1

ARGONNE NATIONAL LABORATORY
P. O. Box 299
Lemont, Illinois

IRRADIATION OF CAST URANIUM-PLUTONIUM BASE ALLOYS

by

K. F. Smith and L. R. Kelman

Final Report - Metallurgy Program 6.5.4

Metallurgy Division

May 1957

Operated by The University of Chicago
under
Contract W-31-109-eng-38

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

LIST OF TABLES

<u>Number</u>	<u>Title</u>	<u>Page</u>
I.	Nominal Compositions of Alloys Irradiated	7
II.	Chemical Analyses of Melting Stock.	7
III.	Isotopic Analysis of Plutonium Melting Stock.	7
IV.	Data for Uranium-Plutonium-Molybdenum Alloy Irradiation Specimens	8
V.	Data for Uranium-Plutonium-Fissium Alloy Irradiation Specimens and Master Alloy	8
VI.	Specimen Data on Uranium-Plutonium Base Alloys	9
VII.	Irradiation Schedule of Uranium-Plutonium Base Alloys	10

LIST OF FIGURES

<u>Number</u>	<u>Title</u>	<u>Page</u>
1.	Loading Fixture to Prevent External Contamination of Capsules	11
2.	Specimen CF-1 After Irradiation.	12
3.	Specimen CF-2 After Irradiation.	12
4.	Specimen CF-3 After Irradiation.	12
5.	Specimen CF-4 After Irradiation.	13
6.	Specimen CF-5 After Irradiation.	13
7.	Specimen CF-6 After Irradiation.	13
8.	Specimen CF-7 After Irradiation.	14
9.	Specimen CF-8 After Irradiation.	14
10.	Specimen CF-10 After Irradiation	14
11.	Specimen CF-12 After Irradiation	15
12.	Specimen CF-14 After Irradiation	15
13.	Specimen CF-15 After Irradiation	15
14.	Specimen CF-16 After Irradiation	16

IRRADIATION OF CAST URANIUM-PLUTONIUM BASE ALLOYS

by

K. F. Smith and L. R. Kelman

INTRODUCTION

Uranium-plutonium binary alloys containing 20 w/o of plutonium have been shown¹ to have very poor metallurgical properties. This fact can be attributed to the presence of small amounts of the brittle zeta phase introduced when the solid solubility limit of plutonium in alpha uranium is exceeded. This limit is about 10 or 11 w/o plutonium at room temperature.

The U-20 w/o Pu alloy in cast form contains microcracks which makes it so brittle that removal from the mold is not possible without cracking the alloy, and it falls apart on thermal cycling. In addition, this alloy is pyrophoric and extremely susceptible to irradiation damage.¹

The addition of molybdenum to uranium suppresses the zeta phase and stabilizes the gamma phase, which is body-centered cubic. It is reasonable to expect that the greater isotropy thereby introduced would be accompanied by improved metallurgical properties.

In the pyrometallurgical process for reprocessing fuel elements, studies have indicated that a group of fission product elements cannot be removed and that these impurities tend to build up to an equilibrium amount after several successive recycles of the fuel. The ratio of the amount of these elements among themselves remains constant, but the level to which they build up can be predetermined and controlled, depending on the original composition of the alloy and the efficiency of the process.

Molybdenum is one of the elements which is retained in the pyrometallurgical process, along with zirconium, ruthenium, rhodium, palladium, and technetium. The presence of molybdenum at least would be expected to be beneficial toward stability. Since the fuel would contain all these elements after a few reprocessing cycles anyway, it was planned to investigate the properties of these "fissium" alloys made up from natural alloying elements, with a view to using the alloy as a starting core material. Such strategy would by-pass the undesirable characteristics of the binary uranium-plutonium alloy. Since technetium does not occur as a natural element, it was necessary to omit this element in the fissium composition.

¹ANL-5706, "Effects of Irradiation on Cast Uranium-Plutonium Alloys," J. H. Kittel and L. R. Kelman. (To be published.)

This report describes experimental results from three groups of U-20 w/o Pu base alloy specimens which were made up at Argonne and irradiated at MTR. Nominal compositions are shown in Table I.

