Written: August 1970

Distributed: November 1970

LA-4512
UC-25, METALS, CERAMICS,
AND MATERIALS
TID-4500

LOS ALAMOS SCIENTIFIC LABORATORY
of the
University of California
LOS ALAMOS • NEW MEXICO

Studies on the U-Pu-Zr Alloy System for Fast Breeder Reactor Applications

by

D. R. Harbur
J. W. Anderson
W. J. Maraman

STUDIES ON THE U-Pu-Zr ALLOY SYSTEM FOR FAST BREEDER REACTOR APPLICATIONS

by

D. R. Harbur, J. W. Anderson, and W. J. Maraman

ABSTRACT

Pure U-Pu-Zr alloys are prepared by conventional comelting and casting techniques using NbC- or Y_2O_3-coated graphite crucibles. The centerline porosity and inverse segregation of zirconium in castings can be minimized by chill-casting.

The as-cast material may be hot extruded. The extruded product, although brittle up to 280°C, is plastic above 450°C. The alloys are very hard at ambient temperatures (400 DPH). The thermal conductivity ranged from 0.03 to 0.07 cal/sec-cm-°C (at 110°C and 892°C, respectively). The densities ranged from 16.6 g/cm^3 for U-15 wt % Pu - 6.8 wt % Zr to 15.0 g/cm^3 for U-15 wt % Pu - 13.5 wt % Zr. For the same composition range, the liquidus temperature increased from 1240 to 1425°C and the solidus increased from 1105 to 1195°C.

Chemical homogenization is accomplished by heat treatment in the γ phase (above 700°C). A thermal gradient (500 to 750°C) causes mass ion transport of zirconium. Anisotropic growth and density decrease result from repeated thermal cycles through the phase transformations.

I. INTRODUCTION

The potential use of metallic U-Pu-Zr alloys in fast breeder reactor applications has been demonstrated by investigators[1,2] at the Argonne National Laboratory (ANL) where the original alloy development, compatibility, and irradiation studies were conducted. The compatibility of these alloys with stainless steel cladding materials has given impetus to further study of this alloy system. Several characteristics of these alloys required additional investigation: their extreme chemical reactivity and oxygen-gettering properties of the molten alloys, the lengthy melt time to achieve complete dissolution of zirconium and their hardness and brittleness at ambient temperature.

This report describes the alloy development program undertaken at the Los Alamos Scientific Laboratory (LASL). These studies include the preparation, fabrication, and characterization of the U-Pu-Zr alloys.

II. EQUIPMENT AND MATERIALS

The alloying materials used in this development program were: (1) standard bomb-reduced uranium that normally contained about 200 ppm, by weight, total detected impurities with carbon ranging between 50 and 100 ppm, (2) electrorefined plutonium that contained about 200 ppm total detected impurities, and (3) crystal bar zirconium that had principal impurities of carbon and oxygen at 110 and 170 ppm, respectively.

Two methods for preparing and casting U-Pu-Zr

alloys evaluated during the course of this investigation were: (1) inductive melting and stirring on a metallic hearth, and (2) inductive melting and mechanical stirring in crucibles. The water-cooled metallic hearth consists of the water-cooled heat concentrator (Fig. 1) horizontally positioned inside a Vycor tube. The Vycor tube is attached to a vacuum source capable of 1×10^{-5} Torr. An induction coil powered by a 25-kW radiofrequency generator is positioned around the bell jar adjacent to the heat concentrator. The longitudinal split in the heat concentrator is maintained in the upright position so that the alloy charge can be contained in the barrel-shaped hole in the center of the heat concentrator.

The crucible method employs the equipment generally used in preparing Pu-base alloys (Fig. 2) and consists basically of a metal mold inside the lower furnace can. Directly above the mold, inside a Vycor tube, are the NbC- or Y_2O_3- coated graphite bottom-pour melt crucible, stopper rod, and cylindrical stirrer. The melt crucible is placed on a magnesia insulating stand and two concentric insulating tubes of MgO are positioned around the crucible.

The stopper rod and stirrer are connected to steel shafts that extend through the lid on top of the Vycor tube. Two steel heat reflecting disks are positioned below the water-cooled lid to protect the silicone rubber lid gasket. The melt crucible is heated by an induction coil placed around the Vycor tube. Inductively heated graphite molds coated with Y_2O_3 and unheated aluminum molds were used.

Extrusion studies on the cast material were performed with a 100-ton hydraulic press. The die materials were made of M-2 tool steel hardened to Rc 60-64. The design limit of the die body at the maximum extrusion temperature of 570°C was 50 tons. Extrusion dies with 60° included angles and shear dies were used. The lubricant was WS_2 commercially available in a pressurized spray can under the trade name "Tungspray".

A Fenn four-die swaging machine with high-temperature dies was also used in the fabrication studies. The dies have a 30% area reduction over a 1.5 in. length. A manual feed mechanism and resistance tube furnace were incorporated as auxiliary equipment that could be used with the swaging machine.

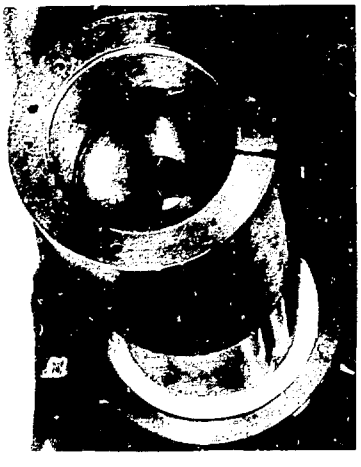


Fig. 1. Water-cooled heat concentrator used in metallic hearth for preparing U-Pu-Zr alloy buttons. Maximum charge is 100 g.

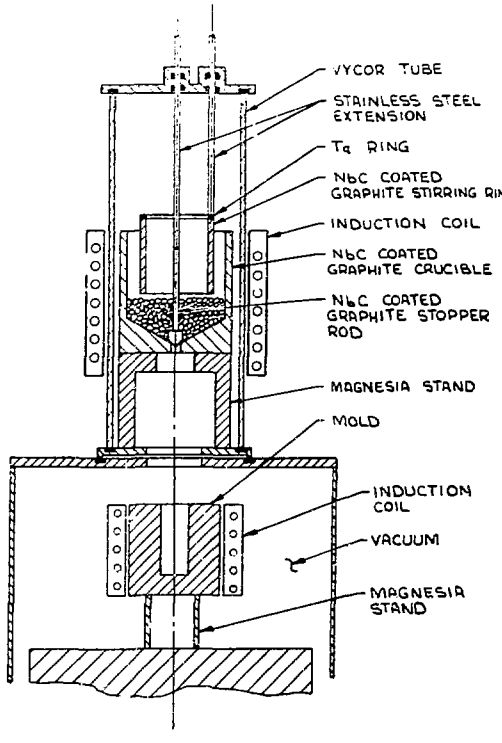


Fig. 2. Conventional vacuum furnace for preparing U-Pu-Zr alloy castings.

