plutonium in thorium was investigated. Two series of alloys were prepared with 2 and 4 w/o uranium as well as various amounts of plutonium. These alloys were heat treated at 700 and 900°C. A liquid phase was observed metallographically at rather low

plutonium concentrations. The composition range of the ternary solid solution was more restricted than had been anticipated; thus, most of the ternary alloys were expected to be two- or three-phase alloys in which an α_{Th} solid solution is in equilibrium with one or two of the phases of the U-Pu system. Because X-ray data raised doubts about this interpretation, the stability range of the β_{Th} phase had to be studied.

Several alloys were investigated by dilatometry and electrical resistance measurements, as well as by high-temperature X-ray diffraction. Since no evidence was found to support the presence of the β_{Th} phase at low temperature, the ternary Th-U-Pu alloys were concluded to consist of the α_{Th} phase in equilibrium with the phases of the U-Pu system. Therefore, alloys in the thorium corner of the system are affected by the solid-state reactions in the U-Pu system.

An analysis of these U-Pu reactions as they enter the ternary phase diagram was made by differential thermal analysis. The important four-phase reactions and their temperatures were determined. The experimental results are presented in a series of isothermal sections and in one isoplethal section.

C. Nomenclature

The following symbols are used to describe the constituents and the phases of the Th-U-Pu system:

(a) α_{Th} designates the fcc allotropic modification of thorium, and includes its binary and ternary solid solutions with uranium and plutonium.

(b) β_{Th} , γ_U , and ϵ_{Pu} are used for either the high-temperature bcc modification of the constituent metals or solid solutions between any two or three of these metals. For an alloy composition close to the thorium or plutonium corner of the system, the corresponding designation β_{Th} or ϵ_{Pu} is used, and γ_U is used for alloys in the uranium corner.

(c) ζ and η are the intermediate phases of the U-Pu system with or without thorium in solid solution.

(d) (U,Pu) designates all or any one of the phases of the U-Pu system with or without thorium in solid solution.

(e) C designates the intermediate Pu_2Th_{1-x} phase of the Th-Pu system with or without uranium in solid solution.

(f) L is the liquid phase where there is complete liquid miscibility.

(g) L_1 and L_2 are the two liquid phases of the miscibility gap of the Th-U system; they also designate equivalent phases in the ternary system.

Most nominal alloy compositions are given without the a/o or w/o sign in the sequence Th-U-Pu, since alloy compositions in either a/o or w/o do not significantly differ. If there is no possibility of misinterpretation, the chemical symbols are omitted for the sake of brevity. The two most important potential fuel alloys contain 80 w/o Th-10 w/o U-10 w/o Pu and 70 w/o Th-20 w/o U-10 w/o Pu, and are designated 80-10-10 and 70-20-10. All phase diagrams and pertinent figures are based on a/o.

III. EXPERIMENTAL METHODS

A. Preparation of Alloys

The glovebox facility and much of the apparatus used in this work have been described by Kelman *et al.*³¹ The very dry nitrogen atmosphere used in the glovebox proved satisfactory to protect the specimens during the various steps of preparation and examination.

The alloys were prepared from crystal-bar thorium obtained from Metal Hydrides, Inc., Beverly, Mass.; dingot uranium from Mallinckrodt Chemical Works, St. Louis, Mo.; high-purity electrolytic uranium and plutonium prepared at ANL; and electrolytic plutonium prepared at the Los Alamos Scientific Laboratory. Analyses of these metals are listed in Table I.

TABLE I. Analyses of Feed Materials
(All data in ppm by weight)

Material	Chemical Analysis							Spectrochemical Analysis ^b											Isotopic Analysis (%)
	H	C	N	O	Si ^a	U	W	Al	B	Fe	Ni	Si	Ti	Y	Zr				
Crystal Bar B750	9-14	26-49	<10	35				4	<1	7	5	18	2			4			
Thorium B794	2	7	5	45	10			7	1	30	<1		0.5	2	10				
Ames Thorium B837 ^c	<1	60	45	190															
Dingot Uranium B759	2	12	24	2				Al	B	Cr	Cu	Fe	Mg	Mn	Ni	Pb	Si		U-235--0.71
								10	<0.1	10	5	40	6	5	10	2	30		
High-purity Electrolytic Uranium								Al	B	Cr	Cu	Fe	Mg	Si					U-235--0.4
HPX 46	Low	13	36	38				5	<0.1	1	2	6	1	13					
HPX 55	Low	20	17	16				5	0.1	<1	1	7	<1	20					
HPX 81	Low	23	<10	40				5	<0.1	<1	<1	<2	1	15					
HPX 176	Low	18	<10	6				<5	0.1	<1	1	<2	6	20					
High-purity Electrolytic Plutonium								Al	Cr	Fe	Ga	K	Li	Mn	Na	Ni	Pb	W	Mo
M 39	6	58	27	12	56	33		10	4	5	40	100	6	0.5	30	10	6	2	
M 40	7	26	10	13	7	18		10	3	10	20	<2	0.1	0.2	<2	10	3	<2	
CM 12	6	20	8	20-116	4	55		10	2	10	<1	<2	0.01	0.2	<2	4	<2	<1	
CM 11	2	26	13	60	15	100		10	0.5	10	<0.5	<2	<0.01	0.1	<2	1	<2	1	
CM 14	4	23	30	30	15	37		<5	1	<5	<1	<2	0.1	0.2	<2	2	<2	<1	
CM 23	0.8	6	10	8	19	55		10	5	20	5	<2	0.02	1	<2	15	<2	<1	
CM 32	1.4	20	20	4	18	16		2	8	10	0.5	<2	0.02	0.5	<2	5	<1	<2	
CM 35	0.9	29	37	55	7	22		10	1	20	<0.1	<2	0.1	<1	<2	2	<1	<2	
M 50	3	38	27	24	100	54		25	<10	40	100	2	3	2	2	50	2	5	2
Los Alamos Electrolytic Plutonium B912	5	5	83	7	1	42	200	Al	Be	Cr	Fe	Mo	Ni	Sn	Ti				Pu-241--0.323
								2	0.04	0.4	20	5	5	2	0.5				

^aSilicon was determined either chemically or spectrochemically. Accuracy by chemical analysis better than ± 1 ppm of amount reported.

^bAll elements not listed are below limits of spectrochemical detection.

^cIncompletely analyzed. Low in most metallic impurities except Na: 40; Si: 60. Tantalum and tungsten estimated to be about 200 ppm each; Ni: 20.

^dPu-241 forms Am-241 by β decay; $\tau = 13.2$ yr. Immediately following electrolysis the Am-241 content is low. The initial breeding rate is about 20 ppm per month. Plutonium stored for some time thus may contain americium in excess of several hundred ppm.