PREPARATION, MEASUREMENT AND ENCAPSULEMENT OF SPECIMENS

Melting and Casting

The melting stock consisted of normal uranium, plutonium, and a master alloy containing the fissium elements and uranium. The uranium and plutonium were as described in Table II, and the isotopic analysis of the plutonium is given in Table III. The master alloy used to make the uranium-plutonium-molybdenum alloy pins contained 10 w/o molybdenum, balance uranium. The composition of the master alloy used to make the uranium-plutonium-fissium alloy pins is given in Table V.

All melts were made by induction heating in vacuo using high-purity MgO crucibles for melts 97, 98, and 104 (capsules CF-1 through 7) and high-purity ThO₂ crucibles for melts 111, 113, 114, and 119 (capsules CF-8 through 16). The castings were heated to 1475° to 1500° C in 1 to 1½ hours and top poured into unheated graphite pin molds. The pin dimensions as cast were nominally 0.140 in. diameter by 1 in. long.

Heat Treatment

All of the pins were in the as cast condition except CF-5, 6, 7, and 8 which were heat treated at 560° C for 25 minutes and slowly cooled at the rate of 1.5° C per minute to 488° C, followed by a rate of approximately 4° C per minute down to room temperature.

Machining

The pins were machined to the finished sizes, shown in Tables IV and V, in a jeweler's-size lathe (Duo-Lathe) using a carbide-tipped tool in the helium atmosphere of gloveboxes. The uranium-plutonium-molybdenum alloy machined without difficulty. The character of the turnings indicated some ductility and the machined surfaces did not tarnish on continued exposure to the glovebox atmosphere. The U-20 w/o Pu-5.4 w/o Fs alloy gave considerable difficulty in machining. Only by frequent changing to a sharp tool and by the use of great care in applying pressure with the tool were the pins machined without fracture. The U-20 w/o Pu-10.8 w/o Fs alloy was somewhat less difficult to machine than the alloy of lower fissium content, but it was not as easy to machine as the uranium-plutonium-molybdenum alloy. Characteristic of all these alloy castings was a thin, hard surface skin that was especially wearing on tools.

Hardness Measurement

Where possible, Rockwell A (60-kg diamond cone indenter) hardness measurements were made on the castings and on the machined pins. The uranium-plutonium-molybdenum alloys tested for hardness without trouble, but the hardness indenter cracked small pieces of metal from the fissium alloys with a conchoidal, fine-grained fracture. Some hardnesses were obtained on the as cast 10.8 w/o fissium alloy pins, but the 5.4 w/o fissium alloy pins were so brittle that no hardness measurements could be made.

Density Measurement

The densities given in Tables IV and V were determined by loss of weight in 1,2,3-tribromopropane. Checks against an Invar standard indicated that the absolute densities should not be relied upon to better than $\pm 0.5\%$.

Other Measurements

Determination of length and of several diameters of the specimens were made by micrometer calipers.

Weights were measured on a standard analytical balance.

This completed the preirradiation series of measurements.

Loading and Sealing

The specimens were loaded into zirconium capsules using a procedure to prevent external contamination. The capsules were fixed in a standard 12-position fixture and the assembly, with plugs and tools, was sealed in a vinyl pouch. A clear vinyl plastic window was used on one face of the housing and a vinyl plastic mitten was sealed into one corner of the housing, as shown in Figure 1.

About 1.4 to 1.45 cc of NaK was introduced into each capsule by a hypodermic syringe. The stems (end plugs) were then screwed into place by a hand wrench. The assembly consisting of the plate with loaded capsules was brought into the open room by an incision seal method. No alpha activity was detected on the capsule or plate. After cutting stems to proper size by hacksaw, the end closure was made by heliarc in an open hood without incident.

The capsules were all leak tested by steam autoclave at a minimum of 170°C for 40 to 48 hours. One capsule (CF-13) failed this test, but all others appeared to be sound. The remaining capsules were then shipped to MTR for irradiation.

RESULTS

A summary of changes resulting from irradiation is given in Table VI and photographs of the specimens after irradiation are shown in Figures 2-14, inclusive. The schedule of irradiation is given in Table VII. Because of the limited number of specimens and because of unintentional differences of exposure between groups, the separation of variables was not as complete as desirable. However, some definite statements can be made even from this limited number of tests.