III. PROCEDURE

Preparation of the alloys by inductive melting and stirring on a metallic hearth is accomplished by placing the charge in the central cavity of the copper heat concentrator, evacuating the chamber to at least 10^{-4} Torr, and heating the charge with the induction coil. Once enough power is supplied to melt the charge, the molten metal conforms to the bottom of the central hole in the heat concentrator. The metal adjacent to the wall of the water-cooled heat concentrator forms a protective frozen skin that prevents reaction between the hearth and the alloy button. The metal on top of the alloy button is heated to several hundred degrees above its melting point and the electromagnetic fields cause this molten portion of the alloy button to be vigorously stirred.

Two ceramic coatings were developed for this reactor program. A 0.002- to 0.003-in. coating of NbC is applied to the graphite crucibles by LASL Group CMB-3. The Y_2O_3 coating, now commercially available from Acheson Colloids Co. (No. EC 3327X), can be easily sprayed onto a graphite or metal surface by using an inert-gas spray gun. The surface of the part being coated is heated to 150 to 200°C on a hot plate and thin coats of the Y_2O_3 are sprayed on to a total thickness of 0.002 to 0.003 in. Any loose particles of Y_2O_3 are rubbed off the surface with steel wool.

The conventional alloying and casting technique adapted for the alloy development program consists of comelting the metals (uranium, plutonium, and zirconium) in a NbC- or Y_2O_3-coated graphite bottom-pour melt crucible after assembling and evacuating the casting equipment as shown in Fig. 2. The molten metals are heated to 1400 to 1500°C and are mechanically stirred for 30 min to assure the dissolution of zirconium into the melt. Finally, the stopper rod is raised and the melt is chill-cast into the ambient-temperature aluminum mold. For those runs in which the alloy was cast into a Y_2O_3-coated graphite mold, the mold was inductively heated to the desired temperature before alloying the three metals.

Extrusion billets were machined, using carbide-tipped tools, from 0.75-in.-diam chill-cast rods. The billets were about 2 in. long with a blunt nose (55° included angle) machined on one end. These cast billets were extruded by standard hot extrusion methods in which the die body and billet were heated to 500 to 570°C in vacuo and then a force of up to 50 tons was applied to the ram. As the material began to flow, the pressure was lowered to maintain a constant extrusion speed of 0.5 in./min throughout the run. The alloy was extruded into a slightly oversize stainless steel tube to keep the extruded rod straight. The WS_2 lubricant was liberally sprayed onto the die, die body, ram, pusher, and billet before each run.

Standard swaging practices were followed in attempts to swage this alloy. The swaging stock was held in the chuck of the mechanical feed mechanism and heated to the desired temperature in the resistance-heated tube furnace. The furnace was then lowered and the material was fed into the swaging dies. In some cases, the swaging stock was placed inside a stainless steel tube. Both ends of the stainless steel tube were swaged down to contain the rod. Finally, the enclosed rod was heated and swaged as above.

To determine the effects of thermal cycling the U-Pu-Zr alloys through their various solid-state transformations, specimens were encapsulated in Type 316 stainless steel tubing and placed in a resistance-heated tube furnace programmed to cycle the specimen between two given temperatures. The specimen was held for 10 min at each temperature; it took about 15 min to heat or to cool the specimens from one temperature to the other. At the two temperature extremes, the temperature of the specimen actually fluctuated 10 to 15°C.

A thermal gradient of 250°C was maintained on a 1-in.-long U-Pu-Zr specimen encapsulated in a special Type 316 stainless steel lined copper tube. One end of the copper tube was embedded in a copper bar heated to 750°C in an enclosed tube furnace. The other end of the copper tube extended out of the furnace and had aluminum cooling fins attached to it.

IV. RESULTS AND DISCUSSION

A. Casting

Two ceramic coatings that can be easily applied to standard bottom-pour graphite crucibles were

developed so that conventional alloying and casting techniques could be used in this alloy development program. The more inert coating to the molten alloy is NbC applied to the graphite surfaces. In general, the NbC-coated graphite crucibles are usable for only one run because the molten alloy completely wets the crucible. If, however, the stopper rod is reseated immediately after the pour and if the crucible is allowed to cool below 100°C in an inert atmosphere before removing it from the furnace, then more than one run is possible. The NbC coating is badly oxidized above 300°C in an air atmosphere. The amount of niobium dissolved into the melt is below 25 ppm and the oxygen pick-up is negligible.

The Y_2O_3 coating was codeveloped by LASL and Acheson Colloids Co., and consists of a water suspension of colloidal Y_2O_3 with a K_2SiO_3 binder added. The Y_2O_3 coating is very abrasion-resistant and is not subject to spalling during thermal cycling. This coating is unwetted by the U-Pu-Zr melt and can be reused. Alloys prepared in Y_2O_3-coated graphite crucibles were contaminated with about 100 ppm of both silicon and oxyge .

The minimum diameter to which a 15-in.-long rod can be gravity-cast in a mold heated to 1050°C is about 0.3 in. These rods are subject to centerline porosity, piping, and inverse segregation. The segregation and porosity can be reduced by chill-casting the metal into an aluminum billet mold with a 0.75-in.-diam cavity. Chemical analyses of three typical batches of the cast U-Pu-Zr alloys made by the chill-casting technique are given in Table I. As is typical for inverse segregation, the longitudinal variation in zirconium content was minimal, whereas the radial variation was as great as 0.8 wt % Zr. The inverse segregation of zirconium in these ternary alloys could not be correlated to any variations in the microstructure.

A photomicrograph of the U-15 wt % Pu-10 wt % Zr alloy in the as-chill cast condition is shown in Fig. 3 along with an EMX scan of a typical area. Powder x-ray diffraction and diffractometer studies by LASL Group CMF-5 identified three phases in this alloy; an αU matrix with a small amount of UZr_2 and a lesser amount of the UPu ζ phase. The location of areas rich in the αU and UZr_2 phases on the EMX scans were readily discernable. Metallographic examination of alloys prepared with more than 200-ppm oxygen showed a small amount of a white globular phase that EMX data showed to be extremely high in zirconium. These particles are similar to the ones purported to be oxygen-stabilized αZr by O'Boyle[3] of ANL. Microhardness readings on these small (1 to 5 μ) particles showed them to be extremely hard with values as high as 2500 DPH. The presence of such particles would no doubt influence the low-temperature tensile properties of these alloys. Isolated areas containing these particles were found even in material that had less than 80 ppm of oxygen.

Attempts to prepare homogeneous U-Pu-Zr alloys by the cold crucible technique, whereby the molten alloy is in contact with a water-cooled hearth, were unsuccessful even though the alloy buttons were broken and inverted several times. These ternary alloys had a minimum zirconium variation from top to bottom of 2 wt % due to a zone refining effect associated with the liquid-solid interface within the alloy button. It has been concluded that this technique, while feasible, would necessitate the development of a process whereby the entire charge could be levitated. It should be noted that there was no pickup of copper found in any of the alloys prepared in this manner.