The alloys (composition shown in Fig. 5) were melted on a water-cooled copper hearth³² in a tungsten arc furnace. A zirconium-gettered atmosphere of 2/3 argon and 1/3 helium was used. The resultant alloy buttons (2 cc in volume), weighing from 20 to 30 g, usually were remelted three times. Preliminary experiments had shown that for the high-thorium alloys melting three times was sufficient to produce uniformly alloyed ingots. For the high-plutonium alloys, multiple melts did not produce a

Fig. 5. Nominal Alloy Compositions
Used for the Th-U-Pu System

positions were used, the results, particularly the X-ray results, were consistent and could be duplicated. Accordingly, the error in using the nominal composition is regarded as small.

uniform composition. Since melting losses were extremely small (0.1% or less of the ingot weight, with an average of 0.04% for 26 ingots), segregation during melting and solidification is assumed to be responsible for the deviation from the nominal composition. Representative analytical data for 37 alloys are shown in Table II. Deviations occur when the nominal composition exceeds 40 a/o plutonium. At 50 and 60 a/o plutonium the deviations are substantial. Nevertheless, nominal compositions were used in the plot of experimental data, since the chemical analysis was not necessarily representative of a particular specimen. When the nominal com-

TABLE II. Analyses of Thorium Alloys

Alloy No.	Name	Composition (w/o)						Impurities (ppm)					Spectrochemical Analysis (ppm)									
		Nominal			By Chem Analysis			by Chem Analysis														
		Th	U	Pu	Th	U	Pu	H	C	N	O	Si	Al	Cr	Cu	Fe	Ga	Mn	Mo	Ni	Zr	
B-752	First Series	90	10	-	89.8	Bal																
753	of Commercial	80	20	-	80.8	Bal																
754	Purity	70	30	-	69.0	Bal																
755		60	40	-	60.7	Bal																
756		50	50	-	49.9	50.2																
772	Th-Pu Series	100	-	-				14	27	183	39	16	15	<0.5	5	15	<0.5	<0.1	<0.5	<1	5	
760	Made from Crystal	90	-	10	89.8		10.0	1.1	11	29	27	13	25	5	10	25	1	<0.1	<0.5	2	10	
767	Bar Thorium and	80	-	20	78.7		20.9	5.7	7	211	99	19	50	25	5	35	5	<0.1	<0.5	5	15	
768	High-purity	70	-	30	69.0		30.9	0.5	13	312	89	4	20	5	<10	20	<0.5	1	100	10	20	
769	Plutonium	60	-	40	60.1		40.0	10	20	14	137	8	20	5	<10	20	<0.5	1	<0.5	10	5	
770		50	-	50	47.1		52.7	11	23	113	78	42	10	10	<10	20	<0.5	1	<0.5	10	10	
773		40	-	60	52.3		47.7	17	37	31	138	16	10	10	<10	20	<0.5	1	<0.5	10	3000	
789	2% U Series Made	100																				
790	from Crystal Bar	98	2	-	47.9			0.5	6	11	55	11	<1	<0.5	15	<5	<0.2	<0.5	<0.5	<1	<1	
795	Th, Dingot U, and	88	2	10	88.4	2.0	10.1	0.9	7	33	79	13	<1	<0.5	<10	<5	<0.2	<0.5	<0.5	<1	<1	
796	High-purity	78	2	20	78.2		20.4	2.8	9	14	71	19	<1	<0.5	<10	<5	<0.2	<0.5	<0.5	<1	<1	
797	Plutonium	68	2	30	68.4		30.1	1	12	17	44	15	<1	<0.5	<10	<5	<0.2	<0.5	<0.5	<1	<1	
807		68	2	30																		
798		58	2	40	58.4		39.3	1.1	11	20	67	20	<1	<0.5	<10	<5	<0.2	<0.5	<0.5	<1	<1	
799		48	2	50	52.6		45.7	10	42	22	71	10	<1	<0.5	<10	<5	<0.2	<0.5	<0.5	<1	<1	
800		38	2	60	46.3		51.7	0.3	7	30	72	8	<1	<0.5	<10	<5	<0.2	<0.5	30	<1	<1	
791	4% U Series Made	96	4		96.3			5.6	40	27	49	9	<1	<0.5	<10	<5	<0.2	<0.5	<0.5	<1	<1	
801	from Crystal Bar	86	4	10	85.8		10.1	12	35	39	39	4	<1	<0.5	<10	<5	<0.2	<0.5	<0.5	<1	<1	
802	Th, Dingot U, and	76	4	20	75.8		19.9	24	30	31	52	9	<1	<0.5	<10	<5	<0.2	<0.5	<0.5	<1	5	
803	High-purity	66	4	30	66.5		29.6	6.8	41	35	31	17	<1	<0.5	<10	<5	<0.2	<0.5	<0.5	<1	5	
804	Plutonium	56	4	40	57.7		38.3	4.9	27	31	15	30	<1	<0.5	10	<5	<0.2	<0.5	<0.5	<1	10	
805		46	4	50	52.7		43.7	12	23	21	13	3	<1	<0.5	<10	<5	<0.2	<0.5	<0.5	<1	<1	
806		36	4	60	45.0		52.2	0.3	4	31	53	13	<1	<0.5	<10	<5	<0.2	<0.5	<0.5	<1	<1	
815	Supplementary	75	0	25				2.1	9	25	54		2	2	10	<5	<0.5	<0.5	<0.5	<1	<2	
816	Series Made from	65	0	35				0.1	4	18	52	1	5	1	<10	<5	<0.5	<0.5	<0.5	<1	1	
818	Crystal Bar Th,	45	0	55				0.4	6	26	40		<1	<0.5	<10	<5	<0.5	<0.5	<0.5	<1	<1	
817	Dingot U, and	40	0	60				0.1	4	17	117	17	5	<0.5	<10	<5	<0.5	<0.5	<0.5	<1	<1	
819	High-purity	83	2	15				0.9	5	31	123	5	<1	<0.5	10	<5	<0.2	<0.5	<0.5	<1	<1	
820	Plutonium	73	2	25				0.3	4	147	60	9	<1	1	<10	<5	<0.2	<0.5	<0.5	2	<1	
919	Made from Crystal	80	10	10	79.3	10.2	10.2	1	9	25	116											
920	Bar Th, High-purity U, and High-purity Plutonium	70	20	10	66.4	22.6	10.8	1	45	20	77											
781	Commercial Purity	60	20	20																		

Early melts showed a high hydrogen content. After leakage of air into the furnace system had been reduced and sources of water vapor had been eliminated, ingots of acceptably low hydrogen content were produced.

Metallic impurities were not a source of trouble. The analytical samples, usually 0.5-g cubes, were cleaned immediately before insertion into the analytical train. Gas manometric methods were used to analyze for H, C, N, O, and Si. The spectrochemical determinations were made by means of the copper spark method.

B. Heat Treatment

Ingots with 80 a/o or more thorium were homogenized for 3 hr at 1000°C prior to heat treatment at 900 for two days or at 700°C for three weeks. Alloys with less than 80 a/o thorium were heat treated at 900°C for two days or at 700°C for three weeks. These heat treatments were made with the bulk material, usually half a button wrapped in 0.2-mm tantalum foil and sealed in Vycor tubes at a vacuum of 10^{-5} Torr. In some cases zirconium turnings were sealed in the tube to getter the residual atmosphere. The sealed tubes were suspended in a vertical-tube resistance furnace for heat treatment. For water quenching, the suspension wire was cut and the tube was mechanically broken before immersion.