Under the specified conditions the following conclusions are drawn:

- (1) All specimens showed good dimensional stability except for isolated cases of end damage in which there was apparently an insufficient quantity of NaK to cover the specimen completely (CF-6, -14).
- (2) Surface finish was noted to be exceptionally good in comparison with other irradiated fissionable materials. The original shiny finish was preserved in many instances, but with some blackening in a few (CF-7, -8, -16).
- (3) Molybdenum, without the other fissium elements, seems to have slightly less embrittling effect than fissium, although it is necessary to realize that binary uranium-plutonium is much more brittle than with either of these additions.
- (4) The apparent softening due to irradiation is too consistent to be accidental. If porosity is used to explain this effect, it would seem that it would be difficult to account for hardening of the many other materials under like exposure.

A comment on interpretation of Table VI should be made. Distortions of diameter are believed to be somewhat smaller than reported because of the large percentage error in measuring small objects. A measure of this error is contained in the divergence of results between columns headed "Calculated Volume Increase" and "Density Decrease."

ACKNOWLEDGMENTS

Assistance is acknowledged in preparation of specimens by H. V. Rhude. Preirradiation measurements and capsule loading were done by J. W. Downey. Postirradiation measurements were made by F. Pausche, Jr. and C. H. Gebo, Jr. Monitor work was performed by A. C. Klank and supervised by J. H. Kittel.

Table I

NOMINAL COMPOSITIONS OF ALLOYS IRRADIATED

Element	Composition		
	U-20 w/o Pu Base Alloy, Plus		
	5 w/o Mo	10.8 w/o Fs	5.4 w/o Fs
	(CF-1 - CF-8, incl.) (w/o)	(CF-9, -10 and -12) (w/o)	(CF-14, -15 and -16) (w/o)
Mo	5	2.80	1.40
Zr	-	0.50	0.25
Ru	-	4.30	2.15
Rh	-	0.70	0.35
Pd	-	2.50	1.25

Table II

CHEMICAL ANALYSES OF MELTING STOCK

	Melting Stock			Melting Stock			Melting Stock.	
	Pu (w/o)	U (ppm)		Pu (w/o)	U (ppm)		Pu (w/o)	U (ppm)
Ag	<0.05	1	Ga	<0.02		Pt	<0.1	
Al	0.01*	<20	K		<20	Sb		< 2
As		<10	La	<0.05		Si		10-30
B	<0.02	< 0.1	Li		< 1	Sn	<0.2	< 5
Ba	<0.2		Mg	<0.02*	< 0.5-3	Sr	<0.0005	
Be		< 0.5	Mn	<0.01	0.5-5	Th	<0.2	
Bi	<0.001	< 2	Mo	<0.1	<50	Ti		<50
C**		475-730	N**		14-43	Tu	<0.01	
			Na		< 2	U	<0.5	
Ca	0.01	<20	Nb	<0.1		V	<0.1	
Cd	<0.1	< 1	Ni	<0.5	5-10	Y	<0.01	
Ce	<0.2		P		<20	Zn	<0.4	<20
Co	<0.1	< 5	Pb	<0.1	1-5	Zr	<0.05	
Cr	<0.01	< 1-2						
Cu		3-20						
Fe	<0.01	10-80						

*Presence uncertain.

**All elements are spectrochemical except C and N;
C and N are reported in ppm.

Table III

ISOTOPIC ANALYSIS OF PLUTONIUM MELTING STOCK

Plutonium Isotope	Per Cent
239	95.00 $\pm$ 0.05
240	4.71 $\pm$ 0.05
241	0.29 $\pm$ 0.01