B. Extrusion

Further fabrication of cast billets was accomplished by standard hot extrusion methods. It was found that when using a 60° included-angle die less force was required to start the material flowing than if a shear die were used. When using a 60° die, a billet with a 55° included-angle nose started flowing at a lower pressure than did a right cylindrical billet or a billet with a 60 or 45° included-angle nose. With a 60° die, 0.75-in.-diam, U-15 wt % Pu-12 wt % Zr billets began to extrude into 0.375-in.-diam rods with a 50-ton force at 510°C. This force was decreased to 45 tons at 520°C and to 40 tons at 530°C. After the material began to flow, the runout force necessary to maintain a given extrusion rate always continued to decrease throughout the run. For the above set of conditions, the runout force was about 30 tons at 520°C.

TABLE I

CHEMICAL ANALYSIS OF CAST U-Pu-Zr ALLOYS[a]

Element	JUZ-98071		JUZ-98069		JUZ-98074	
	Top	Bottom	Top	Bottom	Top	Bottom
Pu	14.79 wt %	14.89 wt %	15.15 wt %	15.10 wt %	14.60 wt %	14.62 wt %
Zr	6.8 to 7.4 wt %	6.6 to 7.0 wt %	10.1 to 10.4 wt %	9.9 to 10.2 wt %	13.3 to 14.1 wt %	13.4 to 13.6 wt %
U	78.1 wt %	77.9 wt %	75.4 wt %	74.7 wt %	72.3 wt %	72.0 wt %
O	90	90	85	80	80	65
C	130		130	130	40	
H	< 5		10	5	5	
Fe	240		58	39	240	
Ga	<12		79	59	< 12	
Nb	14		19	18	24	
Th	17		13	11	18	
W	15		16	16	32	
Li	< 1		< 2	< 2	< 1	
Be	< 1		< 1	< 1	< 1	
B	< 1		< 1	< 1	< 1	
Na	2		< 2	< 2	< 2	
Mg	5		< 5	< 5	< 5	
Al	10		25	25	10	
Si	30		30	30	40	
P	<50		<50	<50	< 50	
Ca	< 5		< 5	< 5	< 5	
Cr	< 5		<10	<10	< 5	
Mn	3		2	2	< 2	
Ni	50		10	10	10	
Cu	5		5	5	< 2	
Zn	20		<10	<10	< 10	
Sr	5		< 5	< 5	< 5	
Cd	<10		<10	<10	< 10	
Sn	< 5		< 2	< 2	< 5	
Pb	< 5		<10	<10	< 5	
Bi	< 2		< 2	< 2	< 2	

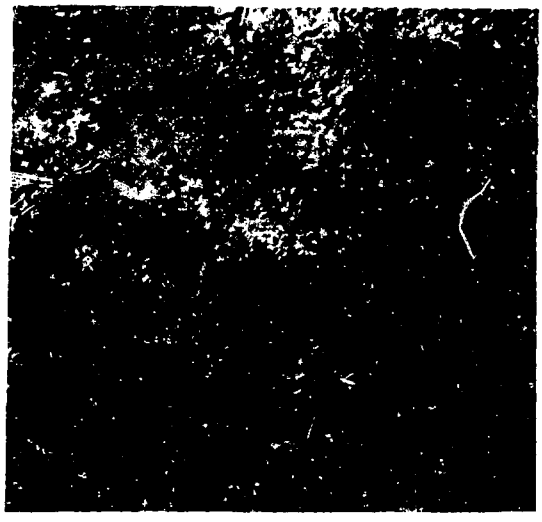
[a]Expressed as parts per million by weight or percent by weight (wt %).

Increasing the extrusion ratio from 4:1 to 9:1 made it necessary to increase the extrusion temperature to 570°C to keep the peak extrusion force at 50 tons, which was the design maximum for the equipment used. The runout force for these extrusions was 35 tons.

About 10 tons less force was necessary to extrude U-15 wt % Pu-6 wt % Zr alloy billets than for U-15 wt % Pu-12 wt % Zr alloy billets. The maximum extrusion temperature used was 570°C, because this is the temperature limit for standard iron-base alloy dies and is below any solid-state transformations in the U-Pu-Zr alloy system. The microstructure of the chill-cast alloy after extrusion is shown in Fig. 4. The extrusion process simply compressed the radial microstructure of the alloy. Some recrystallization occurred in the extruded alloys at extrusion rates below 0.5 in./min; however, the degree of recrystallization was minimal.

C. Swaging

Attempts to swage either the cast or extruded material were not very promising. Neither of these products could be swaged bare even though temperatures well into the γ-phase temperature region were tried. It should be noted that although the rod was heated, the dies were not; and the thinness of the heated rod no doubt resulted in rapid cooling of the rod in the swaging dies. The extruded material could be swaged provided that the material was first placed inside of a thin-walled stainless steel tube. The first pass through the swaging machine could be made at temperatures as low as 300°C. The material was noticeably toughened by the swaging oper-



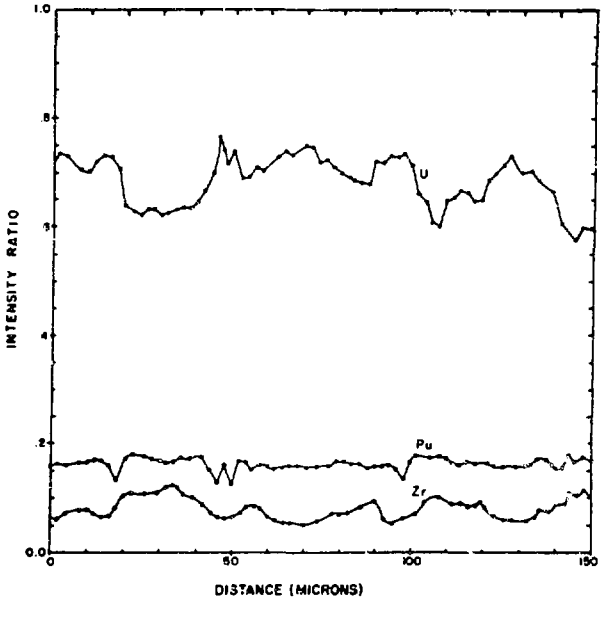


Fig. 3. Photomicrograph and EMX scan of as-cast U-15 wt % Pu-10 wt % Zr alloy.

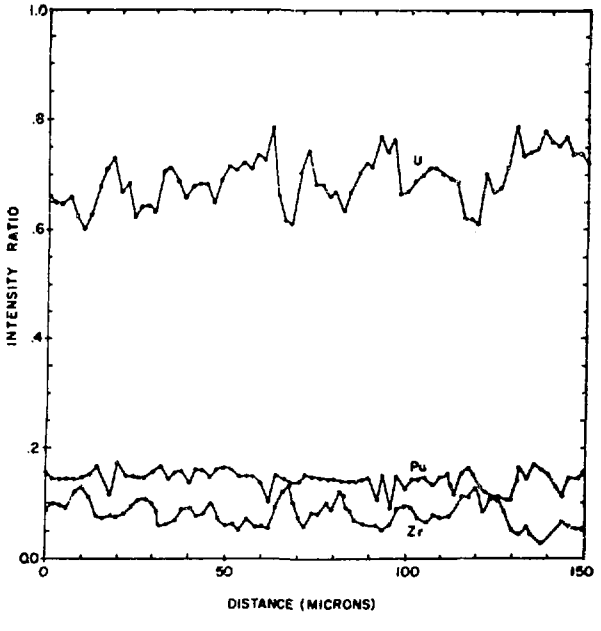


Fig. 4. Photomicrograph and EMX scan of extruded U-15 wt % Pu-10 wt % Zr alloy.

ation. Area reductions of 30% in the alloy were accomplished when using 0.030-in.-wall stainless steel tubing. When a 0.060-in.-wall stainless tubing was used, most of the reduction occurred in the tubing and only 7% area reduction was accomplished in the alloy rod. During the second pass through the swaging machine, the length of the tubing increased more than did the length of the rod, which caused the rod to rupture. Although no physical reaction between the alloy rod and the stainless steel tubing was apparent, there was a mechanical bond that made it necessary to machine the tubing off of the rod.

