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Argonne National Laboratory

PHASE STUDIES ON U-20w/oPu-Fs ALLOYS

by

Owen L. Kruger

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U-20w/oPu-Fs ALLOYS

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Portions of this material have appeared
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<u>ANL</u>	<u>Page</u>
6099	9
6330	10-13
6330	13-15
6516	16
6677	11-14

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TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	7
INTRODUCTION	7
EXPERIMENTAL PROCEDURE	9
RESULTS AND DISCUSSION	14
Properties of As-cast Buttons	14
Melting Points	15
Phases	15
U-20%Pu-Fs Alloys	17
U-20%Pu-5%Fs Alloy	18
U-20%Pu-10%Fs Alloy	18
U-20%Pu-15%Fs Alloy	22
U-20%Pu-3.5%Fs-1.5%Zr Alloy	22
U-20%Pu-7%Fs-3.0%Zr Alloy	22
U-20%Pu-10.5%Fs-4.5%Zr Alloy	23
Pseudoternary Fissium System	23
Crystallographic Data	31
Structure of an Injection-cast U-20%Pu-10%Fs Fuel Pin	33
SUMMARY	36
ACKNOWLEDGMENT	36
REFERENCES	37

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
1.	Densities of Various U-20w/oPu-Fs Alloys	14
2.	Change in Solidus Temperature with Fissium Additions.	15
3.	Microstructures of Annealed and Quenched Specimens from an Alloy of U-20w/oPu-5w/oFs Initially Homogenized 5 days at 800°C and Oil-quenched	19
4.	Microstructures of Annealed and Quenched Specimens from an Alloy of U-20w/oPu-10w/oFs Initially Homogenized 5 days at 795°C and Oil-quenched	20
5.	X-ray Photograms of Specimens from an Alloy of U-20w/oPu-10w/oFs Initially Homogenized 5 days at 795°C and Then Annealed at Various Temperatures and Quenched	21
6.	Microstructures of Annealed and Quenched Specimens from an Alloy of U-20w/oPu-15w/oFs Initially Homogenized 4 days at 740°C and Oil-quenched	24
7.	Microstructures of Annealed and Quenched Specimens from an Alloy of U-20w/oPu-3.5w/oFs-1.5w/oZr Initially Homogenized 5 days at 800°C and Oil-quenched	25
8.	Microstructures of Annealed and Quenched Specimens from an Alloy of U-20w/oPu-7.0w/oFs-3.0w/oZr Initially Homogenized 5 days at 795°C and Oil-quenched	26
9.	Microstructures of Annealed and Quenched Specimens from an Alloy of U-20w/oPu-10.5w/oFs-3.5w/oZr Initially Homogenized 4 days at 740°C and Oil-quenched	27
10.	X-ray Photograms of Specimens from an Alloy of U-20w/oPu-10.5w/oFs-4.5w/oZr Initially Homogenized 4 days at 740°C and Then Annealed at Various Temperatures.	28
11.	Transformations of Matrix Phases Shown as a Vertical Section from the Pseudoternary Fissium System with the Plutonium Concentration Invariant at 20w/o	29
12.	Isothermal Sections Showing Ternary Reactions of the Matrix Phases in the Proposed Pseudoternary U-Pu-Fs System.	30
13.	Solidus Projection for a Portion of the Pseudo U-Pu-Fs System.	31

LIST OF FIGURES

<u>No.</u>	<u>Title</u>	<u>Page</u>
14.	Microstructures of Specimens Taken from the Top, Center, and Bottom of an Injection-cast U-20w/oPu-10w/oFs Alloy	34
15.	Theta Dendrites (Dark) in Gamma Matrix of an Alloy Containing U-20w/oPu-10w/oFs Annealed 1 hour at 650°C and Quenched.	35

LIST OF TABLES

<u>No.</u>	<u>Title</u>	<u>Page</u>
I.	Compositions of Plutonium-containing Alloys under Consideration for EBR-II Fuel	8
II.	Calculated Composition, Nominal Composition, and Chemical Analysis of U-20w/oPu-Fs Alloys	10
III.	Various Heat Treatments for Fissium Alloys	12
IV.	Comparison of Etching Solutions	13
V.	Hardness of Arc-melted U-20w/oPu-Fs Buttons	15
VI.	Room-temperature Phases in Various U-20w/oPu-Fs Alloys as Quenched from the Indicated Annealing Temperatures.	17
VII.	Lattice Constants of the Gamma Phase in Alloys Containing U-20w/oPu-5, 10, and 15w/oFs Quenched from Various Temperatures	32
VIII.	X-ray Data for Theta Phase in an Alloy of U-20w/oPu-10w/oFs Annealed at 775°C for 3 days and Quenched	32
IX.	Lattice Constants of the ZrRu Phase	33

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PHASE STUDIES ON U-20w/oPu-Fs ALLOYS

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ABSTRACT

The phase transformations, microstructures, and melting points of alloys containing U-20w/oPu-Fs were investigated as part of a broad program to evaluate plutonium-containing fuel materials of interest for the second loading of Experimental Breeder Reactor-II. The term "fissium" denotes the elements Ru, Mo, Pd, Te, Rh, Zr, and Nb in the proportions that are left in the fuel after pyrometallurgical refining. Crystallographic data are presented for the alpha and gamma uranium phases and other intermediate phases that occur in these alloys. A primary phase termed "theta" was present in all the alloys to their melting points.

Transformations of the matrix phases appear to be somewhat similar to those in the U-Pu-Mo system. The gamma uranium phase was stable down to 555°C, and at high fissium contents, the beta transformation was entirely suppressed. All alloys contained matrix phases of alpha uranium, gamma-prime, and zeta at 400°C, and these phases appeared to be in equilibrium to room temperature. Analysis of the transformations that occur in the matrix phases has shown that the phase relationships of the fissium alloys can be schematically represented by a pseudoternary system in which U, Pu, and Fs are the components. The microstructures of an injection-cast fuel pin were also examined.

INTRODUCTION

One goal of the fast-reactor program is to incorporate fuel reprocessing into the overall operation of a reactor. This procedure is necessary to remove the fission products that are produced in fuel elements subjected to neutron radiation, thereby repairing the radiation damage to the fuel. Such a scheme is to be demonstrated by the fuel cycle for Experimental Breeder Reactor-II (EBR-II), now in operation at the National Reactor Testing Station in Idaho. Some of the fission products will be removed from spent fuel elements by a pyrometallurgical process called melt refining.⁽¹⁻⁶⁾

The remotely operated process consists of heating a uranium-plutonium fuel alloy between 1300 and 1400°C in a zirconia crucible. The temperature is held for several hours so that the volatile fission products, xenon, krypton, cesium, etc., are removed while the rare-earth elements, barium and strontium, react with the crucible to form a dross. This dross adheres to the crucible surface when the molten metal is poured. Of the other fission products, some of the zirconium is removed, but niobium, molybdenum, technetium, ruthenium, rhodium, and palladium are not removed and would continually increase with repeated fuel reprocessing in the absence of a means for removing them. To avoid a buildup of these elements, which have been collectively called "fissium" (Fs), a small portion of the fuel is removed (dragout) and a percentage of new fuel is added on each cycle. The above elements build up to an equilibrium concentration in the fuel if the following variables are held constant: (1) the fissionable isotope used as fuel, (2) the number of days for irradiation, (3) the percentage burnup, (4) the number of days allowed for cooling, (5) the amount of dragout, and (6) the amount of fissile-element replacement per fuel cycle. The fuel cycle for EBR-II is presently scheduled as 135 days irradiation and 15 days cooling. The first loading of this reactor is an alloy of U-5%* Fs. The transformations, structures, and properties of this alloy have been reported.^(7,8) A plutonium-containing fuel under consideration for loading in EBR-II is an alloy of 70%U-20%Pu-10%Fs. Its estimated fissium composition, based on a 20% enrichment with U²³⁵ plus 20% Pu²³⁹ calculated from the data of Dillon and Burris,⁽⁹⁾ is shown in Table I. Initial plans called for the removal of zirconium from the fissium

