**A STUDY OF PHASE EQUILIBRIA WITH
PLUTONIUM-ZIRCONIUM ALLOYS**

J. M. TAYLOR

SEPTEMBER 1968

**AEC RESEARCH &
DEVELOPMENT REPORT**

FILE NO.	
6-1-Bureau 31425-3782	JAN 10 1969

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.

PACIFIC NORTHWEST LABORATORY

RICHLAND, WASHINGTON

operated by

BATTELLE MEMORIAL INSTITUTE

for the

UNITED STATES ATOMIC ENERGY COMMISSION UNDER CONTRACT AT(45-1)-1830

PRINTED BY/ FOR THE U. S. ATOMIC ENERGY COMMISSION

3 3679 00060 5586

BNWL-402

UC-25, Metals, Ceramics
and Materials

A STUDY OF PHASE EQUILIBRIA WITH
PLUTONIUM-ZIRCONIUM ALLOYS

By

J. M. Taylor

Plutonium Metallurgy Section
Metallurgy Department

September 1968

RECEIVED
DISTRICT 1002 100 2403

BATTELLE MEMORIAL INSTITUTE
PACIFIC NORTHWEST LABORATORY
RICHLAND, WASHINGTON

Printed in the United States of America
Available from
Clearinghouse for Federal Scientific and Technical Information
National Bureau of Standards, U.S. Department of Commerce
Springfield, Virginia 22151
Price: Printed Copy \$3.00; Microfiche \$0.65

TABLE OF CONTENTS

LIST OF FIGURES.	iv
LIST OF TABLES	iv
ABSTRACT	1
INTRODUCTION.	1
SUMMARY AND CONCLUSIONS	1
EXPERIMENTAL PROCEDURE	2
Material	2
Metallography and Hardness	2
X-Ray Diffraction	3
Dilatometry and Thermal Analysis	3
Electron Probe Microanalysis	3
Density Determinations and Density of Various Phases	4
Heat Treatment	5
Isostatic Pressure Technique	5
Pu-Zr PHASE DIAGRAM	5
Liquidus and Solidus	6
Epsilon Plutonium Phase Field	6
Epsilon Plus Delta Phase Fields	6
Delta Plutonium Phase Field.	6
The Low Temperature Phases	6
COOLING RATE STUDIES	10
Liquid and Epsilon Phase Field.	12
Cooling Studies from the Epsilon Phase Field	12
Delta Phase Heat Treatment and Cooling Rate Studies.	17
STABILITY OF BETA PHASE PLUTONIUM.	20
Stability of Beta Phase with Time.	22
Thermal Cycling Studies	24
Pressure Studies	25
Hardness of Retained Beta Phase	27
ACKNOWLEDGMENTS	27
REFERENCES	27
DISTRIBUTION.	29

LIST OF FIGURES

	<u>Page</u>
1 Plutonium Rich End of the Pu-Zr Equilibrium Diagram	7
2 Pu-Zr Alloys Heat Treated at 600 °C for 2 hr and Quenched to Room Temperature	8
3 Microstructures of Pu-Zr Alloys at Equilibrium	11
4 Pu-Zr Alloys Cooled at Different Rates Through the Liquid-Epsilon Phase Field	13
5 Pu-Zr Alloys Cooled 30°/hr Through the Delta-Epsilon Two-Phase Field to 450 °C and then Quenched to Room Temperature	15
6 Etched Structures of Several Pu-Zr Alloys Cooled 30°/hr to 450 °C and Quenched to Room Temperature	16
7 Grain Size Increase as a Function of Cooling Rate Through the Delta-Epsilon Phase Field	18
8 Pu-Zr Alloys Free of Segregation. Alloys held at 600 °C for 2 hr then quenched to room temperature, then heated to 400 °C for 24 hr and quenched to room temperature	19
9 Evidence of Coring in a Pu-6 at.% Zr Alloy that was Held at 400 °C for 8 days After Having Been Cooled Through the Epsilon-Delta Field at 30°/hr.	20
10 Etched Structures of Pu-Zr Alloy Fast Cooled Through the Delta-Epsilon Phase Field then Heated to 400 °C for 24 hr and Quenched to Room Temperature	21
11 Evidence of the Lack of Coring Resulting from Cooling a Homogenized Alloy from 400 °C to Room Temperature at 30°/hr	22
12 Density Change with Time of Several Homogenized Pu-Zr Alloy After Quenching from 400 °C to Room Temperature	23
13 Effect of Thermal Cycle on the Density of Beta Stabilized Pu-Zr Alloys	25
14 Transformation of Retained Beta Phase with Pressure in a Pu-2 at.% Zr and a Pu-3 at.% Zr Alloy	26