C. Metallography

Initially, conventional methods were used for preparation of metallographic specimens. Later, vibratory grinding and polishing as developed by Matras³³ and adapted for plutonium work by Blumenthal and Busch³⁴ proved to be highly effective in producing deformation-free surfaces and in retaining inclusions. Vibratory-ground and polished specimens required electrolytic polishing for only a few seconds to develop the structure. The electrolyte (32 parts of orthophosphoric acid, 9 parts of water, and 59 parts of ethylene glycol monoethylether) was used at a current density of 1 to 2 Amp/cm².

D. Room-temperature X-ray Diffraction

The X-ray examinations were carried out by the Debye-Scherrer method. A Philips camera (Straumanis type of film loading) of 11.46-cm diameter was used with nickel-filtered Cu-K α radiation. The lattice parameters were calculated by using the wavelengths Cu-K α_1 = 1.54051 Å and Cu-K α_2 = 1.54433 Å, and applying the Nelson-Riley function. The least-squares extrapolation was carried out by means of an IBM 704 computer program of Mueller and Heaton.³⁵ The estimated accuracy of each lattice parameter is ± 0.001 Å.

The specimens, needles about 0.4 mm in diameter and 8 mm in length, were similar to those used by Berndt²³ in his investigation of

alpha U-Pu alloys. The specimens were cut from heat-treated buttons, ground to size, re-encapsulated, stress relieved for 15 min at the temperature of the prior heat treatment, quenched, and electropolished.

E. High-temperature X-ray Diffraction

A special Debye-Scherrer camera was built for high-temperature X-ray examination. This water-cooled vacuum camera contains a spherical furnace that permits the specimen needles to be heated to 900°C. The camera is mounted on top of a glovebox so that the interior of the camera is accessible from inside the glovebox. A film cassette is fitted over the camera body, and beryllium windows permit entry and exit of the X radiation and the diffracted rays. The specimen can be rotated and vertically translated to minimize grain-coarsening effects at high temperature.

Nickel-filtered Cu-K α radiation from a GE XRD 5 unit was used. The vacuum system consisted of an Ultek Vapor Ion pump of 50-liters/sec capacity (Model 20-044), an Ultek Foreline trap filled with molecular sieve (Model 50-005), and a mechanical forepump of 2-cfm capacity (Dresser Type DC2). The temperature was measured by means of a Pt/Pt-10% Rh thermocouple calibrated in situ against the lattice parameter of pure platinum. A calibration curve is shown in Fig. 6, two schematic drawings of the camera are given in Figs. 7 and 8, and several photographs of the apparatus are shown in Figs. 9 to 12.

The system worked satisfactorily at temperatures up to 700°C. At 800°C the rate of oxidation of the specimen was fairly high. Oxide layers that formed on the surface of the specimen gave diffraction patterns superimposed on the weakened basic pattern. Although all of the patterns could not be indexed without some ambiguity, the results obtained were sufficient to show the absence of the thorium beta phase in the alloys investigated.

106-8868

Fig. 6. Temperature Calibration of High-temperature X-ray Camera

F. Electrical Resistance

The instrumentation available for the measurement of electrical resistance at elevated temperatures is shown in Fig. 13. The specimen was held in a heat sink in a vacuum resistance furnace positioned horizontally. The vacuum system included an ion pump of 50-liters/sec capacity (Ultek Model 20-044) that produced a vacuum of 1.5×10^{-7} Torr at 600°C. In parallel with the ion pump, a 50-mm-diam oil-diffusion pump and forepump served to evacuate the system. Appropriate valves separated the two systems.

Fig. 7
High-temperature Debye-Scherrer
Camera for Plutonium

106-9139

Fig. 8
Cassette of Debye-Scherrer
Camera for Plutonium

106-8869

106-9157

41045

Fig. 9. High-temperature X-ray Diffraction
Camera on Glovebox, before Closing

106-9158

41051

Fig. 10. Montage of Needle Specimen

106-9159

41049

Fig. 11. Furnace and Finger for Specimen Alignment

106-9160

41047

Fig. 12. Camera without Cassette, Showing Beryllium Windows

106-9141

Fig. 13. Apparatus for Electrical Resistance Measurements at Temperatures up to 900°C

The specimen was a rod of 5-cm length and 0.3-cm diameter. Four platinum leads (of 0.5-mm diameter) were welded to the specimen; two leads conducted current, and two were used to measure the potential drop along the specimen. The distance between the potential leads was 4 cm. Specimen temperature was measured by a Pt/Pt-10% Rh thermocouple welded to the center of the specimen. The cold junction was placed in an aluminum block maintained at a temperature of 30.0°C by a thermistor-controlled heater.

Initially, the heat sink and cover were made of nickel. During high-temperature operation, the nickel cover became bonded to the base and had to be replaced. A molybdenum heat sink and cover proved satisfactory at temperatures up to 1000°C.

The heat sink was fastened to the stainless steel support tube by iodine-coated stainless steel bolts to prevent bonding. The support tube positioned the heat sink in the center of the furnace and carried the various insulated lead wires through the water-cooled furnace heat by means of a high-vacuum feed-through fitting. Copper wire (16 gage) was used to complete the potential, current, and thermocouple circuits to instruments outside the glovebox.

The asymmetry of the heat sink and support produced a temperature gradient along the specimen that induced a thermal emf. Since the instrument was used to determine discontinuities and changes in slope of the temperature-resistance curve, this error did not significantly affect the results.

A block diagram of the furnace-control system is shown in Fig. 14. A Chromel/Alumel thermocouple positioned near the furnace windings was connected to a set-point controller. The error signal, proportional to the difference between the temperature sensed by the thermocouple and the desired furnace temperature as set on the set-point controller, was applied to the null-balance controller, which in turn controlled the saturable-core reactor that supplied power to the furnace. The set-point position could be varied by means of a small motor and gear box; the furnace temperature could be increased or decreased at rates ranging from 0.1 to 5°C/min. A high-limit control protected the furnace from overheating.

106-9150 Rev. 1

Fig. 14. Furnace Control for Electrical Resistance Apparatus

The early measurements were made under thermal-equilibrium conditions at one-half-hour intervals with a Kelvin bridge. At higher temperatures changes in both the lead resistance and the temperature gradient along the specimen proved to be troublesome, and the Kelvin bridge measurements were replaced by the IR method. The block diagram of the measuring circuit is shown in Fig. 15.

106-9146

Fig. 15. Circuit Diagram for Electrical Resistance Measurements by IR Method

A constant current of 1 ± 0.0002 Amp was supplied by a current-voltage calibrator.* The potential drop along the specimen was measured and recorded as a function of time.** The same instrument recorded the specimen temperature. The stability of the current input was checked by measuring the potential drop across a precision standard resistance (1 ohm) and recording it as a function of time. The curve of resistivity vs temperature was derived from data simultaneously recorded on the X-X instrument.

The apparatus was originally designed for operation up to 1000°C . All of the parts met this specification except for the welds that attached the lead and thermocouple wires to the specimens. At 900°C , the welds slowly deteriorated by solid-state diffusion and introduced an uncertainty into some of the results. Since repair and replacement of the thermocouples were time-consuming, and small resistance changes could not be measured satisfactorily, the method was used with only one alloy.