Table I
COMPOSITIONS OF PLUTONIUM-CONTAINING ALLOYS
UNDER CONSIDERATION FOR EBR-II FUEL

Element	Amount (w/o)	
	Normal Fissium	Fissium plus Zirconium (Fizium)
Uranium	70.00	70.00
Plutonium	20.00	20.00
Ruthenium	3.59	2.61
Molybdenum	3.26	2.37
Palladium	1.44	1.04
Technetium	0.99	0.72
Rhodium	0.62	0.45
Zirconium	0.09	2.80
Niobium	0.01	0.01

*All alloy compositions are expressed in weight percent.

by carbide dressing; however, this process resulted in a substantial reduction in the yield of the refining process. Therefore, fuels with additional zirconium were also investigated. The composition of the fissium alloy with zirconium added is shown in Table I. This fuel is designated U-20%Pu-7%Fs-3%Zr* in this report.

The weight ratios of the fissium elements to one another remain about the same over a range of fissium concentration if the number of days of irradiation and the cooling time are held constant. The total fissium content of the fuel is then dependent only on the amount of dragout and makeup fuel added per cycle. Since the dragout can be varied easily, the purpose of this investigation was to determine the effect of fissium concentration on the structures and, if possible, the solid-state transformation temperatures in alloys of U-20%Pu with 5 to 15%Fs. To avoid an extensive study of an extremely complex system, specimens from selected compositions, some with additional zirconium in the fissium, were heat-treated at various temperatures, and their phases were identified by use of metallographic and X-ray-diffraction techniques. No attempt was made to determine the exact transformation temperatures of these alloys because of the many non-isothermal complex phase reactions that could take place in this multicomponent system.

Fuel elements for EBR-II are being made by an injection-casting technique previously described by Yaggee *et al.*⁽¹⁰⁾ The alloy will be in the form of rods 3.6 mm in diameter and 361.2 mm long. Since the fabrication process involves directional cooling, the phases present at the top of the rod might be quite different from the phases in the lower section. To further characterize this reactor fuel material, a microexamination was made of injection-cast rods prepared from the U-20%Pu-10%Fs alloys. Sections from these rods were examined in the as-cast and heat-treated condition.

EXPERIMENTAL PROCEDURE

All work on the alloys used in this study was done in gloveboxes containing an inert atmosphere, or in hoods. When the alloys were handled in air, they were immediately coated with collodion by a procedure described later. These precautions were necessary because plutonium is highly toxic and the alloys oxidized readily when they were left unprotected in air.

Alloys of U-20%Pu-Fs with 5, 10, and 15%Fs and the same alloys with 1.5, 3.0, and 4.5% additional Zr were selected for study. Their complete compositions are listed in Table II. They were made by melting plutonium and uranium with a master alloy containing 75% uranium and 25% fissium. The master alloy was prepared by induction-melting and was

* The compositions containing additional zirconium with the fissium have also been referred to as "fizzium (Fz)" alloys.

analyzed before its use. This procedure assisted homogenization and insured the proper weight ratios between the fissium elements, since chemical analysis for the fissium elements after plutonium additions was less accurate. The plutonium was 99.6% pure with major impurities of iron (0.15%), nickel (0.15%), and carbon (0.04%). The uranium and alloying fissium elements had purities of 99.98 and 99.8%, respectively, or better. Additional molybdenum and ruthenium in equal weights were substituted for technetium. Niobium was not added to these melts because its calculated concentration in the fissium was negligible. The alloyed buttons of about 50 g in weight were inverted and remelted five times. After melting, the buttons were sectioned and metallographically examined for segregation. Careful examination showed that the buttons were homogeneous throughout, as evidenced by their uniform microstructure.

Table II
CALCULATED COMPOSITION, NOMINAL COMPOSITION, AND CHEMICAL ANALYSIS OF U-20w/oPu-Fs ALLOYS

Element	U-20w/oPu-5w/oFs			U-20w/oPu-10w/oFs			U-20w/oPu-15w/oFs		
	Calculated Composition*	Nominal Composition*	Chemical Analysis*	Calculated Composition*	Nominal Composition*	Chemical Analysis*	Calculated Composition*	Nominal Composition*	Chemical Analysis*
Plutonium	20.0	20.3	19.8 ±0.6	20.0	20.0	19.4 ±0.6	20.0	19.5	19.3 ±0.6
Molybdenum	1.63	1.90	2.00±0.10	3.26	3.83	3.90±0.20	4.89	5.79	5.90±0.30
Ruthenium	1.80	2.02	1.90±0.10	3.60	4.09	3.90±0.20	5.40	6.10	5.90±0.30
Palladium	0.72	0.72		1.44	1.45		2.16	2.18	
Rhodium	0.31	0.28		0.62	0.56		0.93	0.85	
Technetium	0.50			0.99			1.48		
Zirconium	0.04	0.046		0.09	0.092		0.14	0.14	
Carbon			0.0440			0.0420			0.0250
Oxygen			0.0010			0.0040			0.0040
Nitrogen			<0.0005			<0.0005			<0.0005
Total Fissium		4.97			10.02			15.06	
U-20w/oPu-3.5w/oFs-1.5w/oZr			U-20w/oPu-7.0w/oFs-3.0w/oZr			U-20w/o-10.5w/oFs-4.5w/oZr			
Plutonium	20.0	19.7	20.1 ±0.6	20.0	20.2	20.2 ±0.6	20.0	20.3	20.6 ±0.6
Molybdenum	1.18	1.31	1.30±0.07	2.36	2.66	2.60±0.13	3.54	3.97	3.80±0.19
Ruthenium	1.30	1.38	1.50±0.08	2.61	2.79	2.80±0.14	3.92	4.17	4.17±0.21
Palladium	0.53	0.53		1.05	1.09		1.57	1.62	
Rhodium	0.23	0.26		0.46	0.53		0.69	0.79	
Technetium	0.36			0.72			1.08		
Zirconium	1.40	1.45	1.50±0.08	2.80	2.94	2.90±0.15	4.20	4.40	4.50±0.23
Carbon			0.0490			0.0280			0.0200
Oxygen			0.0040			0.0040			0.0130
Nitrogen			<0.0005			0.0025			<0.0005
Total Fissium		3.48			7.07			10.55	

*Expressed in weight percent.

Table II shows the results of chemical analysis for plutonium, molybdenum, ruthenium, carbon, oxygen, and nitrogen. Although the plutonium analysis was accurate to only ±3% of the amount present, and the fissium elements to ±5%, there was excellent agreement between the nominal and analyzed compositions. The relatively low carbon, oxygen, and nitrogen contents of these alloys indicate that no contamination was introduced during arc-melting.

Densities of the cast buttons were measured by immersion in a liquid of 1, 2, 3 tribromopropane. The values are accurate to about ±0.02 g/cm³.