LIST OF TABLES

I Average Chemical Analysis of Pu-Zr Alloys	2
II Density of Plutonium Allotropes and Zeta and Theta Phases	4
III The Approximate Density of Beta and Delta Phase Plutonium as a Function of Zirconium Content	5
IV The Densities and Phases Present of Pu-Zr Alloys After Being Heat Treated as Listed Below	9
V Hardness of Several Pu-Zr Alloys Under Equilibrium Conditions	10
VI The Densities and Phases of Pu-Zr Alloys After Being Heat-Treated as Listed Below	14
VII The Densities and Phases of Pu-Zr Alloys After Being Heat-Treated as Listed Below	17
VIII The Densities and Phases of Pu-Zr Alloys After Being Heat-Treated at Listed Below	20
IX Hardness of Retained Beta Phase Pu-Zr Alloys	26

A STUDY OF PHASE EQUILIBRIA WITH PLUTONIUM-ZIRCONIUM ALLOYS

J. M. Taylor

ABSTRACT

A partial Pu-Zr equilibrium diagram is presented which confirms the existence of a solid solution intermetallic beta phase. The diagram developed differs from the equilibrium diagrams previously published. The effect of cooling rate on the retention of high temperature phases at room temperature is discussed along with heat treatments required to homogenize the Pu-Zr alloys. The stability of retained beta phase plutonium with respect to temperature, pressure, and time is also presented.

INTRODUCTION

This report describes a modification to the Pu-Zr phase diagram and gives information on the retention and stability of nonequilibrium phases at room temperature.

The Pu-Zr alloy system has been investigated by Marples et al.;⁽¹⁾ Kutafsev et al.;⁽²⁾ Bochvar et al.;⁽³⁾ and Ellinger.⁽⁴⁾ Differences appear in the equilibrium diagrams produced by these investigations. Marples' work indicated that delta and beta phase of plutonium could be retained to room temperature at low zirconium compositions. The retention of these phases extends the use of plutonium as an engineering material.

Since little information exists concerning the stability of beta phase and dissimilarities appear in the phase diagrams produced by the above investigators, an investigation was undertaken to determine the stability of beta phase plutonium

with respect to temperature, pressure, and time changes and to reconcile the differences among the published phase diagrams.

SUMMARY AND CONCLUSIONS

A partial Pu-Zr equilibrium diagram (0 to 10 at.% Zr) was developed that differed from the previously published British, Russian, and American diagrams. The existence of a zeta intermediate solid solution phase was confirmed. The compositional range (2.5 to 2.7 at.% Zr) of the zeta phase is less than reported in the literature.

Cooling rate studies with Pu-Zr alloys ranging from 2 to 6 at.% Zr indicated that: (1) delta phase or a delta-beta phase mixture is retained at room temperature, depending on the zirconium composition, when the alloys are quenched from the epsilon or delta phase; (2) segregation or coring can be eliminated

at room temperature by holding in the epsilon phase for 2 hr and cooling rapidly (600°/hr or greater) to room temperature, then reheating to 400 °C for 24 hr and furnace cooling to room temperature; (3) the grain size is determined by how fast the alloys are cooled through the delta-epsilon phase region. The faster the cooling rate the smaller the grain size.

Phase stability studies indicated that the retained delta phase transforms to beta phase. The rate of transformation becomes less as the zirconium content increases. The retained beta phase is unstable and transforms to alpha phase in time. The transformation rate increases with decreasing zirconium.

Thermal cycling (-54 to 78 °C) beta retained alloys promoted the beta to alpha transformation. The transformation rate decreased with each succeeding thermal cycle.

The retained beta phase in a 2 and 3 at.% Zr alloy can be compressed isostatically to 25,000 psi without transforming.

The data accumulated indicates that the beta retained Pu-Zr alloy would have limited use as an engineering material due to its instability with time, pressure and temperature changes.

EXPERIMENTAL PROCEDURE

A variety of specialized tools was used to obtain the data included in the report. A brief description is given of the material, apparatus, and techniques used to study the Pu-Zr alloy system.

MATERIAL

Pu-Zr alloys were made by arc melting weighted amounts of plutonium and zirconium on a water-cooled copper hearth in an argon atmosphere to produce buttons. The buttons were in turn melted in a vacuum induction furnace to form ingots approximately 1/2 in. in diameter by 1 1/2 in. long. Discs, cylinders, and small pellets were taken from the ingots for a variety of metallurgical analyses. The nominal compositions of the ingots were 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.5, 8.5, and 10 at.% Zr. The common impurities present in the alloys are listed in Table I.