G. Dilatometry

The dilatometer used to determine transformation temperatures was a quartz push-rod instrument. The cylindrical specimen (of 6.3-mm diameter) was located in the center of a vertical resistance furnace; specimen expansion and contraction were transmitted by a quartz rod to a linear differential transformer. The temperature was measured by a Pt/Pt-10% Rh thermocouple welded to the side of the specimen. The outputs of the thermocouple and the differential transformer were fed to an X-Y recorder. The data taken from the plot were corrected for the expansion of the quartz rod by the method of Lloyd.³⁶ A detailed description of the dilatometer, its control, and calibration is given by Yaggee and Styles.³⁷ In the present research this instrument was used for temperatures to 975°C .

The experimental difficulties encountered above 800°C were reaction of the thorium alloys with the quartz support, loss of contact between the thermocouple and the specimen, and creep of the specimen under its own weight. The reaction of the specimen with the support and guide tube was eliminated by the insertion of a tantalum foil cap over the specimen cup. Creep was controlled by holding the specimen at maximum temperature for a sufficient length of time, usually overnight. Dilatometric measurements could then be duplicated if the original temperature maximum was not exceeded. This behavior is characteristic of the first stage of creep and, once recognized, could be separated from the thermal expansion behavior of the specimens.

*Manufacturer's specification, Fluke Manufacturing Corp., Model 382A.

**Leeds and Northrup X-X recorder (Cat. No. 69955).

H. Differential Thermal Analysis

The apparatus for differential thermal analysis (DTA) was designed to hold a cylindrical specimen, 9 mm in diameter and 21.5 mm in length, with a blind center hole (4 mm in diameter and 11.5 mm in depth) for the thermocouple. The specimen and a high-purity thorium standard of the same dimensions were held in small, yttria-stabilized zirconia or recrystallized-alumina crucibles surrounded by a tantalum heat sink (see Fig. 16). The temperatures of the specimen and the standard were measured by two Chromel/Alumel thermocouples protected by thin-wall (nominally 0.9 mm) thoria or alumina tubes. Details of the measuring circuit are shown in Fig. 17. The reference junction was located in an aluminum block controlled at a temperature of $30 \pm 0.1^\circ\text{C}$.

106-9155

Fig. 16. DTA Apparatus

106-9154 Rev. 1

Fig. 17. Circuit for Differential Thermal Analysis

The output (T) of either of the two thermocouples was recorded on the X axis of an X-Y recorder; the output (ΔT) of the differential couple was recorded after amplification on the Y axis. Usually the signal from the specimen thermocouple was fed to the X axis. The output of the standard couple was used to plot a time-temperature curve for the determination of the rate of heating or cooling.

Heat sink and specimens were heated by a bifilar-wound tantalum furnace insulated by a series of heat shields (see Fig. 18). The two inner shields were made of tantalum sheet, and the outer ones of stainless steel. Power to the furnace was supplied by a silicon-controlled rectifier with a continuously adjusting proportional control unit.* The temperature-sensing device was a Pt/Pt-10% Rh thermocouple located near the furnace winding. A strip-chart controller-recorder was used to regulate the temperature. The controller set-point was moved periodically by three timers that permitted a program of heating, holding, and cooling at rates that could be varied between 0.2 to $5^\circ\text{C}/\text{min}$. This method made the determination of the equilibrium-transformation and reaction temperatures possible by graphic

*Leeds and Northrup Series 60.

extrapolation to slow rates. With thorium as a standard, the base line of ΔT vs T was horizontal for all thorium alloys.

106-9142 Rev. 1

Fig. 18. Furnace for DTA Apparatus

Two phenomena caused the measured transformation temperatures to deviate from the equilibrium-transformation temperatures: one was superheating and supercooling (recalcescence after supercooling was observed for both solid-state transformations of high-purity uranium); the second was inherent in the experiment.

If the specimen were small enough so that the transformation or reaction occurred simultaneously throughout the specimen volume, and if no heat-transfer lag occurred between the specimen and thermocouple, the

DTA curve would have a sharp peak (see Fig. 19a). Most alloy DTA curves, however, resembled skewed distribution curves (see Figs. 19b and 19c). At any time during heating, even when no reaction takes place, a temperature

106-9140

Fig. 19. Schematic DTA Heating Curves

gradient exists between heat sink, crucible, specimen, protection tube, and thermocouple. On heating, the thermocouple measures a lower temperature than exists in the specimen. Since the same phenomenon occurs in the standard, the temperatures of specimen and standard will rise at the same rate, and no temperature difference will be observed between the two thermocouples if the thermal conductivity and specific heat of both the specimen and stan-

dard are the same. When the outer surface of the specimen reaches the temperature of an endothermic reaction, the heat consumed by the reaction will lower the rate of temperature rise of the specimen thermocouple, and a temperature difference will occur between the two couples. As more heat is supplied by furnace and heat sink, the reaction will advance into the specimen, whereby heat is absorbed; the ΔT between the two couples will increase. The largest rate of increase of ΔT will occur when the volume transformation is the largest, which is shortly after the beginning of the reaction. The rate will decrease as the reaction front advances toward the center of the specimen and the transforming volume is getting smaller.

The heat absorbed by the reaction will continue to slow the temperature rise of the specimen thermocouple until the reaction front has reached the center of the specimen and the thermocouple. At that time the difference between the reaction temperature and the temperature indicated by the specimen thermocouple will be at a minimum, while the ΔT between the specimen and the standard thermocouples will be at a maximum. Thereafter, with the reaction completed, the temperature difference between the two couples will decrease and eventually become zero. The specimen temperature at the maximum, the peak temperature, is closest to the temperature of the reaction or transformation. At this point the thermocouple is still shielded by the protection tube and will indicate a somewhat lower temperature than the true reaction temperature. This residual temperature difference, however, should become smaller as the rate of heating is decreased and should become negligible at very slow heating rates. The effect of the heating and cooling rates on the measured reaction temperature was so large that the effect of the thermocouple protection tube appeared to be negligible.

The plots of transformation temperature vs rate of heating or cooling given in this report show that the heating-rate curve approaches equilibrium

conditions more quickly than the cooling-rate curve. The temperature data obtained at the slowest heating rate are closest to the equilibrium-transformation or reaction temperature.

Also, as would be expected, equilibrium is approached more rapidly at higher than at lower temperatures, and, therefore, the two branches of the transformation vs temperature curves for heating and cooling approach each other more rapidly at higher temperatures. These observations are generally applicable to all DTA measurements when the reaction rates are reasonably fast and when macrospecimens with a volume of 1 to 2 cm³ are being analyzed.

Duplication of the reaction temperature indicated by DTA measurements was usually within 1°C. The accuracy of the measurements, of course, is dependent on the material and metrological factors involved. Temperature differences between reactions in different specimens can be determined to about $\pm 1^\circ\text{C}$ if the same thermocouple, crucible, and instrumentation are used for these specimens.

The DTA method was first tried on pure uranium, and the results were in good agreement with data previously reported by Blumenthal.²¹ A typical DTA curve and a plot of transformation temperatures vs rate of heating or cooling are shown in Figs. 20 and 21.