Table IV

DATA FOR URANIUM-PLUTONIUM-MOLYBDENUM ALLOY IRRADIATION SPECIMENS

Specimen No.	CF-1	CF-2	CF-3	CF-4	CF-5	CF-6	CF-7	CF-8
Casting No.	97A	97B	98A	98B	104A	104B	104C	111B
Composition								
Pu (w/o)								
Charge Composition	21.02	21.02	20.29	20.29	21.15	21.15	21.15	21.06
Actual Composition	20.0	20.1	19.2	19.2	20.1	20.2	-	18.0
Mo (w/o)								
Charge Composition	5.01	5.01	5.05	5.05	4.99	4.99	4.99	4.99
Actual Composition	5.2	5.2	5.2	5.4	5.1	5.2	-	5.8
Casting Hardness (R _A)	-	-	68.0	69.2	76.7	76.6	75.7	74.7
Specimen Hardness (R _A)	71.5	72.8	73.0	74.0	77.0	76.4	76.5	76.0
Density (gm/cc)	17.51	17.55	17.71	17.65	17.66	17.69	17.58	17.69
Weight (gm)	2.6797	2.6184	2.6549	2.6509	2.6730	2.6426	2.6441	2.6641
Length (in.)	0.7495	0.7450	0.7500	0.7498	0.7510	0.7510	0.7452	0.7510
Diameter Range (in.)	0.1257- 0.1260	0.1245- 0.1247	0.1241- 0.1245	0.1244- 0.1247	0.1246- 0.1251	0.1240- 0.1243	0.1245- 0.1252*	0.1244- 0.1246

*Oval due to hard spot.

Table V

DATA FOR URANIUM-PLUTONIUM-FISSIUM ALLOY IRRADIATION SPECIMENS AND MASTER ALLOY

Casting No.	Master Alloy	113B	113C	114A		119B/1, 119C/1, 119D/1		
Composition (w/o)	Actual	Charge Composition	Actual	Charge Composition	Actual	Charge Composition	Actual	
Zr	0.77	0.51	-	0.51	-	0.25	-	
Mo	4.20	2.77	2.86	2.78	2.77	1.39	1.43	
Ru	6.54	4.32	-	4.33	-	2.16	-	
Rh	1.18	0.78	-	0.78	-	0.39	-	
Pd	3.83	2.53	2.45	2.54	2.20	1.26	1.22	
Pu	-	20.05	19.9	20.07	20.8	20.04	20.6	
U	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	Bal.	
Capsule No.		CF-9	CF-10	CF-12		CF-14	CF-15	CF-16
Casting Hardness (R _A)		73.2-76.7	76.9-77.9			*	*	*
Specimen Density (gm/cm ³)		16.621	16.638	16.528		17.55	17.66	17.62
Specimen Weight (gm)		2.5026	2.4988	2.4589		2.5032	2.5913	2.6596
Specimen Length (in.)		0.7442	0.7510	0.7465		0.7330	0.7320	0.7460
Specimen Dia. Range (in.)		0.1251- 0.1255	0.1240- 0.1250	0.1243- 0.1244		0.1228- 0.1230	0.1240- 0.1250	0.1251

*Hardness values were not obtained owing to the brittleness of the material.

5
Table VI

SPECIMEN DATA ON URANIUM-PLUTONIUM BASE ALLOYS

Spec. No.	Composition	Approx. C.M.T. (°C)	Calc. Burnup of all Atoms (%)	Changes due to Irradiation					
				Length Increase (%)	Diameter Increase (%)	Calc. Volume Increase (%)	Hardness Change (R _A)	Weight Change (mg)	Density Decrease (%)
CF-1	U-20 w/o Pu-5 w/o Mo	340	0.27	0.74	0	0.74	- 8.3	- 4	0.74
CF-2	U-20 w/o Pu-5 w/o Mo	280	0.43	0.67	0.56	1.80	- 8.3	-16	1.45
CF-3	U-20 w/o Pu-5 w/o Mo	270	0.20	0.79	0.48	1.76	- 8.3	2	0.68
CF-4	U-20 w/o Pu-5 w/o Mo	260	0.38	1.26	0.40	2.07	--**	1	0.62
CF-5	U-20 w/o Pu-5 w/o Mo	190	0.28	0.83	0.48	1.80	-23.9	1	1.08
CF-6	U-20 w/o Pu-5 w/o Mo	120	0.07	***	0	--	-17.2	--	--
CF-7	U-20 w/o Pu-5 w/o Mo	270	0.40	1.05	0.96	3.00	- 7.0	0	1.59
CF-8	U-20 w/o Pu-5 w/o Mo	220	0.15	0.77	0.16	0.40	- 7.7	0	0.23
CF-10	U-20 w/o Pu-10.8 w/o Fs	310	0.92	2.30	0.16	2.63	--	- 1	1.29
CF-12	U-20 w/o Pu-10.8 w/o Fs	280	0.81	0.88	0.40	1.69	--	- 1	0.18
CF-14	U-20 w/o Pu-5.4 w/o Fs	560	0.42	***	1.80	--	--	--	0.46
CF-15	U-20 w/o Pu-5.4 w/o Fs	520	0.40	0.57	0.89	2.37	--	- 1	0.91
CF-16	U-20 w/o Pu-5.4 w/o Fs	450	0.33	0.62	0.08	0.78	--	- 3	0.28

*Heat treated, see text.