TABLE I. Average Chemical Analysis of Pu-Zr Alloys

<u>Element</u>	<u>Analysis,</u> <u>ppm</u>	<u>Element</u>	<u>Analysis,</u> <u>ppm</u>
Al	<5	K	5
Cu	<5	C	50
Cr	<10	Am	230
Cu	10	N ₂	60
Fe	64	O ₂	110

METALLOGRAPHY AND HARDNESS

The metallographic specimens were mounted in catalyzed Thalco polyester resin which completely polymerizes below 70 °C. Wet silicon carbide paper from 180 through 600 grit was used for rough grinding. The lubricant used was carbon tetrachloride.

Fine polishing was used with Syntron vibratory polishers. A two-hour polish using billard cloth with Linde A emulsion in carbon tetra-

chloride, followed by a five-to-fifteen minute polishing period using microcloth with Linde A and carbon tetrachloride, gave an acceptable as-polished surface finish.

Electroetching for grain structure was done with a Zeiss electropolisher which allows the metallographer to observe the metal surface during electropolishing. This proved to be a convenient tool especially when segregated alloys were being etched. The etchant most commonly used for grain structure delineation was 200 ml ethanol, 116 g citric acid, and 10 ml of a solution of 25 g potassium or sodium nitrate per 100 ml of water.

Hardness data were obtained using a Leitz microhardness tester equipped with a 136° diamond pyramid indenter and a 50 g load.

X-RAY DIFFRACTION

X-ray diffraction was used to identify phases at room temperature and at elevated temperatures. Solid specimens that had been metallographically polished and etched for 3 min in a solution of 15 parts water, 75 parts 2-ethoxyethanol, and 10 parts tetraphosphoric acid, were used for X-ray diffraction analysis. It is necessary to point out certain problems that were encountered using X-ray diffraction to identify phases: transformation of the X-ray specimens during metallographic polishing; transformation of unstable phases with time; and inability to detect delta, beta, or

alpha phase in mixtures of phases, unless these phases amounted to about 25% of the volume of the mixture. These problems were overcome by the following methods. The layer of transformed metal that resulted from the polishing operation was removed by electropolishing the specimen for 3 min. The transformations of the unstable phases with time were essentially complete after eleven days. The specimens were held at least that long before they were X-rayed. The insensitivity of the X-rays to detect some of the phases was overcome by using density, metallography and microhardness to identify the phases present.

DILATOMETRY AND THERMAL ANALYSIS

Expansion studies were performed using a conventional quartz tube vacuum dilatometer. Length changes were determined with a linear differential transformer, and the temperature was monitored with a Cr-Al thermocouple embedded in the side of the specimen.

Thermal analysis of the alloy was accomplished using a conventional differential method. The active Pu-Zr alloy specimen was compared with a platinum reference specimen.

ELECTRON PROBE MICROANALYSIS

Qualitative electron probe microanalysis was done on mounted metallographic specimens. The radioactive samples were decontaminated so that

they could be mounted in the sample holder of the electroprobe without contaminating the specimen holder. All analytical measurements entailed the use of 18-keV electrons focused to a beam of 1 to 2 μ in diameter. Standard, curved LiF crystal X-ray optics were used with Xenon sealed proportional detectors and X-ray intensities were recorded on a flexowriter-data scanner for fixed time counting periods. Strip chart recorders were used to monitor the stability of the counting rate for the long counting periods, 100 sec.

Certain problems arose when trying to detect zirconium in a matrix of plutonium using electron-probe microanalysis. The characteristic X-ray spectrum of plutonium masks the X-ray spectrum of zirconium, especially in the wavelength range involving the K emission lines. Using the zirconium L emission lines, however, zirconium could be detected. No standard Pu-Zr samples were made, so quantitative analysis could not be performed. Zirconium concentration variations could be detected by step scanning the surface of the specimen and comparing the relative intensity of the zirconium characteristic lines in the sample. A zirconium standard was used to peak the spectrometers.

DENSITY DETERMINATIONS AND DENSITY OF VARIOUS PHASES

A hydrostatic weighing method that has been described in another report⁽⁵⁾ was used for density measurements.

A knowledge of the density of the various phases that occur in the Pu-Zr alloy system helps to determine what phase or phases exist after a particular heat treatment. The density of the plutonium allotropes and an estimate of the zeta and theta phases is given in Table II.