106-9138

Fig. 20. DTA Curve for High-purity Uranium

106-9117

Fig. 21. Transformation Temperatures of High-purity Uranium as a Function of Heating and Cooling Rate--Peak Temperatures by DTA

IV. EXPERIMENTAL RESULTS

A. Metallography

Metallography of the binary thorium-plutonium alloys quenched from 700°C after three weeks at temperature, and from 900°C after two days at temperature, are shown in Figs. 22 and 23. The unalloyed thorium had impurities at the grain boundaries. A fine precipitate was observed in alloys with 20% or more plutonium when quenched from 700°C and in alloys with 10% or more plutonium when quenched from 900°C. A small amount of liquid phase appeared at 50% plutonium in alloys quenched from 700°C and at 40% plutonium in alloys quenched from 900°C, in agreement with the US-UK phase diagram (Fig. 3).

The two alloy series with 2 and 4 w/o uranium (see Figs. 24 to 27) had more precipitate than the binary alloys. The liquid phase was definitely present in alloys with 20% or more plutonium at 700°C and in alloys with 10% or more plutonium at 900°C. These two alloy series show that even small amounts of uranium greatly restrict the solid solubility of plutonium in thorium.

Two alloys with Th-15U-30Pu and Th-20U-35Pu are shown in Fig. 28. At 700°C they were still below the solidus temperatures, and at 900°C they were well above the solidus. The composition of the two phases of the Th-20U-35Pu alloy was determined by electron probe microanalysis. The light phase contained about 50% uranium and 50% plutonium, with very little thorium; the dark phase was thorium-rich, with 15 to 18% plutonium and only a few tenths of one percent of uranium. The results of the microanalysis are shown in Table III. Although the accuracy of the data is probably less than 4 or 5% of the amount present, the data confirm the low solubility of uranium in α -thorium and show that the phases in equilibrium with α -thorium are those of the uranium-plutonium system.

TABLE III. Electron Probe Microanalysis of
Alloy with Th-20 w/o U-35 w/o Pu

Annealing Temperature (°C)	Phase	Analysis (w/o)		
		Th	U	Pu
700	Light	0.4	51.2	48.4
	Dark	81.2	0.6	18.2
900	Light	3.2	42.8	54.0
	Light	2.1	45.7	52.2
	Dark	84.0	0.4	15.6

35987

Th

100X

35988

10 w/o Pu

200X

35989

20 w/o Pu

200X

35990

30 w/o Pu

200X

36867

40 w/o Pu

200X

36389

50 w/o Pu

200X

36391

60 w/o Pu

200X

NOMINAL COMPOSITIONS

106-9161

Fig. 22. Binary Thorium-Plutonium Alloys Annealed at 700°C,
Water Quenched. (Reduced 35% in reproduction.)

36043 Th 200X

36044 10 w/o Pu 200X

36045 20 w/o Pu 200X

36046 30 w/o Pu 200X

36405 40 w/o Pu 200X

36406 50 w/o Pu 200X

36407 60 w/o Pu 200X

NOMINAL COMPOSITIONS

106-9162

Fig. 23. Binary Thorium-Plutonium Alloys Annealed at 900°C,
Water Quenched. (Reduced 35% in reproduction.)

36590 Th-2 w/o U 200X

36591 10 w/o Pu 200X

36593 20 w/o Pu 200X

36595 30 w/o Pu 200X

36596 40 w/o Pu 200X

36598 50 w/o Pu 200X

NOMINAL COMPOSITIONS

106-9163

Fig. 24. Th-2 w/o U-Pu Alloys Annealed at 700°C, Water Quenched.
(Reduced 35% in reproduction.)

36611 Th-2 w/o U 200X

35858 10 w/o Pu 200X

35859 20 w/o Pu 200X

35860 30 w/o Pu 200X

35867 40 w/o Pu 200X

36906 50 w/o Pu 200X

36907 60 w/o Pu 200X

NOMINAL COMPOSITIONS

106-9164

Fig. 25. Th-2 w/o U-Pu Alloys Annealed at 900°C, Water Quenched.
(Reduced 35% in reproduction.)

36599 Th-4 w/o U 200X

36600 10 w/o Pu 200X

36601 20 w/o Pu 200X

36602 30 w/o Pu 200X

36603 40 w/o Pu 200X

36604 50 w/o Pu 200X

NOMINAL COMPOSITIONS

106-9165

Fig. 26. Th-4 w/o U-Pu Alloys Annealed at 700°C, Water Quenched.
(Reduced 35% in reproduction.)

36605

Th-4 w/o U

200X

36606

10 w/o Pu

200X

36607

20 w/o Pu

200X

36608

30 w/o Pu

200X

36610

40 w/o Pu

200X

NOMINAL COMPOSITIONS

106-9166

Fig. 27. Th-4 w/o U-Pu Alloys Annealed at 900°C, Water Quenched.
(Reduced 17% in reproduction.)

NOMINAL COMPOSITIONS

106-9167

Fig. 28. Alloys with Th-15 w/o U-30 w/o Pu and Th-20 w/o U-35 w/o Pu Annealed at 700 and 900°C, Water Quenched. (Reduced 35% in reproduction.)

B. Room-temperature X-ray Diffraction

The lattice parameters of the binary thorium-plutonium alloys quenched from 700 and 900°C are plotted in Fig. 29 as a function of composition.

106-9151

Fig. 29. α_{Th} Lattice Parameter versus Composition of Binary Th-Pu Alloys

also shows the lattice parameter-concentration curve of Poole, Williamson, and Marples.²⁶ This curve originates at 5.085 Å, the lattice parameter of the highest-purity thorium, and has a steeper slope than the 700°C curve of our study. Since Poole's curve was obtained from powder specimens that were not quenched, the variation is consistent with the present data. Using the slope of the 700°C curve as being least influenced by the impurity effect, the data show that the solubility of plutonium in α -thorium is 47.5 a/o at 700°C and 38.2 a/o at 900°C, in reasonable agreement with Poole's values, namely, 45.6 a/o and 36.2 a/o.

The lattice parameters of two series of ternary alloys with 2 and 4 a/o uranium quenched from 700 and 900°C are shown in Figs. 30 and 31. The curve of lattice parameter vs concentration is shown in Fig. 32 for a section A-A at constant uranium concentration in a simplified isothermal section. With increasing plutonium content, the lattice parameter decreases linearly from a to b until the boundary of the $\alpha_{Th} + \gamma_U + L$ three-phase region is reached. The lattice parameter then remains constant for concentrations from b to c in the three-phase region. After entering the next two-phase field at c, the lattice parameter continues to decrease. Now, however, the relationship between lattice parameter and concentration is no longer linear. The distance between the tie lines decreases for constant

Investigations by Evans and Raynor³⁸ and later by Blumenthal and Sanecki³⁹ have shown that the lattice parameter of thorium varies greatly with impurity content and heat treatment. The smallest lattice parameters apply to the purest material slowly cooled from its annealing temperature such that a minimum amount of the impurity content and particularly of the oxygen content is in solid solution. The two lines shown in Fig. 29 that represent the present results do not have the same slope. This difference in slope is probably due to the simultaneous effect of impurity content and quenching temperature. Figure 29

intervals of plutonium concentration along A-A, and successively smaller concentration changes will occur along B-B from tie line-to-tie line intercept. The lattice parameter concentration curve will follow the course c-d.