Hardness measurements were taken on the bottom of the as-cast buttons with a portable hardness tester. Some comparative observations on the ductility of these alloys were made during the preparation of specimens.

Pieces from the buttons were homogenized by heating them for various times at temperatures below the melting point. To establish the homogenization time, annealed samples were placed in crucibles made from tantalum foil, heated above the solidus temperature in a quartz-tube vacuum-quenching furnace, and dropped into NaK alloy. This arrangement allowed the samples to be quenched rapidly by virtue of the excellent heat-transfer properties of the eutectic alloy. A button was adjudged "homogeneous" if heating a piece of it slightly above the solidus temperature caused a resulting liquid phase to nucleate uniformly at all grain boundaries. The pre-quench distribution of the liquid phase in pieces so heated could be readily established by microexamination of the pieces after they had been quenched in NaK alloy.

Once the homogenization time was established, the solidus temperatures of the 5, 10, and 15%Fs alloys were determined by examining the microstructure of samples that had been heat-treated and quenched at temperatures above the homogenization temperature. For this part of the study, the presence of the quenched liquid phase at the grain boundaries was an indication that the solidus temperature had been exceeded. Incipient melting was observed at a temperature of about 50°C below the true melting point in samples from the 10%Fs alloy that were not homogenized.

Pieces from the arc-melted buttons were initially homogenized for 200 hr at 805, 795, and 740°C for the 5, 10, and 15%Fs alloys, respectively. This homogenization time was reduced to 100 hr when the alloys were slowly heated to temperature in the manner suggested by Rhines⁽¹¹⁾ so that no liquid phase formed during the entire heat treatment. Throughout the homogenization and all subsequent annealing treatments, the specimens were wrapped in tantalum foil and sealed in evacuated Vycor glass tubes.

Samples for metallographic and X-ray diffraction examination were taken from homogenized material. Pieces weighing from 0.2 to 0.4 g were used for metallography samples. Needle-shaped samples about 0.05 cm in diameter and 1 cm in length were used to obtain X-ray photograms. To retain the more ductile high-temperature phases, the homogenized material was quenched. One specimen of each type from each of the six alloys was weighed to 0.1 mg and loaded into a single capsule. Nine capsules were made up, and each was heat-treated at a different one of the nine temperatures listed in Table III for the time indicated.

Table III
VARIOUS HEAT TREATMENTS
FOR FISSION ALLOYS

Temperatures (°C)	Time (days)
775	3
700	5
625	18
600	15
570	30
540	30
510	50
490	18
400	57

The capsules were positioned in the heat sink of a vertical resistance furnace. Samples were quenched by dropping the capsule into a predetermined position below the furnace, where it was smashed by a spring-loaded plunger. The contents of the capsule fell into a quenching liquid of silicone oil. The total time for the quenching operation was usually less than 0.5 sec. This technique assured the same annealing treatment and quenching rate for all specimens from the different alloys within a capsule. Specimens were weighed after the heat treatment to separate them from one another.

Selection of the temperatures and times of heat treatment was based on preliminary work by the author comprising some thermal-expansion measurements and examination of annealed metallographic and X-ray samples. The data were then correlated with transformation temperatures of similar alloys of U-20%Pu-Mo.⁽¹²⁾ The samples were held at their annealing temperatures for a longer time than needed to obtain equilibrium in all cases, with one exception. The 490°C heat treatment was made to help determine the maximum temperature for the presence of the alpha uranium phase, and the relatively short annealing time for the temperature was sufficient to obtain adequate X-ray patterns for identification of this phase.

The metallographic samples were cold-mounted in a polyester resin by a method previously described.⁽¹³⁾ They were ground on silicon carbide papers through the 600 grit manually or by using an automatic grinder and polisher. Polishing was done on nylon and silk velvet cloths using 6- and 0.25-micron diamond pastes, respectively. A solution composed of trichloroethylene and kerosene was used as a lubricant for both the grinding and polishing operations. The samples were cleaned ultrasonically in ethyl alcohol. To avoid severe relief polishing of one or more of the several compounds (θ , U_2Ru , and $ZrRu$) that were present in the alloys, the time for final polishing on the wheel containing 0.25-micron diamond paste was held to less than one minute.

Some of the etching solutions tried on these alloys are listed in Table IV. Solutions Nos. 1 through 5 are common etches of the type used on uranium and uranium-plutonium alloys.⁽¹⁴⁾ Orthophosphoric acid was substituted for tetraphosphoric acid in solutions Nos. 6 through 9, and the ratio of water to acid was varied to get the good etching characteristics obtained with Solution No. 4. When the ratio of water to acid was increased, the etch became more corrosive. The right combination was achieved in solution No. 9, which was an excellent etchant for all the fission alloys and

has since been employed widely by other investigators in their work on various plutonium-containing alloys. Metallographic samples were etched electrolytically for 30 sec at a current density of about 100 mA/cm².

Table IV
COMPARISON OF ETCHING SOLUTIONS

Solution No.	Composition*	Type	Effect
1	1 HNO ₃ 2 HF 20 Glycerin	Chemical	The specimen was overetched in 6 sec. This etch was too corrosive and did not preferentially attack the phases in the matrix.
2	5 H ₃ PO ₄ 5 Glycol 8 Ethanol	Electrolytic	The areas around the θ phase were preferentially attacked, leaving θ in relief. There was no preferential attack of the phases in the matrix.
3	8 H ₃ PO ₄ 5 Ethanol 5 Glycerol	Electrolytic	This etch reacted much like solution No. 2. However, there was some preferential attack of the phases in the matrix.
4	20 H ₆ P ₄ O ₁₃ 30 H ₂ O 50 Ethoxyethanol	Electrolytic	This etch was good. Preparation of the etch with tetraphosphoric acid was difficult, and the solution was hard to remove from the surface of specimens.
5	7 H ₆ P ₄ O ₁₃ 36 H ₂ O 57 Ethoxyethanol	Electrolytic	Some phases in the matrix were stained by the etch. The etch was difficult to prepare and was too corrosive for general use.
6	32 H ₃ PO ₄ 18 H ₂ O 50 Ethoxyethanol	Electrolytic	This etch attacked the matrix about the same as solution No. 5.
7	32 H ₃ PO ₄ 68 Ethoxyethanol	Electrolytic	The matrix was under-etched. Increasing the etching time left θ in relief. The matrix was attacked slightly greater than with solution No. 3.
8	32 H ₃ PO ₄	Electrolytic	The etch was good. However, the θ phase showed slight preferential attack.
9	32 H ₃ PO ₄ 9 H ₂ O 59 Ethoxyethanol	Electrolytic	This etch was excellent. There was slight staining of one phase in the matrix.

*Parts by volume.

Several X-ray-diffraction techniques were investigated to determine the best method of obtaining good X-ray photographs of the fissium alloys. The Debye-Scherrer method was used on needle and powder specimens, and the reflection technique was employed to obtain the diffractometer traces of a metallography sample. Needle-shaped samples gave by far the sharpest peaks and the most lines on the X-ray patterns. Therefore they were used throughout this investigation. After annealing, the X-ray samples were cleaned electrolytically in etching solution No. 9.