TABLE II. *Density of Plutonium Allotropes and Zeta and Theta Phases*

<u>Phase or Allotrope</u>	<u>Density, g/cm³</u>	<u>Remarks</u>
Alpha	19.82	Density - room temperature determined from X-ray data
Beta	17.70	Density - 150 °C, X-ray data
Gamma	17.14	Density - 235 °C, X-ray data
Delta	15.92	Density - 320 °C, X-ray data
Delta Prime	16.00	Density - 477 °C, X-ray data
Epsilon	16.51	Density - 510 °C, X-ray data
Zeta	17.42	Estimate from a density versus zirconium composition curve of Pu-Zr alloys at equilibrium
Theta	17.13	Estimate from a density versus zirconium composition curve of Pu-Zr alloys at equilibrium

Estimates of the beta and delta phase densities are also given at room temperature for different Pu-Zr alloy compositions, Table III. The estimated beta densities were determined by using the density of a 2 at.% Zr alloy that had a single phase microstructure and a uniform hardness of 100 DPHN and the density of unalloyed beta plutonium at room temperature. Using these values, a plot was made that gave some idea how the beta density changed with zirconium composition at room temperature. The delta densities were obtained using Pu-Zr alloys that retained the delta phase to room temperature. From the density of these alloys a plot was made from which the delta density could be estimated at a particular zirconium composition.

TABLE III. The Approximate Density of Beta and Delta Phase Plutonium as a Function of Zirconium Content

Zr Composition, at. %	Beta Phase Density, g/cm ³	Delta Phase Density, g/cm ³
0	18.06	15.80
1	17.77	15.79
2	17.48	15.70
3	17.19	15.60
4	16.90	15.51
5	16.60	15.42
6	16.32	15.32

HEAT TREATMENT

The heat-treating facility consisted of an evacuable stainless steel tube surrounded by a tube furnace that is capable of temperatures

up to 1000 °C. Specimens for heat treating were contained in a basket that was attached to a movable shaft. This shaft, supported by O-rings, passes through a flange that fits on top of the furnace tube. The movable shaft allows the specimens to be heated and quenched under vacuum. The quenching medium is vacuum oil that is contained in the bottom of the furnace tube. By means of water coils on the outside of the furnace tube the oil is maintained at room temperature.

ISOSTATIC PRESSURE TECHNIQUE

The pressure chamber consists of a steel supporting ring and a cylindrical insert which contains two cylindrical follower blocks. Pressure is transmitted to the follower blocks by a ram attached to the platen of a 200 ton hydraulic press. Alloy specimens were subjected to pressure in steps of 3500 to 10,000 psi up to a maximum of 150,000 psi. The specimens being pressurized were surrounded by a soft rubber compound that provided uniform pressure on the specimen.

Pu-Zr PHASE DIAGRAM

A partial phase diagram (0 to 10 at.% Zr) is presented showing the equilibrium phases that exist at a particular temperature and alloy composition. The individual phase and phase fields are discussed, proceeding down and across the diagram.

LIQUIDUS AND SOLIDUS

The liquidus and solidus curves ascend with increasing zirconium composition in a smooth manner (Figure 1). The liquid-epsilon phase field extends over a large temperature range, some 100° at the 10 at.% Zr composition. The solidus and liquidus temperatures are higher for a particular zirconium composition than reported by Marples⁽¹⁾ and Bochvar.⁽³⁾

EPSILON PLUTONIUM PHASE FIELD

The epsilon plutonium phase and the beta zirconium phase are shown to be completely miscible in the British and Russian diagram. No evidence of immiscibility was seen in a series of alloys quenched from the epsilon phase (Figure 2). These alloys had been held at 600 °C for 2 hr prior to quenching them in oil at room temperature.

EPSILON PLUS DELTA PHASE FIELDS

The epsilon-delta phase field does not exist over a great temperature range. Good agreement exists between the British data, the Russian data, and the data presented in Figure 1 as to the temperature range the epsilon-delta field covers. As seen in Figure 1, the epsilon phase transforms eutectoidally to delta prime plus delta phase at approximately 1.7 at.% Zr. Bochvar indicates that a eutectoid reaction occurs with epsilon phase at around a 3 at.% Zr composition. Marples' diagram indicates no such reaction.

The delta prime plutonium field is shown to extend to 1 at.% Zr, see Figure 1. Evidence of the delta prime phase was observed in the dilatometer traces of the 1 and 2 at.% Zr alloys. The phase boundaries of the delta prime phase were arbitrarily drawn based on the dilatometer data.

DELTA PLUTONIUM PHASE FIELD

The single phase delta field extends over a wide range of zirconium composition, Figure 1. The temperature range over which the delta phase exists is also extensive and amounts to several hundred degrees. The lowest temperature to which it is stable is 270 °C. At this temperature the delta phase undergoes a eutectoid transformation ($\delta \rightarrow \zeta + \theta$), the eutectoid composition being about 3.3 at.% Zr. The data presented in Figure 1 for the delta phase agrees well with the diagrams produced by Marples⁽¹⁾ and Bochvar.⁽³⁾

THE LOW TEMPERATURE PHASES

The low temperature phases are represented on the diagram (Figure 1) by alpha, beta, and gamma plutonium plus two intermetallic compounds, zeta and theta. The greatest differences that exist in the published Pu-Zr diagrams involve the low temperature phases. Due to the complexity and similarity of the X-ray diffraction patterns of the low temperature phases and the long heat treatment that must be used to obtain equilibrium conditions, it is understandable how differences could exist.