106-9120

Fig. 30. Lattice Parameter of α -Thorium Phase of Th-U-Pu Alloys at 700°C

106-9116

Fig. 31. Lattice Parameter of α -Thorium Phase of Th-U-Pu Alloys at 900°C

Fig. 32

Scheme of Lattice-parameter Changes in Simplified Ternary System

106-9113

If the section A-A cuts the three-phase region near the thorium-rich corner (point P), the horizontal portion of the curve (b-c) will be small and difficult to detect. The composition ranges in Figs. 30 and 31, where there should be short horizontal sections, are indicated by broken lines. At 700°C the $\alpha_{Th} + \beta_U + \eta$, the $\alpha_{Th} + \eta$, and the $\alpha_{Th} + \eta + \gamma_U$ phase fields are so close together that they could not be separated.

Early in this study, we felt that a reasonable interpretation of the lattice-parameter measurements could be made by assuming that the β_{Th} phase extends to low temperatures, as shown by Bochvar.²⁹ This interpretation could not be confirmed by subsequent work. The curves of lattice parameter vs concentration (drawn in Figs. 30 and 31) are in agreement with the metallographic observation that the α_{Th} phase is in equilibrium with appropriate phases of the uranium-plutonium system.

The alloys with a nominal composition of Th-20U-35Pu and Th-15U-30Pu have α_{Th} lattice parameters of 5.023 and 5.026 Å, respectively, at 700°C and of 5.0285 and 5.0284 Å, respectively, at 900°C. These lattice parameters are equivalent to plutonium contents of about 25% at both 700 and 900°C, which is somewhat different from the microanalysis of 15 to 18% plutonium in the α_{Th} phase of the alloy with 45% thorium. None of the X-ray patterns showed second-phase lines sufficiently distinct to be identified. Only the Th-20U-35Pu alloy quenched from 900°C showed a second fcc pattern (observed in the low-angle region) that was sharp enough to be measured. The lattice parameter indicated by the pattern was 5.157 Å, which possibly corresponds to a lower oxide, $(Th,Pu)O$, with a lattice parameter intermediate between those of ThO (5.20 Å) and PuO (4.958 Å). The Debye-Scherrer patterns of the two alloys contained no indication of the ζ phase of the U-Pu system.

C. High-temperature X-ray Diffraction

One alloy, Th-2U-40Pu, was investigated by high-temperature X-ray diffraction at 800°C. The lattice parameter of the α_{Th} phase was 5.043 ± 0.001 Å as compared with 4.997 ± 0.001 Å at room temperature. An alloy of the same nominal composition, but quenched from 700 or 900°C, had room-temperature lattice parameters of 5.0025 ± 0.0001 Å and 5.0038 ± 0.0001 Å, respectively. In addition to the lines of the α_{Th} phase, the pattern showed the lines of the fcc ThO_2 ($a_0 = 5.635 \pm 0.001$ Å) and PuO_2 ($a_0 = 5.313 \pm 0.001$ Å) phases that result from surface contamination during the exposure. The former, as expected, is higher and the latter unexpectedly lower than the corresponding room-temperature lattice constants of the pure bulk materials (5.591 and 5.3960 Å). No indication was found for the presence of the bcc β_{Th} phase.

D. Electrical Resistance Measurements

Electrical resistance measurements of a Th-30Pu alloy showed no discontinuities in the range from 490 to 965°C when heated or cooled at a rate of 2.4°C/min. The two curves are shown in Fig. 33. The curves give no indication of the presence of the β_{Th} phase between 650 and 700°C nor of a solidus temperature at 770°C as required by the diagram proposed by Bochvar.²⁹

106-9118

Fig. 33. Electrical Resistance of
Th-30 w/o Pu Alloy

two or three cycles before consistent arrests were obtained; other specimens, particularly when the observed arrests were weak, required up to ten cycles to obtain reproducible results. At temperatures above 700°C some of the specimens crept under their own weight. (The load on the specimen by push rod and sensing device was about 8 g.) With each successive cycle the decrease in specimen length became less, provided the maximum temperature of the preceding cycle was not exceeded. When the temperature was subsequently raised, creep occurred again, but came to a halt after the specimen was held at the new temperature for a few hours. This behavior is characteristic of the first stage of creep. Once this behavior was recognized, reproducible results could be obtained on the second or third cycle by holding the specimen at the highest test temperature for a number of hours.

Figure 34 shows the dilatometric curves (the cooling curve is displaced downward) of an alloy with a nominal composition of Th-30 w/o Pu. No discontinuities were observed up to 947°C, which is below the solidus temperature of 990°C, obtained by extrapolation of the US-UK phase diagram.

106-9137

Fig. 34

Dilatometric Curve of
Th-30 w/o Pu Alloy

E. Dilatometry

Most of the dilatometric specimens exhibited an erratic behavior during the initial heating and cooling cycles in spite of prior homogenization heat treatment. Aside from instrumentation difficulties,* the most important causes of trouble appeared to be local inhomogeneities within the specimens and creep. The irregularities tended to disappear with each successive cycle. Some specimens required only

*The difficulties encountered were sensitivity of the slide wire of one of the X-Y recorders to contamination, noise from external sources (particularly at high temperatures), sticking of the push rod, and seating problems.

Figure 35 shows four cycles that are typical of the alloy with a nominal composition of Th-10U-10Pu. Cycle I shows the heating and cooling loop resulting from creep at the maximum temperature of 840°C. The loop is smaller during Cycle IV. In Cycle VIII the temperature was raised to 975°C and held for about 2 hr. No additional creep was observed in Cycles IX and X. Beginning with Cycle VIII, reproducible data for the two observed phase transformations were obtained. By observing the precautions described above, good data were obtained in Cycle II for an alloy with nominally Th-20U-10Pu as shown in Fig. 36.

The dilatometric curves in Fig. 37 were obtained from two ternary alloys that were most likely to show the thorium-beta phase transformation, if it should occur at a low temperature. These alloys were Th-1U-41Pu and Th-2U-40Pu. The latter alloy was subsequently examined by high-temperature X-ray diffraction. Both alloys show a contraction at

106-9125

Fig. 35. Effect of Dilatometric Cycling on Thermal-expansion Curve

106-9126

Fig. 36. Dilatometric Curve of Th-20 w/o U-10 w/o Pu Alloy for Cycle II

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Fig. 37. Dilatometry of Four-phase Reaction
 $\alpha_{Th} + \gamma_U + L \rightleftharpoons Th_2Pu$

about 630°C, their solidus temperature. Contraction during melting is characteristic of plutonium, since the density of the liquid phase is higher than that of the ϵ_{Pu} phase, according to Serpan and Wittenberg.⁴⁰ In the present case the formation of the liquid phase is part of the peritectic four-phase reaction $C \rightleftharpoons \alpha_{Th} + \epsilon_{Pu} + L$, where C is the compound Pu_2Th_{1-x} , as shown in Fig. 44.

F. Differential Thermal Analysis

The DTA method was used for two purposes: (a) to establish the important four-phase reactions in the uranium corner of the ternary system, and (b) to determine the transformation temperatures and, if possible, the solidus temperatures of the two technologically interesting alloys Th-10U-10Pu and Th-20U-10Pu.