This treatment was followed by ultrasonic cleaning in ethyl alcohol to remove the etching solution and any loosely adhering particles. The needles were then placed in clean vials and transferred from the glovebox to a hood in polyvinyl chloride pouches. In the hood, the pouches were slit and the needles were removed and completely coated with collodion. After coating, the needles were placed in inserts, and the coated surface was examined for integrity with a 10X magnifier. This technique prevented any spread of contamination during subsequent handling and exposure outside the glovebox and retarded the oxidation of the surface of the specimens without affecting the quality of the X-ray photograms. With this procedure, no oxide lines were observed on the X-ray-diffraction patterns of the coated needles after exposure to air for several days. Longer times resulted in deterioration of the coating because of alpha bombardment from the plutonium in the alloy. If additional exposures were needed, the sample was put into the glovebox and taken through the above procedure a second time. Diffraction patterns were obtained with a 114.6-mm Debye-Scherrer camera, together with $\text{CuK}\alpha$ radiation. Precision lattice constants were determined by use of the method described by Mueller *et al.* (15,16)

RESULTS AND DISCUSSION

Properties of As-cast Buttons

Curves showing the change in densities of the arc-melted buttons with additions of fissium (including zirconium) are shown in Figure 1.

40738

Figure 1. Densities of Various U-20w/oPu-Fs Alloys

As expected, there was a gradual decrease in density with increasing fissium content. The alloys containing additional zirconium had a slightly lower density than the normal fissium alloys when compared on a percent addition (Fs + Zr) basis.

Hardness values of the buttons given in Table V ranged from RA 73 to 95. There was no apparent systematic relationship between the hardness values with fissium addition. The 5%Fs composition was the only ductile button in the as-cast condition. The 10%Fs, 7%Fs-3%Zr, and 10.4%Fs-4.5%Zr alloys were extremely tough. Alloys of 15%Fs and 3.5%Fs-1.5%Zr

were very brittle. Homogenization followed by quenching made all the buttons somewhat more ductile; however, careful handling techniques had to be employed to obtain X-ray needle samples of alloys with 15%Fs and 3.5%Fs-1.5%Zr.

Table V
HARDNESS OF ARC-MELTED U-20w/oPu-Fs BUTTONS

Composition	Hardness (R_A)*
U-20w/oPu-5w/oFs	75
U-20w/oPu-10w/oFs	95
U-20w/oPu-15w/oFs	76
U-20w/oPu-3.5w/oFs-1.5w/oZr	84
U-20w/oPu-7.0w/oFs-3.0w/oZr	75
U-20w/oPu-10.5w/oFs-4.5w/oZr	73

*Measured on the bottom of each button.

Melting Points

The solidus temperature, as a function of fissium addition for normal fissium alloys, is shown in Figure 2. The values for the 5, 10, and 15%Fs alloys are thought to be accurate to about $\pm 10^\circ\text{C}$. This rather large

40737

Figure 2. Change in Solidus Temperature with Fissium Additions

temperature error was due to the very slight change in the amount of liquid formed with increasing temperature because of a large difference between the solidus and liquidus temperatures. The liquidus temperature of the 10%Fs alloy was $1010 \pm 10^\circ\text{C}$, which gave a liquid-plus-solid range of 190°C for this composition. The point for zero-percent Fs was taken from the U-Pu phase diagram published by Ellinger et al.⁽¹⁷⁾ From the shape of the solidus curve in Figure 2, additions of Fs to 20 or 25% would probably reduce the solidus temperature only slightly below 800°C .

The solidus temperatures were not determined for the alloys containing additional zirconium; however, their solidus temperatures would not be expected to deviate substantially from the values found for the normal fissium alloys when considered on a percent-fissium basis. This point is discussed more in the following sections of this report.

Phases

The major phases found in the alloys prepared for this investigation are described below. The nomenclatures for the gamma, gamma-naught,

alpha-prime, and gamma-prime phases are in accordance with the system adopted by Lehmann and Hills⁽¹⁸⁾ in their investigations of the U-Mo phase diagram.

Gamma uranium (γ): Well-known, body-centered cubic allotropic modification of uranium, which has complete solid solubility for B.C.C. epsilon plutonium at high temperatures.

Gamma-naught (γ^0): A tetragonal modification of the gamma phase, with a c/a ratio of approximately 0.98. This phase is apparently isomorphous with the tetragonal γ phase found by Anselin⁽¹⁹⁾ in an alloy of U-20%Pu-3%Mo.

Alpha-prime (α'): A phase thought to be a metastable modification of orthorhombic α uranium, which has been widely designated "distorted alpha."⁽¹⁸⁾ The lines of this phase on the X-ray photograms were spotted and diffused so that the line positions could not be accurately determined.

Gamma-prime (γ'): A phase that occurs in the binary U-Mo system at a composition of U_2Mo . Its crystal structure has been reported by Halteman⁽²⁰⁾ to be tetragonal of the $MoSi_2$ -type, and it is believed to be an ordered state of the cubic gamma phase.

Alpha and beta uranium (α and β): Well-known allotropic modifications of uranium that have orthorhombic and tetragonal crystal structures, respectively.

Eta and zeta (η and ξ): Two intermediate phases that exist in the U-Pu system.⁽¹⁷⁾ They have wide ranges of homogeneity. In the binary system, eta phase is stable only at high temperatures, and it usually transforms to zeta on quenching.

Theta (θ): A primary phase, thought to be composed of U, Pu, and Pd, which was present to room temperature in all the alloys studied. Solubility for uranium, plutonium, and/or some of the fission elements was indicated by a slight shift in lines on the X-ray-diffraction photograms with changes in fission concentration. The change in line positions, along with an apparent complex crystal structure, prohibited positive identification of this phase, although there was a similarity between the line positions on an X-ray pattern from this phase and one from the orthorhombic ThPd phase.⁽²¹⁾

U_2Ru : A phase whose X-ray-diffraction pattern indicates that it is isostructural with the U_2Ru phase reported by Berndt.⁽²²⁾

ZrRu: A phase that appears to be isostructural with the CsCl-type phase, ZrRu, studied by Dwight.⁽²³⁾ It occurred in an identifiable concentration only in the high zirconium alloys.

The gamma-prime, U_2Ru , and $ZrRu$ phases may have had slight solubility for other components in these alloys that would cause them to deviate from their binary compositions. The above nomenclature was retained, regardless of this possibility.

U-20%Pu-Fs Alloys

The results of X-ray diffraction and metallographic examination of annealed and quenched specimens are shown in Table VI. Theta phase was present in all alloys from room temperature to their melting points. The U_2Ru phase was found only in alloys containing normal fissium. Additions of zirconium to the fissium suppressed the formation of the U_2Ru phase, and $ZrRu$ was found instead. The gamma uranium phase apparently transformed to alpha-prime and gamma-naught in alloys with less than 10% fissium that were quenched to room temperature. However, gamma was retained without difficulty in compositions that contained more than 10%Fs. No change was observed in the microstructure of the gamma phase when it transformed to gamma-naught or alpha-prime on quenching. This behavior was thought to be due to the presence of other phases in the microstructure that concealed the transformation products when specimens were observed under polarized light.