FIGURE 1. Plutonium Rich End of the Pu-Zr Equilibrium Diagram

Pu-2 at.% Zr 80X

Pu-3 at.% Zr 80X

Pu-4 at.% Zr 80X

Pu-5 at.% Zr 80X

Pu-6 at.% Zr 80X

FIGURE 2. Pu-Zr Alloys Heat Treated at 600 °C for 2 hr and Quenched to Room Temperature.

The main differences that are apparent among the diagrams of Marples,⁽¹⁾ Bochvar,⁽³⁾ Kutaifsev,⁽²⁾ and Ellinger⁽⁴⁾ are the range of composition of the plutonium phases and the existence of zeta phase. To better define the extent of the plutonium phases and determine whether zeta phase exists, homogenized alloys ranging from 1 to 10 at.% Zr were heat-treated for six weeks at 200 °C and quenched to room temperature. Following the heat treatment an X-ray analysis was made on the alloy specimens. The X-ray patterns indicated a phase was present, (Table IV) the line positions of which did not correspond to the theta phase line position published by Marples or to any line position for the plutonium allotropes. To determine whether the pattern was due to zeta phase, X-ray diffraction data for the zeta phase was obtained from Ellinger.⁽⁶⁾ Using his data, good agreement was obtained between the unknown and the zeta pattern.

By the use of room temperature X-ray and elevated temperature X-ray analysis the phases present at the different alloy compositions and temperatures were determined. The actual zirconium solubility in the alpha, beta, and gamma phases was not accurately determined. It can be assumed to be less than 1 at.% Zr, since zeta phase was detected at elevated temperature in the 1 at.% Zr alloy.

Going across the diagram from low zirconium to higher zirconium compositions the alpha, beta, and gamma allotropes are in equilibrium with zeta phase up to about 2.5 at.% Zr. Here the zeta phase forms and exists over a narrow composition range extending from approximately 2.5 to 2.9 at.% Zr. The compositional range has not been accurately determined. From 2.9 at.% Zr to 9 at.% Zr the zeta phase is in equilibrium with theta phase and beyond 9 at.% Zr only theta phase could be detected on the X-ray patterns. The low

TABLE IV. The Densities and Phases Present of Pu-Zr Alloys After Being Heat Treated as Listed Below

Nominal Compositions, at.% Zr	Heat Treatment	Density, g/cm ³	Phases Present X-ray Determination
2	Specimens held at 600 °C	18.65	$\alpha + \gamma$
3	for 2 hr and quenched to	17.36	$\zeta + \theta$
4	room temperature. Re-	17.33	$\zeta + \theta$
6	heated to 400 °C for 24	17.28	$\theta + \zeta$
7.5	hr and quenched to room	17.16	$\theta + \zeta$
8.5	temperature, then re-	17.03	$\theta + \zeta$
10	heated to 200 °C for 6	16.92	θ
	weeks and quenched to		
	room temperature.		

zirconium boundary for the theta phase is only approximate.

The small two phase field of zeta plus delta, to the left of the $\delta \rightarrow \zeta + \theta$ eutectoid, was not detected by elevated X-ray diffraction. It was constructed to satisfy certain phase rules.

Above 270 °C and to the left of the $\delta \rightarrow \zeta + \theta$ eutectoid, gamma and delta phases exist together. To the right of the eutectoid, delta and theta phases are in equilibrium. These phases have been observed by all the other investigators at the temperatures and compositions shown in Figure 1.

Single phase beta plutonium was not observed in any of the alloy compositions studied at room temperature. Only above 100 °C does it exist and then below the 1 at.% Zr composition. The zeta phase exists over a much narrower composition range than Ellinger indicated. As seen from Table II and Table III the zeta phase has a density similar to beta phase plutonium. As the zeta phase is diluted with the theta phase the density decreases (Table IV). The densities are probably a little low in that complete diffusion has not taken place.

Etched structures of the alloys appear in Figure 3. The structures are mixtures of phases. The 2 at.% Zr alloy is a mixture of alpha and zeta phase. The 3 at.% is mostly all zeta with a little theta phase being present. The 4, 6, 7.5 and 8.5 at.% are mixtures of zeta and theta.