The fabrication studies on this alloy system show that the most practical method developed for making 0.144-in.-diam rods with a large length-to-diameter ratio lies in the bare extrusion of the chill-cast billets. With a 100-to 150-ton press, no difficulty should be

encountered in extruding 0.75-in.-diam billets down to the final EBR-II size.

D. Physical Properties

The tensile properties of several U-Pu-Zr alloys are given in Table II. The room-temperature tensile strength of the extruded material was at a maximum of 97,000 psi for the U-15 wt % Pu-6 wt % Zr alloy decreasing to a minimum of 70,000 psi for the U-15 wt % Pu-10 wt % Zr alloy and again increasing to 84,000 psi for the U-15 wt % Pu-13.5 wt % Zr alloy. All these alloys were of high purity, having 125, 70, and 180 ppm oxygen, respectively. The maximum tensile strength for a U-15 wt % Pu-12.2 wt % Zr alloy in the as-cast condition was 61,000 psi. Tensile strengths as much as 17,000 psi lower than this value were obtained, but small cavities were always evident at the fracture surface. These small cavities were a result of centerline porosity that occurred during the casting operation. All U-Pu-Zr tensile bars fractured in a brittle manner when tested at ambient temperature. The U-15 wt % Pu-10 wt % Zr alloy began to exhibit some ductility at 350°C, and became quite plastic at 400°C having an elongation of 53% over the 2-in. gauge section of the tensile bar. The U-15 wt % Pu-6 wt % Zr alloy was quite plastic at 290°C, elongating 11% during a short-time creep test at 5360 psi. The short-time creep data between 290 and 500°C for three different U-Pu-Zr alloys are given in Table III. The specimens were held at constant load during test so that the indicated stresses are the initial ones and the strain rate was not controlled. All tensile-creep test bars were reduced to a tapered point at the fracture interface even though the entire 2-in.

TABLE II

TENSILE PROPERTIES OF U-Pu-Zr ALLOYS[a]

Alloy Composition Nominal wt %			Temp. °C	UTS psi	Y.S.[b] psi	Elongation %	Fabrication History	E psi x 10^6
U	Pu	Zr						
75	15	10	25	70,000	-	Nil	as-extruded	2.2
			300	39,000	-	Nil	as-extruded	2.1
			350	44,000	44,000	3	as-extruded	0.9
			400	14,000	10,000	53	as-extruded	0.4
73.3	14	11.7	25	76,000	-	Nil	as-extruded	2.3
			100	80,000	-	Nil	as-extruded	2.2
72.5	15	12.5	25	95,700	-	Nil	as-extruded	2.7
			300	64,800	-	Nil	as-extruded	2.6
			350	55,700	55,000	Nil	as-extruded	2.5
			450	8,140	6,800	31	as-extruded	0.4
			525	5,740	4,100	62.5	as-extruded	0.5
71.5	15	13.5	25	84,000	-	Nil	as-extruded	1.9
79	15	6	25	97,000	-	Nil	as-extruded	2.5
72.8	15	12.2	25	61,000	-	Nil	as-cast	1.4

[a] Tensile test performed at a strain rate of 0.015 in./in./min.
[b] Yield strength at 0.2% offset.

TABLE III

TIME (MIN) TO ATTAIN 2% STRAIN IN U-Pu-Zr ALLOYS IN THE AS-EXTRUDED CONDITION

Alloy Composition Nominal wt %			Stress, psi	Temperature, °C			
				290	350	400	500
U	Pu	Zr					
75	15	10	2,000	-	-	-	20
			3,000	-	-	-	5
			8,000	-	-	30	failed
			10,000	-	-	9	failed
			11,000	-	-	3	failed
			20,000	-	300	failed	failed
			30,000	-	20	failed	failed
			40,000	-	9	failed	failed
72.5	15	12.5	2,000	-	-	-	8
			3,000	-	-	-	4
			15,000	-	-	15	failed
			17,000	-	-	8	failed
			19,000	-	-	4	failed
79	15	6	1,000	-	-	-	0.3
			5,000	30	failed	failed	failed
			6,000	9	failed	failed	failed

gauge section was carefully maintained at the test temperature, which shows the extreme ductility of the material at these temperature.

The variation in densities with zirconium content in both the cast and extruded conditions is given in Fig. 5. Hardness values for the as-cast and as-extruded material were identical, with the value of the 6 and 10 wt % Zr material being 440 DPH, whereas the 13.5 wt % Zr material had a hardness of 380 DPH. The elevated temperature (hot) hardness of a U-15 wt % Pu-6.8 wt % Zr alloy was determined between 400 and 800°C using a 200-*g* load. These data are summarized in Table IV.

E. Thermal Conductivity

The thermal conductivity of an extruded U-15 wt % Pu-6.8 wt % Zr alloy specimen was determined between

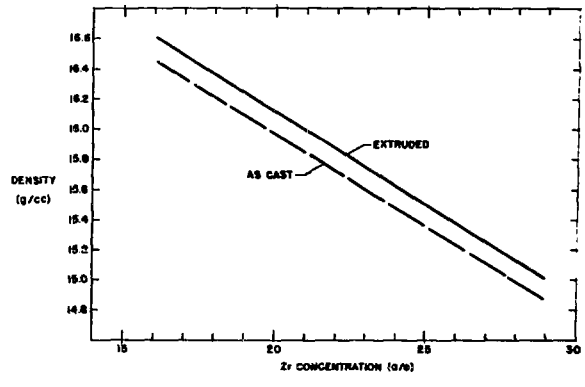


Fig. 5. Variation of density with Zr content of U-15 wt % Pu-X wt % Zr alloys in the as-cast and extruded condition.

Table IV

HOT HARDNESS OF U-15 wt % Pu-6.8 wt % Zr
(200 g LOAD)

Temperature (°C)	DPHN	Temperature (°C)	DPHN
800	3.4	625	18.2
725	4.3	610	20.2
730	5.4	600	39.6
720	5.6	590	46.6
710	7.4	580	59.1
700	6.4	570	60.9
690	8.8	550	83.5
680	8.8	500	148
670	10.0	450	202
650	11.0	400	256

110° and 892°C. The values obtained increased from 0.0305 to 0.0757 cal/sec-cm-°C.