Table VI
ROOM-TEMPERATURE PHASES IN VARIOUS U-20w/oPu-Fs ALLOYS AS QUENCHED FROM THE INDICATED ANNEALING TEMPERATURES

Annealing Temperature (°C)	Fissium and Zirconium Content					
	5w/oFs	10w/oFs	15w/oFs	3.5w/oFs 1.5w/oZr	7.0w/oFs 3.0w/oZr	10.5w/oFs 4.5w/oZr
775	$\gamma^0 + \theta$	$\gamma U + \theta$	$\gamma U + \theta + U_2Ru$	$\gamma^0 + \theta + ZrRu$	$\gamma^0 + \theta + ZrRu$	$\gamma U + \theta + ZrRu$
700	$\gamma^0 + \theta$	$\gamma U + \theta + U_2Ru$	$\gamma U + \theta + U_2Ru$	$\gamma^0 + \beta U + \zeta + \theta + ZrRu$	$\gamma^0 + \theta + ZrRu$	$\gamma U + \theta + ZrRu$
625	$\gamma^0 + \alpha' + \beta U + \zeta + \theta + U_2Ru$	$\gamma U + \theta + U_2Ru$	$\gamma U + \theta + U_2Ru$	$\gamma^0 + \beta U + \zeta + \theta + ZrRu$	$\gamma^0 + \theta + ZrRu$	$\gamma U + \theta + ZrRu$
600	$\gamma^0 + \alpha' + \beta U + \zeta + \theta + U_2Ru$	$\gamma U + \theta + U_2Ru$	$\gamma U + \theta + U_2Ru$	$\gamma^0 + \beta U + \zeta + \theta + ZrRu$	$\gamma^0 + \beta U + \theta + ZrRu$	$\gamma U + \theta + ZrRu$
570	$\gamma^0 + \alpha' + \beta U + \zeta + \theta + U_2Ru$	$\gamma U + \theta + U_2Ru$	$\gamma U + \theta + U_2Ru$	$\gamma^0 + \beta U + \zeta + \theta + ZrRu$	$\gamma^0 + \beta U + \zeta + \theta + ZrRu$	$\gamma U + \theta + ZrRu$
540	$\gamma' + \beta U + \zeta + \theta + U_2Ru$	$\gamma U + \gamma' + \zeta + \theta + U_2Ru$	$\gamma U + \gamma' + \zeta + \theta + U_2Ru$	$\gamma' + \beta U + \zeta + \theta + ZrRu$	$\gamma' + \beta U + \zeta + \theta + ZrRu$	$\gamma U + \gamma' + \zeta + \theta + ZrRu$
510	$\gamma' + \beta U + \zeta + \theta + U_2Ru$	$\gamma' + \zeta + \theta + U_2Ru$	$\gamma' + \zeta + \theta + U_2Ru$	$\gamma' + \beta U + \zeta + \theta + ZrRu$	$\gamma' + \beta U + \zeta + \theta + ZrRu$	$\gamma' + \zeta + \theta + ZrRu$
490	$\alpha U + \gamma' + \zeta + \theta + U_2Ru$	$\alpha U + \gamma' + \zeta + \theta + U_2Ru$	$\gamma' + \zeta + \theta + U_2Ru$	$\alpha U + \gamma' + \zeta + \theta + ZrRu$	$\alpha U + \gamma' + \zeta + \theta + ZrRu$	$\alpha U + \gamma' + \zeta + \theta + ZrRu$
400	$\alpha U + \gamma' + \zeta + \theta + U_2Ru$	$\alpha U + \gamma' + \zeta + \theta + U_2Ru$	$\alpha U + \gamma' + \zeta + \theta + U_2Ru$	$\alpha U + \gamma' + \zeta + \theta + ZrRu$	$\alpha U + \gamma' + \zeta + \theta + ZrRu$	$\alpha U + \gamma' + \zeta + \theta + ZrRu$

The following figures that show microstructures are divided into parts a, b, c, etc., depending upon heat treatment. Those that are as-cast are indicated by (a). Coring of the matrix can be seen in those as-cast compositions with more than 10%Fs. X-ray patterns had diffuse lines, and no attempt was made to identify the phases present in these alloys. Phase changes in the various alloys after homogenization and annealing are discussed below.

U-20%Pu-5%Fs Alloy

A two-phase structure of gamma-naught plus θ was found in specimens from this alloy that were quenched from above 700°C (see Figures 3b and 3c). In alloys quenched from below 700°C, alpha-prime formed with the gamma-naught phase. At the 625°C heat treatment (Figure 3d), small quantities of U_2Ru , beta, and zeta were also detected in the X-ray photograms. The microstructure shows additional phases that appear light in color when etched. The amount of these phases increased as the annealing temperature was decreased. Delineation of the phases in the microstructure of the specimen annealed at 600°C was not good, as shown in Figure 3e. However, heat treatment at 570°C produced a well-defined microstructure (see Figure 3f). Theta and U_2Ru look the same and are gray with a black outline. The beta and zeta phases also cannot be distinguished from one another, and they appear gray with a dark outline in a matrix of gamma-naught and alpha-prime. At the 540 and 510°C heat treatments, gamma-prime existed with beta, zeta, θ , and U_2Ru . Only a fine precipitate is visible at 540°C (see Figure 3g) with the θ and U_2Ru phases. However, in Figure 3h, the multiphase structure is quite evident for the 510°C anneal. The existence of beta uranium apparently terminated below about 500°C, and alpha was formed in its place. The complex microstructure of the matrix as-quenched from 400°C was not resolved at 500X, as shown in Figure 3i.

U-20%Pu-10%Fs Alloy

The gamma uranium and θ phases were retained in this alloy when annealed at 775°C, as shown in Figure 4b. Below about 700°C, θ appeared at the grain boundaries and as a Widmanstätten precipitate in the grains (see Figures 4c through 4f). Precipitation of U_2Ru began at about 700°C and was easily distinguished at the 625, 600, and 570°C anneals because it appeared dark gray. Gamma-prime and zeta started to precipitate at 540°C, and at 510°C gamma was completely replaced by these phases. This transformation was accompanied by a change in microstructure that resulted in a very dark matrix, as shown in Figures 4g and 4h for the 540 and 510°C heat treatments, respectively. In Figure 4h, θ and U_2Ru phases appear light in an almost black matrix of coprecipitated gamma-prime and zeta. Below about 500°C, light islands of θ and U_2Ru are surrounded by an unresolved matrix of alpha, gamma-prime, and zeta (see Figure 4i). The X-ray-diffraction patterns of this alloy annealed at various temperatures are shown in Figure 5. Although some of the lines for the different phases have been lost in reproduction, the change from gamma to alpha, gamma-prime, and zeta (not present in reproduction) can be seen. The θ phase lines are evident in the photogram from the 775°C anneal (Figure 5a).

Figure 3. Microstructures of Annealed and Quenched Specimens from an Alloy of U-20w/oPu-5w/oFs Initially Homogenized 5 days at 800°C and Oil-quenched. Photomicrographs taken with bright field illumination. (Etchant: Phosphoric Acid)

Figure 4. Microstructures of Annealed and Quenched Specimens from an Alloy of U-20w/oPu-10w/oFs Initially Homogenized 5 days at 795°C and Oil-quenched. Photomicrographs taken with bright field illumination. (Etchant: Phosphoric Acid)

(a) 775°C, 3 days; gamma plus θ

(b) 700°C, 5 days; gamma plus θ plus U₂Ru

(c) 625°C, 18 days; gamma plus θ plus U₂Ru

(d) 600°C, 15 days; gamma plus θ plus U₂Ru

(e) 570°C, 30 days; gamma plus θ plus U₂Ru

(f) 540°C, 30 days; gamma plus gamma-prime plus zeta plus θ plus U₂Ru

(g) 510°C, 50 days; gamma-prime plus zeta plus θ plus U₂Ru

(h) 400°C, 57 days; alpha plus gamma-prime plus zeta plus θ plus U₂Ru

Figure 5. X-ray Photograms of Specimens from an Alloy of U-20w/oPu-10w/oFs Initially Homogenized 5 days at 795°C Then Annealed at Various Temperatures and Quenched.