The 6, 7.5, 8.5, and 10 at.% Zr alloy structures look essentially the same, but the boundary that separates the zeta and theta phases from the theta phase is between 8 and 10 at.% Zr. This is based on X-ray diffraction analysis and dilatometry. The 10 at.% Zr alloy contains just theta phase. Hardness data from the different compositions at room temperature, shown in Table V, indicate that the zeta phase is not too hard (≈ 111 DPHN). Combinations of zeta and alpha and zeta and theta phases are much harder than zeta, as shown in Table V.

TABLE V. Hardness of Several Pu-Zr Alloys Under Equilibrium Conditions

Zr Composition, at. %	Hardness, (a) DPHN
1	280
2	190
3	117
4	145
6	157
7.5	160
8.5	170
10	170

(a) 50 g load

COOLING RATE STUDIES

The influence of cooling rate through the various phase fields on microsegregation and retention of phases at room temperature was studied using alloys ranging from 2 to 6 at.% Zr. Alloys above (up to

Pu-2 at.% Zr

400X

Pu-3 at.% Zr

400X

Pu-4 at.% Zr

400X

Pu-6 at.% Zr

400X

Pu-7.5 at.% Zr

400X

Pu-8.5 at.% Zr

400X

Pu-10 at.% Zr

400X

FIGURE 3. Microstructures of Pu-Zr Alloys at Equilibrium

≈15 at.% Zr) and below these compositions responded to the thermal treatments in essentially the same way as a 6 or a 2 at.% Zr alloy.

LIQUID AND EPSILON PHASE FIELD

To determine how the cooling rate through the liquid-epsilon phase field influences the grain structure within the Pu-Zr alloys, two Pu-6 at.% Zr alloy specimens were cooled from 800 °C (liquid phase) into the epsilon phase at different rates. One specimen was cooled at 30°/hr to 640 °C and quenched to room temperature, and the other was cooled to 640 °C at 600°/hr and oil quenched to room temperature. The as-polished surface for the alloy cooled 600°/hr shows a cored structure (Figure 4). The darker areas are zirconium-rich areas (determined by X-ray microprobe analysis) which react with the lubricant used in polishing differently than the zirconium depleted zones which appear as the light areas. Based on the slope of the liquidus and solidus curves, the dark areas should include the center of grains.

The as-polished surface for the alloy cooled 30°/hr has a uniform color and the alloy appears homogeneous. At 640 °C a 6 at.% Zr alloy has cooled 15° below the solidus; this means that the slower cooled alloy was heat-treated for about one-half hour in the epsilon field. This time at temperature was apparently long enough for the zirconium to diffuse and eliminate coring.

The etched structures in Figure 4 reveal a grain size that is nearly the same for the alloys cooled at different rates. This is surprising since the grain size for the slow-cooled alloy was expected to be larger than that for the fast-cooled alloy. The reason this is not observed might be explained by the appearance of the dark inclusions seen in the etched structure of the fast-cooled specimen. These dark inclusions are remnants of the large dark areas seen in the as-polished photomicrograph. This was determined while observing the as-polished surface being etched using the Zeiss electropolisher. The dark inclusions are seen to cover several of the etched grains. Since the dark inclusions are remnants of the center of grains that developed on cooling through the liquid-epsilon region, it can be concluded that the etched grain structure seen in the photomicrographs was developed on cooling through a lower temperature two-phase field. The grain size should be uniform since the alloys were cooled through the low temperature phases at the same rate (quenched from 640 °C).

COOLING STUDIES FROM THE EPSILON PHASE FIELD

Quenching alloys from the epsilon phase to room temperature does not retain the epsilon phase. X-ray diffraction analysis of the alloys indicated that delta phase was

*As-Polished**200X* *Etched**200X*

*Pu-6 at.% Zr alloy cooled from the melt
at 600°/hr to 640 °C and quenched to
room temperature*

*As-Polished**200X* *Etched**200X*

*Pu-6 at.% Zr alloy cooled from the melt
at 30°/hr to 640 °C and quenched to
room temperature*

FIGURE 4. *Pu-Zr Alloys Cooled at Different Rates through
the Liquid-Epsilon Phase Field.*

present in the 4, 5, and 6 at.% Zr alloys, with evidence of beta phase being present in the 4 at.% Zr alloy. The 2 and 3 at.% Zr alloys were predominantly beta phase.

Densities of the quenched alloys confirmed the presence of delta phase in the 4, 5, and 6 at.% Zr alloys (Table VI). The density of the 2 and 3 at.% Zr alloys indicated that beta and delta phases were being retained. The reasons are not clear as to why the delta and beta phases are present after quenching from the epsilon phase field. All the alloys pass through the delta field at a rapid rate. The exact cooling rate is not known. Since the temperature over which the delta phase exists is extensive, the alloys could have been cooled at such a rate that delta formed during cooling. Another possibility is that the epsilon is retained for a very short time at room temperature and then transforms to delta.