F. Differential Thermal Analysis

The thermal transitions of two samples of extruded U-Pu-Zr alloys have been observed by using differential thermal analysis (DTA) techniques. Thermocouples were used for observation of solid transformations below 1000°C. The observed temperatures of solid transformations are listed in Table V. The temperature ranges of energy absorption or release listed here are the ranges covered by sample temperatures between the beginning of the arrest and the time of maximum lag of sample temperature behind reference temperature. It is estimated that not less than 75% (and in many cases more than 90%) of the energy involved in the transition is transferred in this interval. The transformations listed in Table V are labeled "A" and "B" to allow easy comparison of temperatures observed for the two different alloys.

The thermal arrests of the U-15 wt % Pu-6.8 wt % Zr specimen could not be separated into additional arrests. Cooling arrest B of the U-15 wt % Pu-13.5 wt % Zr alloy could, however, be separated into two overlapping arrests with a reasonable degree of confidence. The minor transition was in the range 626° to 618°C, but a transition involving four times as much energy covered the range 618 to 610°C. The energy of Transition A was about equal to that of transition B for the alloy with the higher zirconium content. For the lower zirconium content alloy, the energy of transition B was about four times that of transition A.

TABLE V

THERMAL ARRESTS RANGES OF TEMPERATURE OVER WHICH A MAJOR FRACTION OF ENERGY RELEASE OR ABSORPTION OCCURS IN U-Pu-ALLOYS

Alloy	Transition	Heating Arrests Start (°C)	Heating Arrests Range (°C)	Cooling Arrests Start (°C)	Cooling Arrests Range (°C)
U-15 wt % Pu-6.8 wt % Zr	A	588	588-598	594	594-586
U-15 wt % Pu-6.8 wt % Zr	B	643	643-658	634	634-626
U-15 wt % Pu-13.5 wt % Zr	A	588	588-593	593	593-586
U-15 wt % Pu-13.5 wt % Zr	B	638	638-653	626	626-610
100% U	α-β	665 (standard)	665-669	supercooled	
100% U	β-γ	775	775-776	supercooled	

No high-temperature x-ray data were obtained to help delineate the transformation responsible for the heat effects detected at transitions A and B.

Solidus and liquidus temperatures of the two alloys are as follows:

Alloy	Solidus °C	Liquidus, °C
U-15 wt % Pu-6.8 wt % Zr	1105 ± 10	1240 ± 20
U-15 wt % Pu-13.5 wt % Zr	1195 ± 10	1425 ± 20

The solidus was determined from DTA heating curves whereas the liquidus was determined from the DTA cooling curves. These temperatures are in fair agreement with those predicted from the solidus and liquidus lines of the isopleth between U-15 wt % Pu and pure zirconium, using the assumption of ideal liquid and solid solution behavior.

G. Thermal Stability

The effects of holding the extruded material in the γ-phase temperature region are shown by the photomicrograph and EMX scan in Fig. 6. After 17 days at 750°C, the alloy has become almost completely homogenized. The density of this specimen decreased 0.07 g/cm^3 during this heat treatment, presumably due to homogenization and the resultant redistribution of phases.

The photomicrograph shown in Fig. 7 of a specimen heated at 650°C in a multiphase region depicts the development of a duplex microstructure. The EMX data shows that the microstructure developed at 650°C resulted in alternating αU-UZr_2 grains with the plutonium being mutually soluble in each. Again the density decreased 0.09 g/cm^3 during heat treatment due to the resultant redistribution of phases.

By holding the extruded material for 19 days in

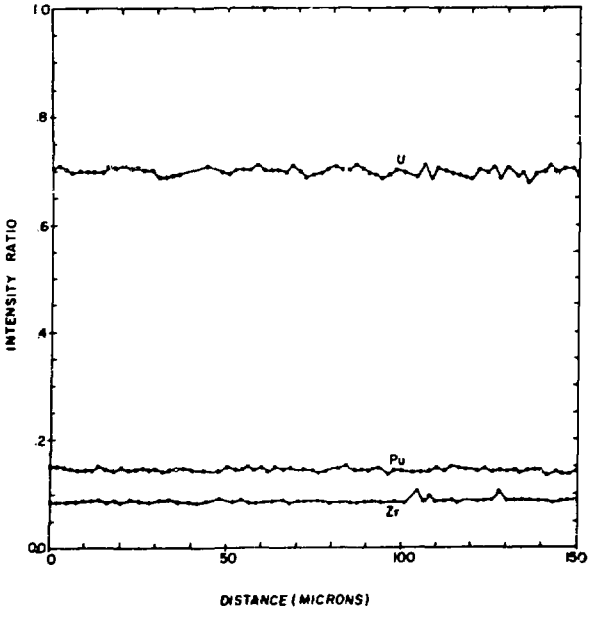


Fig. 6. Photomicrograph and EMX scan of extruded U-15 wt % Pu-12 wt % Zr alloy after a 17-day heat treatment in the γ phase at 750°C. Material contains 300 ppm oxygen. Note α zirconium particles in photomicrograph.

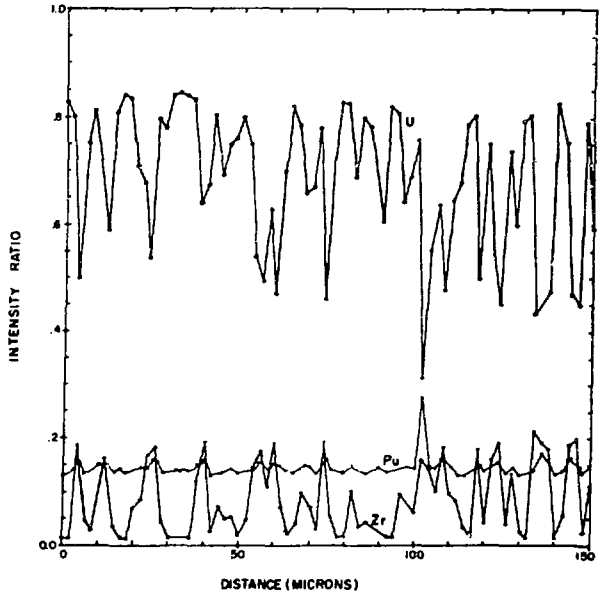


Fig. 7. Photomicrograph and EMX scan of extruded U-15 wt % Pu-12 wt % Zr alloy after an 18-day heat treatment in the multiphase region at 650°C.

the high α-phase temperature region at 500°C, the complex microstructure and EMX scan shown in Fig. 8 developed. These data indicate the presence of the three phases (αU, UZr_2, and UPu ζ) found in the as-cast microstructure with the plutonium much less soluble in the αU phase causing the more extensive formation of the UPu ζ phase. The density decrease caused by this heat treatment was only 0.02 g/cm^3. Comparison of the plutonium distribution resulting from the 500 and 650°C heat treatments indicate that plutonium is much more soluble in the βU phase than in the αU phase.