U-20%Pu-15%Fs Alloy

The three-phase microstructure of gamma, θ , and U_2Ru present in this alloy after annealing at 775°C is shown in Figure 6b. Comparison of the etching characteristics of the phases present in this alloy with those in the 10%Fs alloy indicates that θ is probably the light gray phase with a black outline, while U_2Ru is dark gray. The θ and U_2Ru phases increase in quantity with lower annealing temperatures as shown in the microstructures in Figure 6c through 6f. At the 570°C annealing temperature, there is almost a continuous network of θ and U_2Ru . The gamma-prime and zeta phases precipitated at 540°C, and at 510°C gamma was no longer detected by X-ray diffraction. Only slight changes were seen in the microstructures of specimens annealed at 540 and 510°C because the large amount of θ and U_2Ru masked the structure of the other phases (see Figures 6g and 6h). Gamma-prime and zeta were the stable phases, along with θ and U_2Ru , down to about 400°C, where a small amount of alpha rejection was detected in the X-ray photograms. The resulting microstructure in Figure 6i was not resolved at the 500X magnification.

U-20%Pu-3.5%Fs-1.5%Zr Alloy

A three-phase structure of gamma, θ , and ZrRu was present in this alloy from the melting point down to about 775°C, as shown in Figure 7b. Gamma transformed to gamma-naught on quenching. Specimens annealed in the temperature range of 700 to 570°C contained gamma-naught, beta, zeta, θ , and ZrRu. Their microstructures are shown in Figures 7c through 7f. The light-etching phase with a black outline is apparently ZrRu, and θ is dark gray in Figure 7c. The matrix shows light and dark etching phases at the 625 and 600°C heat treatments, with some evidence of a fine precipitate. At 570°C, the appearance of the microstructure changes abruptly, although the quenched phases remained the same. This change can be explained by the fact that in the binary U-Pu system the high-temperature eta phase is difficult to retain and usually transforms to zeta on quenching. Since the peritectoidal transformation of eta to zeta occurs at 590°C in the binary alloys, the fissium alloys quenched from 700 to 600°C were assumed to contain eta at these annealing temperatures, while zeta was formed at the 570°C treatment. The microstructures shown here are consistent with this behavior. At 540 and 510°C (see Figure 7g and 7h), gamma-prime existed with beta and zeta in a fine coprecipitate, similar to the 5%Fs composition without additional Zr. Alpha was stable with gamma-prime, zeta, θ , and ZrRu at 490°C and below.

U-20%Pu-7%Fs-3.0%Zr Alloy

Specimens from this alloy annealed at 775, 700, and 625°C contained θ and ZrRu in a gamma-naught matrix as shown in Figures 8b, 8c, and 8d. The ZrRu phase appears light on etching. Coprecipitation of θ and

ZrRu from the melt is evident in these microstructures. Annealing at 600°C produced a light-etching beta-uranium phase in the matrix, as shown in Figure 8e. The very dark phase with a black outline is θ , while ZrRu appears light with a black outline. Coprecipitation of beta and zeta was well-advanced at 570°C, as shown in Figure 8f. Beta and zeta are indistinguishable and appear as a light-gray phase with a black outline. In the temperature range of 540 to 510°C, gamma was no longer present and gamma-prime existed with beta, zeta, θ , and ZrRu. The structures of these phases are shown in Figures 8g and 8h. At 510°C, θ (dark) and ZrRu (light with a black outline) were concentrated at the grain boundaries. The matrix was not resolved at this magnification. Beta was not stable below about 500°C, and alpha was present in its place along with the other phases (see Figure 8i).

U-20%Pu-10.5%Fs-4.5%Zr Alloy

Theta and ZrRu were stable in a gamma matrix of this alloy from its melting point down to 570°C (see Figures 9b to 9f). No photomicrograph was available for the 700°C heat treatment. Therefore Figure 9c was omitted so that the remaining photomicrographs could be compared on the basis of their letter designation. At 540°C, a rejection of gamma-prime and zeta was detected by X-ray-diffraction examination. The gamma uranium phase was not present at 510°C, and at this temperature the stable phases were gamma-prime, zeta, θ , and ZrRu. A gradual change in microstructure accompanied these phase changes, as shown in Figures 9g and 9h. Although magnification was not sufficient to resolve the fine particles, a general increase in their number can be seen. Dark areas are present in the microstructure of the specimen annealed at 510°C. A rejection of alpha took place between 510 and 490°C, and the remaining phases were apparently stable to room temperature. Annealing at 400°C produced a microstructure (see Figure 9i) comparable with the microstructures of the other alloys annealed at this temperature. X-ray photograms of this alloy annealed at various temperatures are shown in Figure 10. These patterns are similar to the ones for the U-20%Pu-10%Fs alloy, except that strong lines of the ZrRu phase are present. Here again some lines have been lost in reproduction. The phases that were detected from the original patterns are indicated.

Pseudoternary Fissium System

The U-Pu-Fs alloys contain seven components, and as many as five phases have been detected in equilibrium. Transformations in this multiphase system are extremely complex and do not lend themselves to analysis in their present form. If, for the purpose of simplification, it is assumed that the θ , U_2Ru , and ZrRu phases do not take part in the transformations, and in so doing their presence is disregarded, then the remaining matrix phases and their possible transformations can be examined in detail.

Figure 6. Microstructures of Annealed and Quenched Specimens from an Alloy of U-20w/oPu-15w/oFs Initially Homogenized 4 days at 740°C and Oil-quenched. Photomicrographs taken with bright field illumination. (Etchant: Phosphoric Acid)

Figure 7. Microstructures of Annealed and Quenched Specimens from an Alloy of U-20w/oPu-3.5w/oFs-1.5w/oZr Initially Homogenized 5 days at 800°C and Oil-quenched. Photomicrographs taken with bright field illumination. (Etchant: Phosphoric Acid)

775°C, 3 days; oil-quenched

700°C, 5 days; oil-quenched

30187

500X

(a) As-cast

27949

500X

(b) Gamma-naught plus θ plus ZrRu

27978

500X

(c) Gamma-naught plus θ plus ZrRu

625°C, 18 days; oil-quenched

600°C, 15 days; oil-quenched

570°C, 30 days; oil-quenched

27973

500X

(d) Gamma-naught plus θ plus ZrRu

30124

500X

(e) Gamma-naught plus beta (light) plus θ plus ZrRu

32122

500X

(f) Gamma-naught plus beta plus zeta plus θ plus ZrRu

540°C, 30 days; oil-quenched

510°C, 50 days; oil-quenched

400°C, 57 days; oil-quenched

32271

500X

(g) Gamma-prime plus beta plus zeta plus θ plus ZrRu

32284

500X

(h) Gamma-prime plus beta plus zeta plus θ (dark) plus ZrRu (light)

32296

500X

(i) Alpha plus gamma-prime plus beta plus θ plus ZrRu

Figure 8. Microstructures of Annealed and Quenched Specimens from an Alloy of U-20w/oPu-7.0w/oFs-3.0w/oZr Initially Homogenized 5 days at 795°C and Oil-quenched. Photomicrographs taken with bright field illumination. (Etchant: Phosphoric Acid)

Figure 9. Microstructures of Annealed and Quenched Specimens from an Alloy of U-20w/oPu-10.5w/oFs-4.5w/oZr Initially Homogenized 4 days at 740°C and Oil-quenched. Photomicrographs taken with bright field illumination. (Etchant: Phosphoric Acid)