Cooling rapidly (quenching) through the delta prime-delta or the delta-epsilon phase field produced little or no coring, as was seen in the

photomicrographs, Figure 2. However, an X-ray microprobe analysis was made on a Pu-6 at.% Zr alloy that had been quenched from the epsilon phase field. A qualitative analysis revealed that a very narrow band or zone near the grain boundary was low in zirconium compared to the center of the grain. Coring does occur if the quench rate is not fast enough.

Cooling slowly (30°/hr) through the delta-epsilon phase field to 450 °C and quenching to room temperature produced cored structures (Figure 5). The darker areas have a higher concentration of zirconium than do the lighter areas. Since the boundaries of the delta-epsilon phase field are rising (Figure 1) the dark areas will be the center of the grains. The etched structures (Figure 6) show grain boundaries that are large due to the different etching rates which are caused in part by the different concentration of zirconium. The apparent lack of coring in the 2 at.% Zr alloy was probably due to its being near the eutectoid composition.

TABLE VI. The Densities and Phases of Pu-Zr Alloys After Being Heat-Treated as Listed Below

Nominal Compositions, at.% Zr	Heat Treatment	Density, g/cm ³	Phases Present X-ray Determination
2	Specimens held for 2 hr	17.04	β
3	at 600 °C and quenched	16.38	$\beta + \delta$
4	to room temperature in	15.57	$\delta + \beta$ (?)
5	oil	15.47	δ
6		15.36	δ

*Pu-2 at.% Zr**200X* *Pu-3 at.% Zr
As-Polished**200X* *Pu-4 at.% Zr
As-Polished**200X* *Pu-5 at.% Zr
As-Polished**200X* *Pu-6 at.% Zr
As-Polished**200X*

FIGURE 5. Pu-Zr Alloys Cooled 30°/hr Through the Delta-Epsilon Two-Phase Field to 450 °C and then Quenched to Room Temperature.

Pu-2 at.% Zr

80X

Pu-3 at.% Zr

80X

Pu-4 at.% Zr

80X

Pu-5 at.% Zr

80X

Pu-6 at.% Zr

80X

FIGURE 6. Etched Structures of Several Pu-Zr Alloys Cooled 30°/hr to 450 °C and Quenched to Room Temperature.

The densities of the alloys taken after cooling and quenching from 450 °C indicated that delta phase was being retained at the higher zirconium compositions, as shown in Table VII.

In general, the density increases as the zirconium concentration decreases, indicating that delta phase plutonium becomes more unstable at the lower zirconium compositions. The fact that the density for the 5 at.% Zr alloy is higher than the 4 at.% Zr alloy cannot be explained. It does indicate that the delta phase is more unstable in the 5 at.% Zr alloy than in the 4 at.% Zr alloy.

X-ray patterns showed delta and beta phase present in the 3, 4, and 5 at.% Zr alloy. The X-ray pattern for the 2 at.% Zr alloy was mostly beta with some indication of alpha being present, and for the 6 at.% Zr alloy a strong delta pattern appeared with some very weak beta lines (Table VII).

The grain size at room temperature is influenced by the rate of cooling through the delta-epsilon phase field. The grain size is larger for the slow-cooled alloy than for the faster cooled alloy (Figure 7).

TABLE VII. The Densities and Phases of Pu-Zr Alloys After Being Heat-Treated as Listed Below

Nominal Compositions, at.% Zr	Heat Treatment	Density, g/cm ³	Phases Present X-ray Determination
2	Specimens held at 600 °C,	17.50	$\beta + \alpha$ (?)
3	cooled 30°/hr to 450 °C	16.53	$\beta + \delta$
4	and quenched to room	15.35	$\delta + \beta$
5	temperature in oil	15.62	$\delta + \beta$
6		15.21	$\delta + \beta$ (?)

DELTA PHASE HEAT TREATMENT AND COOLING RATE STUDIES

A series of heat treatments and cooling rate studies was conducted with several Pu-Zr alloys holding in the delta field. The object of study was to determine the length of time necessary to homogenize the alloys after cooling through the delta-epsilon phase field and to determine the influence of the lower temperature transformations on the grain structure and coring of the alloys.