**Blanks indicate breakage by indenter.

***Loss of material.

Table VII

IRRADIATION SCHEDULE OF URANIUM-PLUTONIUM BASE ALLOYS

Spec. No.	Composition ^(a)	MTR Cycle		Date in (1956)	Date out (1956)	Location in MTR	Approx. C.M.T. (°C)	Calculated Flux (nv) ($\times 10^{-13}$)	Calculated Burnup of all atoms (%)
		No.	MWD						
CF-1	U-20 w/o Pu-5 w/o Mo	66	648	2/27	3/19	A-37NE	340	2.07	0.27
CF-2	U-20 w/o Pu-5 w/o Mo	66	648	2/27	3/19	A-37NE	280	1.64	0.43
		68	677	4/9	4/30	A-11SW			
CF-3	U-20 w/o Pu-5 w/o Mo	66	648	2/27	3/19	A-37NE	270	1.56	0.20
CF-4	U-20 w/o Pu-5 w/o Mo	66	648	2/27	3/19	A-37NE	260	1.48	0.38
		68	677	4/9	4/30	A-11SW			
CF-5	U-20 w/o Pu-5 w/o Mo	66	648	2/27	3/19	A-37NE	190	1.01	0.28
		68	677	4/9	4/30	A-11SW			
CF-6	U-20 w/o Pu-5 w/o Mo	66	648	2/27	3/19	A-37NE	120	0.55	0.07
CF-7	U-20 w/o Pu-5 w/o Mo	66	648	2/27	3/19	A-37NE	270	1.56	0.40
		68	677	4/9	4/30	A-11SW			
CF-8	U-20 w/o Pu-5 w/o Mo	66	648	2/27	3/19	A-37NE	220	1.22	0.15
CF-9	U-20 w/o Pu-10.8 w/o Fs	67-70	2541	3/19	6/11	A-37SE	Missing and presumed lost at MTR		
CF-10	U-20 w/o Pu-10.8 w/o Fs	67-70	2541	3/19	6/11	A-37SE	310	1.9	0.92
CF-12	U-20 w/o Pu-10.8 w/o Fs	67-70	2541	3/19	6/11	A-37SE	280	1.7	0.81
CF-14	U-20 w/o Pu-5.4 w/o Fs	69	605	4/30	5/21	A-11NE	560	3.56	0.42
CF-15	U-20 w/o Pu-5.4 w/o Fs	69	605	4/30	5/21	A-11NE	520	3.28	0.40
CF-16	U-20 w/o Pu-5.4 w/o Fs	69	605	4/30	5/21	A-11NE	450	2.78	0.33

(a) All specimens are as cast except CF-5, -6, -7, and -8, which were held at 560°C for 25 minutes and slowly cooled.

//

Figure 1. Loading Fixture to Prevent External Contamination of Capsules.

Plate 127

2X

Figure 2. Specimen CF-1 After Irradiation.

Macro 20166

2X

Figure 3. Specimen CF-2 After Irradiation.

Macro 20167

2X

Figure 4. Specimen CF-3 After Irradiation.

Macro 20168

2X

Figure 5. Specimen CF-4 After Irradiation.

Macro 20169

2X

Figure 6. Specimen CF-5 After Irradiation.

Macro 20170

2X

Figure 7. Specimen CF-6 After Irradiation.

Macro 20171

2X

Figure 8. Specimen CF-7 After Irradiation.

Macro 20172

2X

Figure 9. Specimen CF-8 After Irradiation.

Macro 20173

2X

Figure 10. Specimen CF-10 After Irradiation.

Macro 20174

2X

Figure 11. Specimen CF-12 After Irradiation.

Macro 20175

2X

Figure 12. Specimen CF-14 After Irradiation.

Macro 20176

2X

Figure 13. Specimen CF-15 After Irradiation.

Macro 20177

2X

Figure 14. Specimen CF-16 After Irradiation.

Macro 20178

2X