(a) 775°C, 3 days; gamma
plus θ plus ZrRu

(b) 700°C, 5 days; gamma
plus θ plus ZrRu

(c) 625°C, 18 days; gamma
plus θ plus ZrRu

(d) 600°C, 15 days; gamma
plus θ plus ZrRu

(e) 570°C, 30 days; gamma
plus θ plus ZrRu

(f) 540°C, 30 days; gamma
plus gamma-prime plus
zeta plus θ plus ZrRu

(g) 510°C, 50 days; gamma-
prime plus zeta plus θ
plus ZrRu

(h) 400°C, 57 days; alpha
plus gamma-prime plus
zeta plus θ plus ZrRu

Figure 10. X-ray Photographs of Specimens from an Alloy of U-20w/oPu-10.5w/oFs-4.5w/oZr Initially Homogenized 4 days at 740°C and Then Annealed at Various Temperatures

The matrix phases from Table VI (omitting the transformation products due to quenching and θ , U_2Ru , and $ZrRu$) are shown in Figure 11 as a vertical section from a pseudoternary diagram where uranium, plutonium, and fissium are the components and the plutonium concentration is invariant at 20%. Probable transformation temperatures and the phase boundaries have been indicated, although their exact positions are not accurately known. Here the fissium term designates the fissium elements soluble in the matrix. Obviously, the matrix was depleted in palladium and ruthenium in all alloys, and in palladium, ruthenium, and zirconium in the alloys containing additional zirconium, but the exact amounts of these elements remaining in the matrix were unknown. Therefore, the total fissium concentration* in each alloy was plotted for convenience. In alloys containing additional zirconium, only the fissium content was used; this accounts for the nomenclature U-20%Pu-Fs plus Zr. This vertical section corresponds to a region in the U-Pu-Mo system⁽¹²⁾ in which the concentration of plutonium is about 20% and the molybdenum concentration varies between about 2 and 10%. In this region, three four-phase reactions occur in the temperature range of 605 to 525°C. These reactions are:

- (1) $\gamma + \beta + \eta \rightarrow \xi$ at 605°C; (2) $\beta \rightarrow \alpha + \gamma + \xi$ at 565°C;
 (3) $\gamma \rightarrow \alpha + \gamma' + \xi$ at 525°C;

40736

Figure 11. Transformations of Matrix Phases Shown as a Vertical Section from the Pseudo-ternary Fissium System with the Plutonium Concentration Invariant at 20w/o

*i.e., the concentration by weight of fissium that would exist if there had been no depletion of palladium, ruthenium, and zirconium.

The transformation temperatures and the phases present above and below the first transformation agree well with the fissium system. The reaction scheme of a class III reaction,

for the fissium system is represented by the isotherms presented in Figures 12a and 12b. The positions of the phase fields on these and subsequent diagrams were determined from the above vertical section, the binary U-Pu system, and some theoretical considerations.

The eutectoidal decomposition of beta at 565°C by reaction (2) apparently does not occur in the fissium system as shown by the presence of beta below the 565°C transformation temperature. Instead, the gamma-prime phase appears at about 555°C and exists with beta and zeta phases to 500°C . The presence of beta, gamma-prime, and zeta phases in this temperature range indicates that a class II reaction,

has taken place at 555°C . The proposed reaction scheme is shown in Figures 12c, 12d, and 12e.

At 500°C , beta apparently transforms eutectoidally according to the class I reaction,

40740

Figure 12. Isothermal Sections Showing Ternary Reactions of the Matrix Phases in the Proposed Pseudoternary U-Pu-Fs System

as represented in Figures 12e and 12f. The resulting low-temperature phases, alpha, zeta, and gamma-prime are the same as those found in the U-Pu-Mo system.

Solidus isotherms for the U-Pu-Fs pseudoternary system were constructed from the available melting-point data⁽²⁴⁾ and are shown as projections in Figure 13. The solidus temperatures of alloys with additional zirconium were plotted according to their fissium content. There is an appreciable drop in the solidus temperature with additions of fissium to the binary uranium-plutonium alloys. This behavior is quite different from the U-Pu-Mo alloys, although molybdenum is the primary element of the fissium in solution.

The above isothermal sections can be used to predict the phases present in fissium alloys over a rather wide range of plutonium and fissium concentration. Any composition can be prepared through variations in the amounts of dragout and changes in quantities of make-up fissile elements added per fuel cycle.

40739

Figure 13. Solidus Projection for a Portion of the Pseudo U-Pu-Fs System

Crystallographic Data

There was a gradual increase in the c/a ratio of the tetragonal gamma-naught phase with increasing fissium content. Alloys containing U-20%Pu with 3.5%Fs-1.5%Zr, 5%Fs, and 7.0%Fs-3.0%Zr had c/a ratios of 0.97, 0.99, and almost 1.00, respectively, when quenched from 775°C.

Precision lattice constants of the gamma phase were determined on some of the U-20%Pu-10 and 15%Fs alloys. These values are reported in Table VII, along with the a_0 and c_0 values for the tetragonal U-20%Pu-5%Fs alloy. The lattice constants of gamma decreased from 3.4196Å to 3.3956Å as the fissium content increased from 10 to 15%. The c/a ratio of the 5%Fs alloys decreased from 0.99 to 0.98 with a decrease in the annealing temperature from 775 to 625°C. X-ray photograms of the high zirconium alloys in general did not have gamma phase lines of sufficient quality for precision lattice-constant determinations.

The alpha uranium lattice constants for an alloy of U-20%Pu-3.5%Fs-1.5%Zr quenched from 400°C were $a_0 = 2.8613 \pm 0.0001\text{Å}$, $b_0 = 5.8531 \pm 0.0001\text{Å}$, and $c_0 = 4.9627 \pm 0.0001\text{Å}$. These values are very close to the values of $a_0 = 2.8625\text{Å}$, $b_0 = 5.8562\text{Å}$, and $c_0 = 4.9631\text{Å}$ obtained by Berndt⁽²⁵⁾ as the weighted average of the values found on alloys in the two-phase, alpha-plus-zeta region of the binary U-Pu system after annealing at 400°C.

Table VII

LATTICE CONSTANTS OF THE GAMMA PHASE IN ALLOYS CONTAINING
U-20w/oPu-5, 10, AND 15w/oFs QUENCHED FROM VARIOUS TEMPERATURES

Annealing Temperature (°C)	Lattice Constants		
	5w/oFs (Å)	10w/oFs (Å)	15w/oFs (Å)
775	$a_0 = 3.46$ $c_0 = 3.43$ $c_0/a_0 = 0.99$	$a_0 = 3.4196 \pm 0.0001$	$a_0 = 3.3956 \pm 0.0001$
700	$a_0 = 3.56$ $c_0 = 3.41$ $c_0/a_0 = 0.99$	$a_0 = 3.430 \pm 0.001$	$a_0 = 3.4005 \pm 0.0001$
625	$a_0 = 3.46$ $c_0 = 3.40$ $c_0/a_0 = 0.98$	$a_0 = 3.4284 \pm 0.0002$	

As mentioned earlier, θ appeared as a primary phase in both the normal fissium and high-zirconium fissium alloys. Some of the θ lines on the X-ray photograms shifted with changes in fissium concentration; however, alloys containing the same amounts of fissium, independent of the zirconium content, had almost identical line positions for this phase. The "d" spacings of θ in an alloy of U-20%Pu-10%Fs, annealed at 775°C, are shown in Table VIII. Since some of the lines for θ may be missing, because of its obviously complex crystal structure and the small amount present in these alloys, this phase could not be positively identified by X-ray techniques. Microprobe studies by Savage⁽²⁶⁾ on alloys of U-10%Pu-10%Fs have shown that a primary phase, thought to be θ , contained uranium and plutonium with palladium as its main constituents.