To differentiate the effects of thermal cycling from

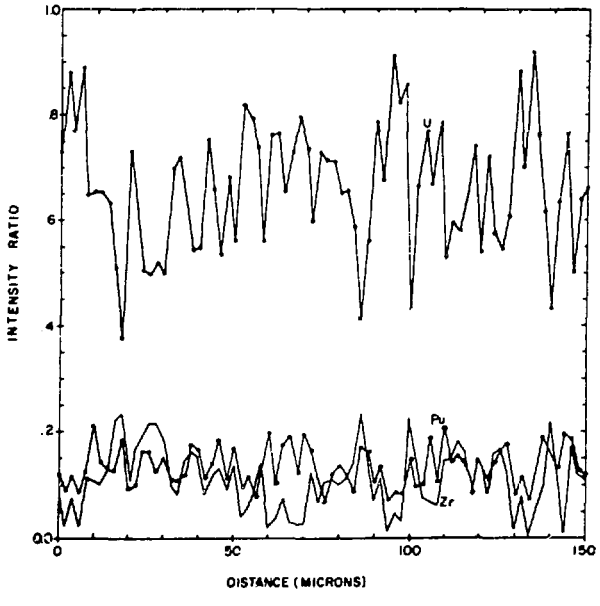


Fig. 8. Photomicrograph and EMX scan of extruded U-15 wt % Pu-12 wt % Zr alloy after a 19-day heat treatment in the high α-matrix phase temperature region at 500°C.

those due to irradiation, thermal cycling experiments were performed on U-15 wt % Pu-12 wt % Zr rods in the as-extruded condition. Three separate thermal cycles were investigated: (1) 500° (α matrix phase) to 650°C (multiphase region); (2) 500° (α matrix phase) to 750°C (γ phase); and (3) 630°C (multiphase region) to 750°C (γ phase). The behavior of this material during the various thermal cycles is shown in Fig. 9.

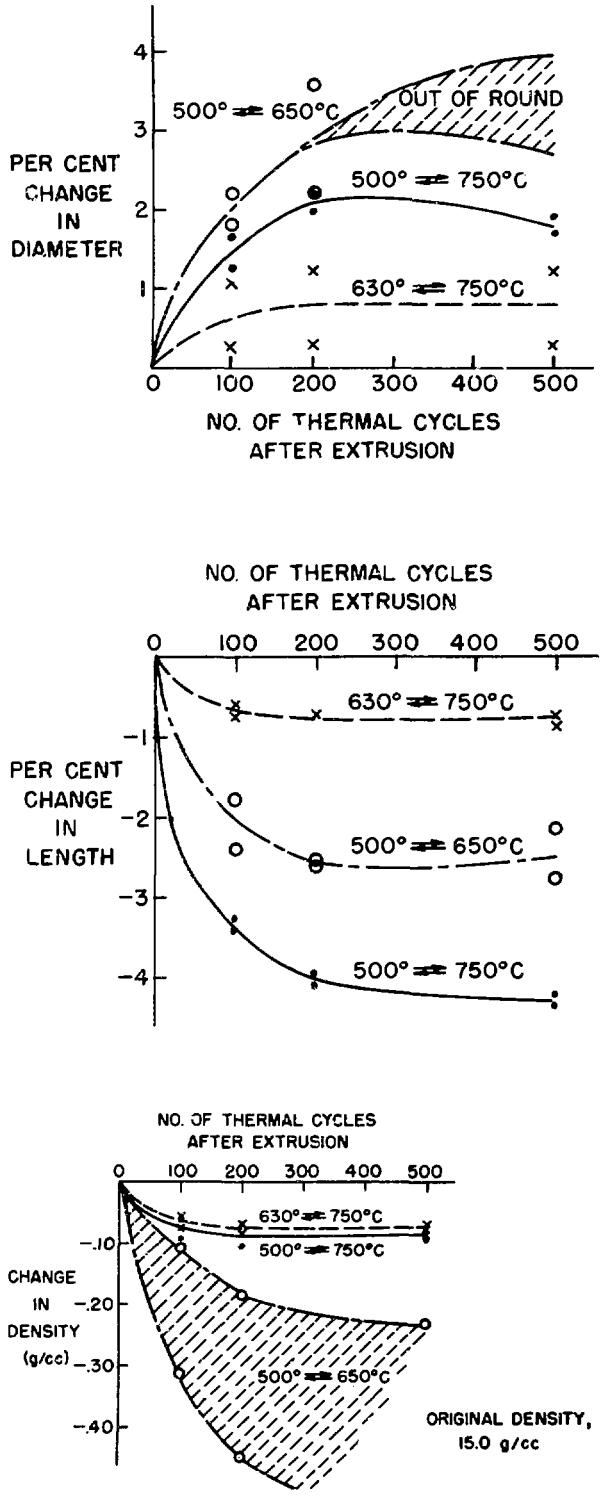


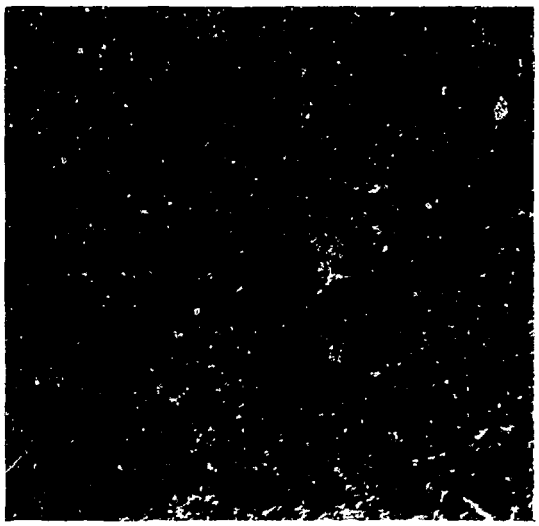
Fig. 9. Physical changes in as extruded U-15 wt % Pu-12 wt % Zr alloy due to thermal cycling.

Each of the three thermal cycles caused the extruded material to exhibit aniostropic growth patterns (that is, increase in diameter and decrease in length) up through 200 cycles. This aniostropic growth is no doubt caused by the preferred orientation that exists due to the extrusion process. Metallographic examination of these specimens after 100 thermal cycles showed all specimens to have a recrystallized-equiaxed grain structure; however, the preferred orientation of the specimen had not been fully eliminated. The EMX data for the specimens after 100 cycles showed that a great deal of homogenization had occurred during all three thermal cycles, especially those cycled in the γ-phase temperature region.

The resulting microstructures after 500 thermal cycles, together with typical EMX scans, are shown in Figs. 10, 11, and 12 for the three different thermal cycles investigated. The material cycled between 500 and 650°C became very fine grained, such that an almost equal distribution of phases was picked up by the 1-μ-wide microprobe beam. At about 100-μ intervals there were 20-μ-wide bands that contained a large concentration of the UZr_2 phase. The reason for the development of the UZr_2 rich areas is unknown. Metallographic examination of this matrix reveals at least a two-phase microstructure with only a 0.5 μ separation between phases. Because the EMX readings were taken at 2-μ intervals, the multiple phase nature of this fine-grained matrix could not be delineated.

A catastrophic density decrease occurred in the specimens cycled between 500 and 650°C. After 500 thermal cycles, the density decrease was 0.23 to 0.68 g/cm^3. Both specimens had developed shallow longitudinal grooves. A 0.030-in.-diam hole had opened in the center of the specimen that had the greater density decrease. The center of the other specimen had numerous smaller holes. Before the thermal cycling experiments, no internal voids in the extruded rods were detectable by radiography. It should be noted, however, that centerline porosity was present in the cast material and that these voids were closed, but probably not welded shut, during the extrusion operation.