(a) The preceding experiments indicated that the Th-U-Pu ternary system is one in which the phases of the U-Pu binary system are in equilibrium with α -thorium. Thus, reactions that occur in the uranium corner of the system should occur also in alloys in the thorium corner. Since the volume of the (U,Pu) phases in the thorium-rich alloys is small, it was experimentally easier to seek and determine the four-phase reaction temperatures in uranium-rich alloys. Three alloys: U-25Pu, Th-67.5U-22.5Pu, and Th-60U-20Pu, were investigated. DTA data at rates ranging from 0.2 to 4°C/min were obtained for the binary alloy and for the Th-60U-20Pu alloy. Only one DTA curve, at 3°C/min, was obtained with the intermediate alloy Th-62.5U-22.5Pu. A typical DTA curve is shown in Fig. 38. The

106-9136

Fig. 38. DTA Curve of 20 a/o Th-60 a/o U-20 a/o Pu Alloy

The absolute value of the reaction temperature is not the determining factor, but it is the relative position of the binary and ternary reaction temperatures which establishes that the reaction is a Class III peritectoid reaction.

The reaction temperature of 594°C for the formation of the ζ -phase in the binary system is in agreement with the published temperature of 590°C. In the ternary system the ζ -phase is formed at 610°C, also by a peritectoid reaction.

transformation temperatures are shown in Figs. 39 and 40 as a function of heating or cooling rate for the U-25Pu and Th-60U-20Pu alloys.

Three isothermal solid-state transformations occur in the ternary system. The first transformation occurs at 714°C, distinctly 2 to 4°C higher than the temperature of 712 or 710°C of the binary peritectoid reaction $\beta_U + \gamma_U \rightleftharpoons \eta$. These data place the temperature of the binary peritectoid reaction 5 to 7°C higher than the temperature of 705°C reported in the U-Pu phase diagram by Schonfeld.²⁷

106-9149

Fig. 39. Solid-state Reactions in 75 a/o U-25 a/o Pu Alloy--Peak Temperatures by DTA

106-9153

Fig. 40. Solid-state Reactions in 20 a/o Th-60 a/o U-20 a/o Pu Alloy--Peak Temperatures by DTA

No evidence of the $\beta_U \rightleftharpoons \alpha_U + \zeta$ reaction was found in the U-25Pu alloy at 560°C (see Fig. 39), which suggests that the two-phase $\alpha_U + \zeta$ region of the U-Pu system does not include the alloy with 25 a/o Pu. The $\alpha_U + \zeta$ two-phase field apparently is narrower than was shown by Schonfeld.²⁷ Earlier evidence for the restricted $\alpha_U + \zeta$ two-phase region has been obtained by Wittenberg and Etter.²⁵ The diagram shown in Fig. 2 takes this into consideration. The Th-60U-20Pu ternary alloy undergoes a third transformation at about 595°C (see Fig. 40), which belongs to the Class II reaction $\alpha_{Th} + \beta_U \rightleftharpoons \alpha_U + \zeta$.

(b) The DTA curves of the 70-20-10 alloy show four arrests at 738, 690 (weak), 681, and 587°C (see Fig. 41). The equivalent temperatures obtained by dilatometry: 739, 679, and 587°C, were in good agreement (see Fig. 36). In the 80-10-10 alloy a small amount of second phase is present, and only two arrests were observed at 730 and 680°C (see Fig. 42). Comparative dilatometric data for the 80-10-10 alloy confirmed the highest temperature arrest of 738°C, but the other transformations did not appear in all dilatometric cycles (see Fig. 35). The reaction at 680°C is seen in Cycle IV. For the reaction observed dilatometrically at 600°C there was no indication of a differential thermal output in the DTA curves. These arrests occur when the alloy passes from one phase field into another except the arrest at 587°C, which is the temperature

106-9152

Fig. 41. Solid-state Reactions in Th-20 a/o U-10 a/o Pu Alloy--Peak Temperatures by DTA

at 587°C, which is the temperature

106-9148

Fig. 42. Solid-state Reactions in Th-10 a/o U-10 a/o Pu Alloy--Peak Temperatures by DTA

$\alpha_{Th} + \gamma_U$ field into the $\alpha_{Th} + \gamma_U + L$ field, and since the amount of liquid formed initially is small, the solidus temperatures should appear as a slight change in the slope of the base line. Specimens examined metallographically after being heated to 900°C showed no indication of the presence of a liquid phase. The most reasonable results were obtained when the first DTA peak on heating above 800°C was chosen as the solidus temperature. The next DTA peak then corresponds to the temperature at which the alloys pass from the $\alpha_{Th} + \gamma_U + L$ field into the $\alpha_{Th} + L$ field. This choice resulted in solidus data that fitted into the ternary reaction scheme. The following solidus and transition temperatures were obtained at a rate of 2°C/min:

Alloy (w/o)	Solidus Temperature $\alpha_{Th} + \gamma_U \rightleftharpoons \alpha_{Th} + \gamma_U + L$ (°C)	Transition Temperature $\alpha_{Th} + \gamma_U + L \rightleftharpoons \alpha_{Th} + L$ (°C)
Th-10U-10Pu	918	990
Th-20U-10Pu	955	1000

of the Class II four-phase reaction that was found in the Th-60U-20Pu alloy at 595°C. During this reaction β_U is transformed to α_U and ζ by the reaction $\alpha_{Th} + \beta_U \rightleftharpoons \alpha_U + \zeta$. The temperature difference of 7°C is not significant in view of the wide separation of the alloy compositions.

An attempt was made to determine the solidus temperatures of the 80-10-10 and 70-20-10 alloys by DTA. Since solidus temperatures of these alloys are those temperatures at which, upon heating, the alloys pass from the

V. DISCUSSION OF RESULTS

A. Liquidus Surface

The Th-U-Pu system contains no ternary intermediate phases. It is believed that the liquid miscibility gap is restricted to the binary Th-U side of the system, as shown in Fig. 43. Since the alloys in this region are not expected to be potential reactor fuels, the boundaries of the miscibility gap were not determined. If in the Th-Pu binary system the α_{Th} phase is formed by the peritectic reaction $\beta_{Th} + L \rightarrow \alpha_{Th}$, the reaction might reasonably join the $\beta_{Th} \rightarrow \alpha_{Th} + L$ reaction of the Th-U binary system. The liquidus isotherms in the thorium corner were determined metallographically during the preparation of experimental alloys and probably are accurate to $\pm 20^\circ\text{C}$. A eutectic trough connects the Th-U side with the Th-Pu side. The peritectic reaction $\alpha_{Th} + L \rightarrow C$ of the Th-Pu binary system at 615°C joins the eutectic trough in a ternary peritectic reaction at 630°C , as determined by dilatometry. The scheme of this four-phase reaction is shown in Fig. 44. All reactions that involve the liquid are shown in Fig. 45.

B. Solid-state Reactions

The solid-state reactions in the intermediate temperature range are shown in Fig. 46. Both the η and the ζ phases are formed by ternary peritectoid reactions. The peritectoid points should lie close to the binary U-Pu side at temperatures above those of the equivalent binary reactions.