Table VIII

X-RAY DATA FOR THETA PHASE IN AN ALLOY OF
U-20w/oPu-10w/oFs ANNEALED AT 775°C
FOR 3 DAYS AND QUENCHED

Intensity	d (Å)	$\sin^2 \theta$	Intensity	d (Å)	$\sin^2 \theta$
W	3.398	0.0514	VVW	1.538	0.2512
S	2.756	0.0782	VVW	1.459	0.2790
W	2.655	0.0843	VVW	1.438	0.2875
W	2.568	0.0901	VVW	1.412	0.2980
VVW	2.280	0.1143	VVW	1.372	0.3155
S	2.277	0.1198	VVW	1.289	0.3575
VVW	1.877	0.1686	VVW	1.267	0.3701
VVW	1.688	0.2086	VVW	1.195	0.4162
VVW	1.647	0.2190	VVW	1.143	0.4552

Lattice constants of the gamma-prime phase in a U-20%Pu-15%Fs alloy quenched from 400°C were: $a_0 = 3.35\text{Å}$, $c_0 = 9.22\text{Å}$, and $c/a = 2.75\text{Å}$. These approximate values are not in good agreement with

the values of $a_0 = 3.427\text{\AA}$, $c_0 = 9.834\text{\AA}$, and $c/a = 2.871\text{\AA}$, reported by Halteman⁽²⁰⁾ for a single-phase alloy. This variation is probably due to solubility for plutonium or the other fissium elements.

Values for the lattice constant of the ZrRu phase in alloys annealed at different temperatures are shown in Table IX. Their average value of $3.262 \pm 0.002\text{\AA}$ is between the value of $3.27\text{\AA}$ found by Nevitt and Zegler⁽⁷⁾ in U-Fs alloys, and a value of $3.253\text{\AA}$ obtained by Dwight⁽²³⁾ on the pure compound.

Table IX
LATTICE CONSTANTS OF THE ZrRu PHASE

Composition	Annealing Temperature ($^{\circ}\text{C}$)	Lattice Constant ($\text{\AA}$)
U-20w/oPu-3.5w/oFs-1.5Zr	700	3.260 ± 0.001
U-20w/oPu-7.0w/oFs-3.0Zr	775	3.2624 ± 0.0001
U-20w/oPu-7.0w/oFs-3.0Zr	700	3.2623 ± 0.0001
U-20w/oPu-7.0w/oFs-3.0Zr	625	3.263 ± 0.001
U-20w/oPu-10.5w/oFs-4.5Zr	775	3.2611 ± 0.0001
U-20w/oPu-10.5w/oFs-4.5Zr	700	3.2612 ± 0.0001
U-20w/oPu-10.5w/oFs-4.5Zr	625	3.2641 ± 0.0001

None of the diffraction photograms yielded patterns of the beta, zeta, or U_2Ru phases of sufficient line quality for lattice constant measurements.

Structure of an Injection-cast U-20%Pu-10%Fs Fuel Pin

The injection-casting process is being used to make fuel pins for EBR-II. In this process, the top of the fuel pin is cooled more quickly than the bottom, which is near the melt. In fuel alloys that undergo sluggish phase transformations upon cooling, the high-temperature phases can be expected in regions of rapid cooling, and the low-temperature phases will be present in the slow-cooled regions. This behavior was first evident in the injection-cast fuel pins by the fact that the tops of the pins were relatively more ductile than their bottoms.

Several pins with a U-20%Pu-10%Fs composition were prepared by injection-casting, and samples from the top, center, and bottom of the pins were examined for evidence of phase changes. The photomicrographs of Figure 14 show the change in microstructure of the as-cast pins from top to bottom. The primary dendrites of θ in the specimen taken from the bottom of the pin had a much greater degree of development than the dendrites in specimens taken from the center and top of the same pin. The matrix of the top specimen was cored-gamma. The bottom and center

26265

150X

26264

750X

(a) TOP: Theta (dark) in matrix of cored gamma

26270

150X

26271

750X

(b) CENTER: Theta dendrites with gamma (light) at the center of the grains and low temperature phases at the grain boundaries

26261

150X

26260

750X

(c) BOTTOM: Theta dendrites in a matrix of almost completely transformed gamma

Figure 14. Microstructures of Specimens Taken from the Top, Center, and Bottom of an Injection-cast U-20w/oPu-10w/oFs Alloy (Etchant: Phosphoric Acid)

specimens appeared to retain gamma at the center of the grains, while the grain boundaries partially transformed to the low-temperature alpha, gamma-prime, and zeta phases. As indicated in Figure 9, this transformation begins as soon as the temperature drops below about 550°C. The low-temperature structure was removed by a one-hour anneal at 700°C, followed by quenching, as shown in Figure 15.

26269

150X

26268

750X

Figure 15. Theta Dendrites (Dark) in Gamma Matrix of an Alloy Containing U-20w/oPu-10w/oFs Annealed 1 hour at 650°C and Quenched (Etchant: Phosphoric Acid)

SUMMARY

The solidus temperatures of the U-20%Pu-Fs alloys decreased from about 930 to 800°C with additions of Fs to 15%. An intermediate phase termed " θ ," which is thought to contain U, Pu, and Pd, was present to the melting point in all of the alloys. A U_2Ru phase was also present with θ in most of the alloys; however, additions of zirconium to the fissium suppressed the formation of U_2Ru and instead formed ZrRu. Alloys containing less than 10%Fs undergo transformations involving the three allotropic forms of uranium, gamma-prime (U_2Mo), eta, and zeta phases from the U-Pu system and two of the previously mentioned intermediate phases, either θ plus U_2Ru or θ plus ZrRu. Less-complicated transformation characteristics are exhibited by the alloys containing more than 10%Fs in that the formation of beta uranium is entirely suppressed and gamma-plus- θ phases are stable with either U_2Ru or ZrRu from the melting point to about 550°C.

If the fissium system is simplified by disregarding the θ , U_2Ru , and ZrRu phases, then this system appears to be similar to the U-Pu-Mo system in the region of about 2 to 10%Mo and 20%Pu. A pseudoternary system has been proposed where the components are uranium, plutonium, and fissium. In this system, three four-phase reactions occur as follows:

- (1) $\gamma + \beta + \eta \rightarrow \xi$ at 610°C;
- (2) $\beta + \gamma \rightarrow \xi + \gamma'$ at 555°C;
- (3) $\beta \rightarrow \alpha + \xi + \gamma'$ at 500°C.

Quenching of alloys containing less than 10%Fs did not produce the retention of gamma uranium as expected. Instead, a tetragonal modification of the gamma phase called gamma-naught and a distorted-alpha resulted. Gamma was retained in alloys with more than 10%Fs. An increase in the sluggishness of the gamma transformation accompanied an increase in fissium content. Fuel pins of U-20%Pu-10%Fs prepared by injection-casting retained gamma phase at the top, but a considerable amount of the low-temperature phases assumed to be alpha, gamma-prime, and zeta appeared in the microstructure of the bottom section of the pins. Therefore, substantial changes in properties may occur over the length of cast fuel pins from variations in the phases present.

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