The EMX data of the specimens cycled into the



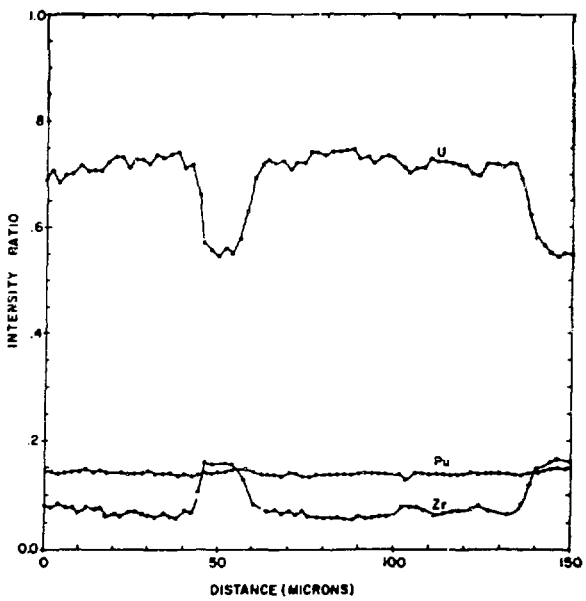


Fig. 10. Photomicrograph and EMX scan of extruded U-15 wt % Pu-12 wt % Zr alloy after 500 thermal cycles between 500°C (α-matrix phase) and 650°C (multiphase).

γ phase at 750°C from either 500 or 650°C shows a coarsening of grain size with grains 10- to 20-μ wide rich in the UPu ζ-phase. The areas between these grains are rich in the αU-UZr_2 phases, with the plutonium concentration lower than the apparent solubility of plutonium in δU and higher than the apparent solubility of plutonium in αU. From the photomicrographs, the areas rich in the UPu ζ phase are less extensive in the material cycled no lower

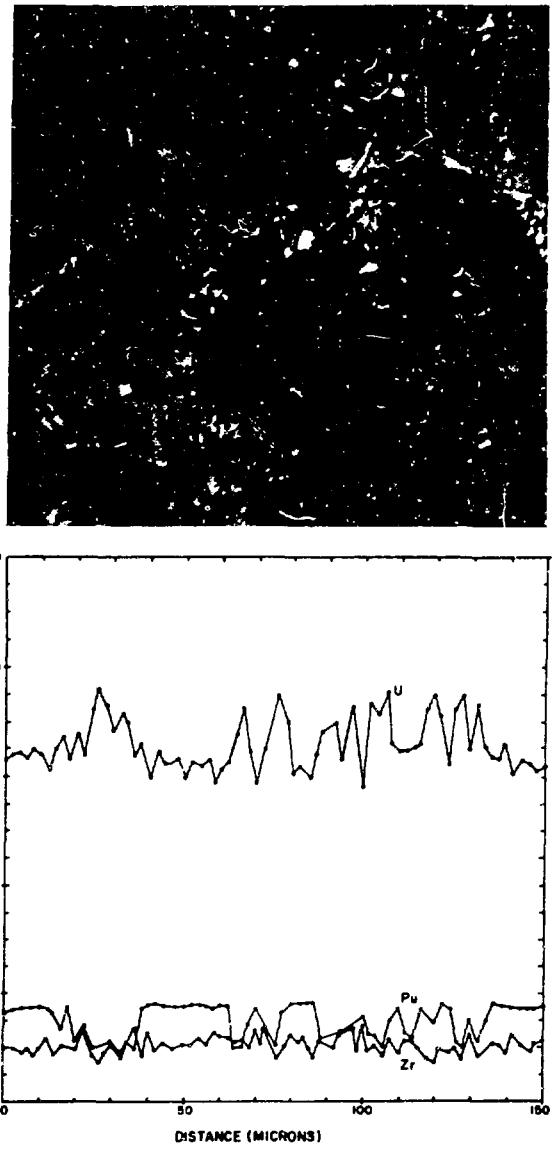


Fig. 11. Photomicrograph and EMX scan of extruded U-15 wt % Pu-12 wt % Zr alloy after 500 thermal cycles between 500°C (α-matrix phase) and 750°C (γ phase).

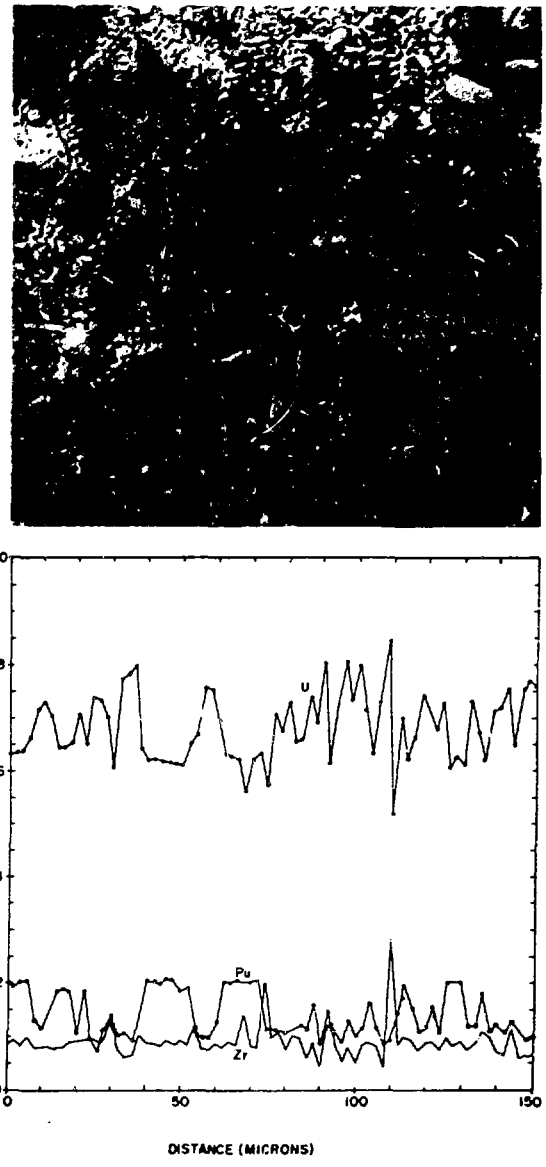


Fig. 12. Photomicrograph and EMX scan of extruded U-15 wt % Pu-12 wt % Zr alloy after 500 thermal cycles between 630°C (multiphase) and 750°C (γ phase).

than 630°C.