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Fig. 43. Liquidus Surface for Th-U-Pu System

106-9115

Fig. 44. Class III Four-phase Reaction $\alpha_{Th} + \epsilon_{Pu} + L \rightarrow C$ at 630°C , Schematic

Binary Reactions			Ternary Reactions	
Th-U	Th-Pu	U-Pu	Th-U-Pu	
1350° $L_1 \rightarrow \beta_{Th} + L_2$	1390° $\beta_{Th} + L \rightarrow \alpha_{Th}$			
1265° $\beta_{Th} \rightarrow \alpha_{Th} + L$				
1086° $L \rightarrow \alpha_{Th} + \gamma U$				
			<div style="border: 1px solid black; padding: 5px; text-align: center;"> III 630° $\alpha_{Th} + \epsilon_{Pu} + L \rightarrow C^{**}$ </div>	
			$\alpha_{Th} + C + L$	$\epsilon_{Pu} + C + L$
	615° $\alpha_{Th} + L \rightarrow C$			
	605° $L \rightarrow \epsilon_{Pu} + C$			
			$\alpha_{Th} + C + \epsilon_{Pu}$	
			To low temperature reactions in Pu corner	

*The symbols γU and ϵ_{Pu} are interchangeably used for the continuous series of b.c.c. solid solutions between γU and ϵ_{Pu} .
 **C designates the intermediate phase $Pu_2Th(1-x)$.

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Fig. 45. Th-U-Pu System. Scheme of Reactions Involving the Liquid.

106-8906

Fig. 46. Th-U-Pu System. Solid-state reactions in intermediate temperature range.

at 900 and 700°C are supported by metallographic examination, X-ray diffraction, dilatometry, and electron probe microanalysis. These were the sections that first showed evidence that the solubility of plutonium in thorium is greatly restricted by the addition of uranium, and that the liquid phase appears at 20% plutonium in the presence of 2% uranium at 700°C and at 10% plutonium at 900°C. The very low solid solubility of uranium in the (Th, Pu) solid solution was further confirmed by microanalysis of Th-20U-35Pu. The thorium-rich phase of this alloy contained less than 1% U, and the second phase was U-50Pu with little thorium. The experimental data justify the description of most of the ternary Th-U-Pu alloys as alloys in which a (Th, Pu) solid solution is in equilibrium with the phases of the U-Pu system.

The peritectoid temperatures were determined by DTA. The third reaction (that at 595°C) is a Class II reaction wherein the remainder of the β_U reacts to form ζ . This reaction was observed by DTA in the 70-20-10 and 80-10-10 alloys in the thorium corner. The reaction scheme of Fig. 46 accounts for all the binary three-phase reactions of the Th-U system and the uranium-rich U-Pu alloys. It explains the reactions found in individual alloys by dilatometry and DTA, and shows the three-phase fields that, upon further cooling, move toward the plutonium corner where they participate in the various plutonium transformations. The reactions in the plutonium corner were not investigated.

A series of isothermal sections at selected temperatures are shown in Figs. 47 to 59. The isothermal sections

Fig. 47. Th-U-Pu 1400°C Isotherm, Schematic

Fig. 48. Th-U-Pu 1200°C Isotherm, Schematic

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Fig. 49. Th-U-Pu 1100°C Isotherm, Schematic

106-9131

Fig. 50. Th-U-Pu 1000°C Isotherm

106-9132

Fig. 51. Th-U-Pu 955°C Isotherm

106-9147

Fig. 52. Th-U-Pu 900°C Isotherm

106-9130

Fig. 53. Th-U-Pu 800°C Isotherm

106-9144

Fig. 54. Th-U-Pu 714°C Isotherm. $\alpha_{Th} + \beta_U + \gamma_U \rightarrow \eta$.

106-9145

Fig. 55. Th-U-Pu 700°C Isotherm

106-9128

Fig. 56. Th-U-Pu 650°C Isotherm

106-9129

Fig. 57. Th-U-Pu 610°C Isotherm.
 $\alpha_{Th} + \beta_U + \eta \rightarrow \zeta$.

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Fig. 58. Th-U-Pu 595°C Isotherm.
 $\alpha_{Th} + \beta_U \rightarrow \alpha_U + \zeta$.

reaches below 10% plutonium, and it is this reaction that determines the amount of ζ in the alloys of potential interest as fast reactor fuel. The solubility of ζ for thorium appears to be extremely small. At 575°C (see Fig. 59) the $\alpha_U + \zeta$ phase field necessitates that the solubility of β_U for thorium be smaller than that of ζ . A small amount of β_U will exit into the binary U-Pu system with the reaction $\beta_U \rightarrow \alpha_U + \zeta$ at 560°C. At room temperature the potential fuel alloys consist of α_{Th} and α_U and a very small amount of ζ . In alloys with a higher plutonium content, the amount of ζ increases.

C. Isopleth at 10 a/o Plutonium

An isopleth for alloys with a constant plutonium content of 10 a/o is shown in Fig. 60. This isopleth shows several of the characteristic structural features of the 80-10-10 and 70-20-10 alloys. The solidus temperature

106-9143

Fig. 60. Isopleth for Th-U-Pu System at 10 a/o Plutonium

of $\alpha_{Th} + \gamma_U \rightarrow \alpha_{Th} + \gamma_U + L$ increases slowly with increasing uranium content. Between 675 and 700°C the η phase temporarily appears in the structure. The two other three-phase fields are very narrow and should not have much of an effect on the properties of the alloys. There was no indication of the presence of the ζ phase in alloys quenched from 700°C. Whether any zeta is retained at room temperature on slow cooling is uncertain. The bulk of the α_U phase is formed at about 600°C, and small quantities of α_U precipitated at lower temperatures would be difficult to distinguish from a small quantity of zeta.

D. Discussion and Conclusions

The study of the ternary phase diagram has confirmed that most of the ternary alloys are alloys in which the

phases of the U-Pu system are in equilibrium with α_{Th} . Since the addition of uranium to the (Th, Pu) solid solution greatly lowers the solid solubility of plutonium in thorium, the potentially useful fuel alloys are restricted to a range of compositions with no more than 10% plutonium and up to 25% uranium (see Fig. 61). Even though the solidus temperatures of these alloys are relatively low (920 to 960°C; see Fig. 60), the fact that the second phase is completely surrounded by the high-melting thorium matrix makes them acceptable as fuels. A drastic increase in the amount of liquid phase does not occur below about 1100°C.

106-9127

Fig. 61. Th-U-Pu Isothermal Section at 900°C
with Range of Useful Fuel Compositions

The ternary system may be looked upon as a system in which thorium is added to the U-Pu alloys; then the system resembles other U-Pu systems to which a third element has been added, notably: U-Pu-Mo, U-Pu-Ti, U-Pu-Zr. In all four systems the ζ -phase forms by a peritectoid Class III reaction. No such uniformity applies to the formation of the η -phase.

There are still many details to be filled in to make the present diagram complete. Even though the β_{Th} phase was shown not to exist at the low temperatures, as

required by the phase diagram of Bochvar *et al.*,²⁹ the actual transformation temperatures must still be determined. Also, many of the two- and three-phase fields shown in the isothermal sections are approximations that need further experimental verification. The effect of thorium on the solid-state transformations in the plutonium corner is completely unknown. Nevertheless, the investigation has fulfilled its purposes of outlining the essential features of the system, of making possible the selection of alloys suitable as fast reactor fuels, and of establishing the temperatures and other conditions required for their preparation and heat treatment.

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