Because most of the original irradiation data were determined at ANL for this alloy while both radial and longitudinal thermal gradient were imposed upon the fuel pin, it was felt desirable to determine the effects of such a thermal gradient upon an unirradiated rod. Thus, one end of a 1-in.-long, 0.178-in.-diam U-15 wt % Pu-13.4 wt % Zr rod was held for 17 days in the γ-phase temperature region at 750°C and the other end was maintained in the α-phase temperature region at 500°C. Subsequent examination of the rod using metallographic and EMX techniques showed an abrupt change between the area held in the γ-phase temperature region and the adjacent area held in the multiphase temperature region (Fig. 13). The homogeneous matrix of the material heat-treated in the γ phase abruptly changed into a large duplex grain

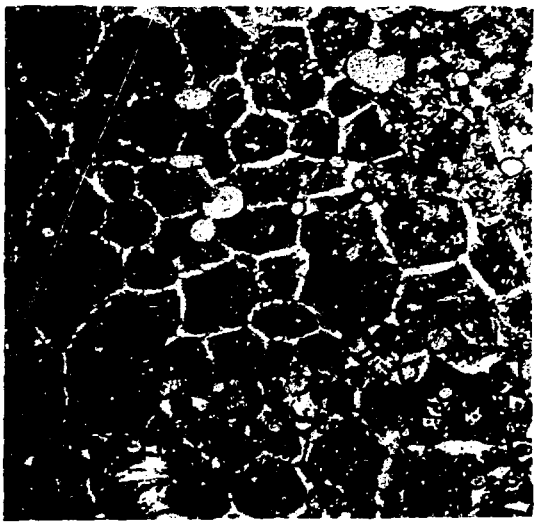


Fig. 13. U-15 wt % Pu-13.4 wt % Zr alloy rod held for 17 days with a thermal gradient along the length of the rod. End to left of photomicrograph toward 750°C end. Depicts γ phase microstructure at left changing into a multiphase microstructure at right.

structure.

Two chemically different phases were identifiable by EMX techniques in the duplex grain region adjacent to the homogeneous material. One phase contained 85 wt % U-15 wt % Pu with almost no zirconium, and the other phase contained 65 wt % U-15 wt % Pu-20 wt % Zr. The large duplex grains gradually decreased in size and the microstructure finally evolved into one similar to the material held at 500°C for 19 days (Fig. 8).

Chemical analysis of approximately 0.15-in.-long sections along this rod gave the composition profile shown in Fig. 14. The section of rod designated 2A contained the region that had the large duplex grain structure, as well as some material on either side of the region. The actual decrease of zirconium in the large duplex grain region, which was the area held at ~645°C, was about 7.5 wt % over a length of about 200 μ. The microprobe data indicate that most, if not all, of this zirconium diffused toward the colder region of the rod. During the life of a fuel pin, the magnitude and the relative position of the inherent thermal gradient are continually shifting. It is not known whether the shifting of the thermal gradient

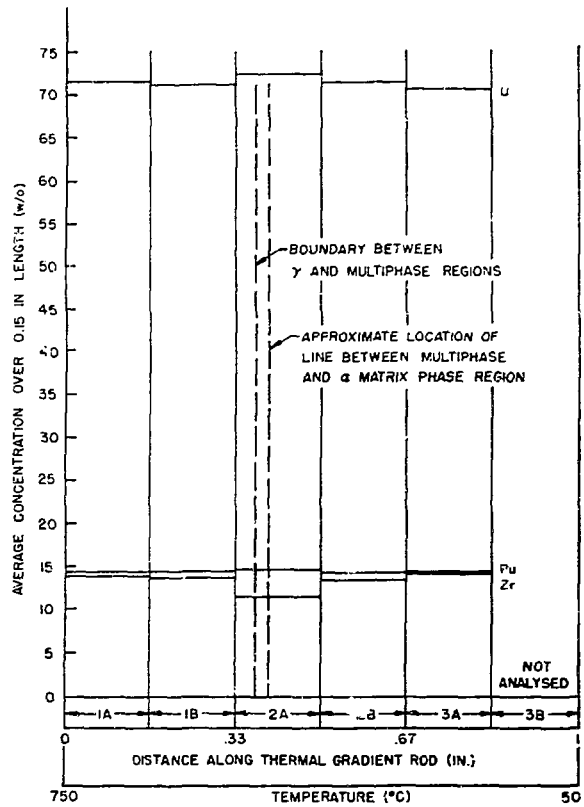


Fig. 14. Composition profile along the length of a U-15 wt % Pu-13.4 wt % Zr rod held in a thermal gradient. Obtained by dissolving and analyzing ~0.15-in.-long sections of the rod.

will tend to diminish or magnify the mass ion transport of zirconium observed in this study.

V. SUMMARY

Alloys of the U-Pu-Zr ternary system can be prepared by conventional casting techniques with little addition of impurities provided that NbC- or Y_2O_3-coated graphite crucibles are used. The cast product is subject to inverse segregation of zirconium and centerline porosity that can be minimized by chill-casting into metal molds. The chill-cast material can readily be hot extruded in the range of 520 to 570°C.

The extruded material is quite brittle up to 280°C, becoming plastic above 450°C. The alloys are very hard at ambient temperature (400 DPH) and require the use of carbide-tipped tools for machining. For the alloys tested, the density varied from 16.5 g/cm^3 for the low zirconium

alloys down to 15.0 g/cm^3 for the high zirconium alloys.

As the zirconium content is lowered from 13 to 6.8 wt %, the liquidus temperature decreases from 1425 to 1240°C and the solidus temperature decreases from 1195 to 1105°C. Chemical homogenization of the three major components of this alloy system can be accomplished by γ-phase heat treatment above 700°C. Microstructural phase coarsening, caused by growth of the three major phases present in this alloy system at ambient, resulted from heat treatments between 500 and 650°C. Maintaining a thermal gradient (500 to 750°C) on a U-Pu-Zr rod for 17 days caused the mass ion transport of zirconium from a narrow (200 μ) band, at about 645°C, toward the colder end of the rod.

Anisotropic growth (diameter increases as length decreases), as well as decreases in densities, occurred in the extruded rods when subjected to thermal cycles through the phase transformations. The most severe density decrease (0.23 to 0.68 g/cm^3) occurred in the specimens that were cycled 500 times through the lowest temperature transformation (500 to 650°C).

ACKNOWLEDGMENTS

We are indebted to C. F. Metz for analytical data, to E. A. Hakkila for microprobe examinations, to C. C. Land and F. H. Ellinger for x-ray studies, to J. R. Reavis for differential thermal analysis, to K. A. Johnson for metallography, to K. W. R. Johnson for thermal conductivity data and to M. Tokar for hot hardness measurements. We thank B. N. Robbins for his assistance in many aspects of the program and R. M. Brick and M. C. Flemings, consultants to the Laboratory, for their suggestions and discussions.

REFERENCES

1. L. R. Kelman, H. Savage, C. M. Walter, B. Blumenthal, R. J. Dunworth, and H. V. Rhude, "Status of Metallic Plutonium Fast Power-Breeder Fuels," in: Plutonium 1965, A. E. Kay and M. B. Waldron (Eds.) (Chapman and Hall, London, 1967), pp. 458-526.
2. W. N. Beck, "Performance of Advanced U-Pu-Zr Alloy Fuel Elements Under Fast Reactor Conditions, Trans. Am. Nucl. Soc. 10 (1), 106 (1967).
3. F. G. Foote, S. T. Zegler, D. R. O'Boyle, B. Blumenthal, C. M. Walter, and H. V. Rhude, "Annual Progress Report for 1965 Metallurgy Division, Argonne National Laboratory Report No. ANL-7155, p. 16 (1966).