To determine the time necessary to homogenize alloys that had been quenched from the epsilon field, a series of alloys (2 to 6 at.% Zr) was held at 400 °C for 1, 2, and 7 days and quenched to room temperature. All the heat treatments produced similar microstructures. A qualitative X-ray microprobe analysis of a 6 at.% Zr alloy, heat-treated for 1 day at 400 °C, indicated the absence of a zirconium gradient in the grain structure of the alloy. The as-polished surfaces of the alloys heat-treated for 1 day indicated a

Pu-6 at.% Zr 200X

Quenched from 600 °C to Room Temperature. Grain Size - 0.028 mm

Pu-6 at.% Zr 200X

Held at 600 °C for 2 hr, then cooled to 450 °C at 30°/hr and quenched to room temperature. Grain Size - 0.11 mm

FIGURE 7. Grain Size Increase as a Function of Cooling Rate through the Delta-Epsilon Phase Field.

core-free condition (Figure 8). Heat treating at 400 °C for less than 1 day was not investigated.

Alloys cooled slowly (30°/hr) through the delta-epsilon phase field require a much longer time at 400 °C to become fully homogenized. A 6 at.% Zr alloy that was heat treated at 400 °C for 8 days still has evidence of coring (Figure 9).

The etched structures of the alloys held for 24 hr at 400 °C and quenched

to room temperature indicate that a mixture of phases were present in the alloys containing less than 6 at.% Zr (Figure 10). Through the use of X-ray analysis and density determinations, the phases present were identified in the lower zirconium composition alloys as shown in Table VIII. The 2 at.% Zr alloy is a mixture of alpha and beta phase, while the 3, 4, and 5 at.% are mixtures of varying amounts of beta and delta phases. The lighter or white phases shown in the photomicrograph of the 2 at.% Zr is alpha phase plutonium. This phase has a hardness of 266 DPHN, which correlates well with the hardness for unalloyed alpha plutonium. The darker or beta phase shown has a hardness of 100 DPHN and this corresponds to the hardness of beta phase plutonium at room temperature. To identify the delta or beta phase from the 3, 4, and 5 photomicrographs is difficult. Hardness measurements taken across the sample varied in value and were not consistent. Holding in the delta field and quenching retains delta phase to room temperature in all the alloys except the 2 at.% Zr. Also, beta phase is present in all the alloys except the 6 at.% Zr. Since no beta phase exists beyond the 2.5 at.% Zr under equilibrium conditions (see Figure 1), it must be concluded that the delta transforms to the beta. The beta phase appears to be a transition structure that the delta phase assumes as it transforms to the equilibrium structure.

*Pu-2 at.% Zr
As-Polished*

200X

*Pu-3 at.% Zr
As-Polished*

200X

*Pu-4 at.% Zr
As-Polished*

200X

*Pu-5 at.% Zr
As-Polished*

200X

*Pu-6 at.% Zr
As-Polished*

200X

FIGURE 8. Pu-Zr Alloys Free of Segregation. Alloys held at 600 °C for 2 hr then quenched to room temperature, then heated to 400 °C for 24 hr and quenched to room temperature.

TABLE VIII. The Densities and Phases of Pu-Zr Alloys After Being Heat Treated as Listed Below

Nominal Compositions, at.% Zr	Heat Treatment	Density, g/cm ³	Phases Present X-ray Determination
2	Specimens held at 600 °C	17.54	$\beta + \alpha$
3	for 2 hr and quenched to	16.66	$\beta + \delta$
4	room temperature, then	15.30	$\delta + \beta$ (?)
5	reheated to 400 °C for	15.45	$\delta + \beta$
6	24 hr and again quenched	15.23	δ
	to room temperature.

FIGURE 9. Evidence of Coring in a Pu-6 at.% Zr Alloy That Was Held at 400 °C for 8 days After Having Been Cooled Through the Epsilon-Delta Field at 30°/hr.

The equilibrium structure is only established after holding in the high alpha-zeta or zeta-theta fields for many weeks. This allows the zirconium to diffuse and form the zeta and theta phases which are stable at room temperature.

As mentioned above, quenching alloys from the delta phase to room temperature produced alloys free of segregation. It was also determined that cooling a homogenized delta alloy at 30°/hr from 400 °C to room temperature produced a core-free structure (Figure 11). The as-polished surface shows no dark or light areas, and the etched surface

shows a grain structure similar to the homogenized delta alloy that was quenched to room temperature. It can be concluded from this that zirconium diffuses slowly below 325 °C and no coring results from cooling through the lower temperature two-phase fields.

STABILITY OF BETA PHASE PLUTONIUM

Little information exists on beta phase plutonium at room temperature. Since the beta phase is present in Pu-Zr alloys at room temperature after quenching from the delta field, it would be of interest from an engineering standpoint to determine the stability of beta phase.

All Pu-Zr alloys used in the stability studies were homogenized by holding them at 600 °C for 2 hr and quenching to room temperature, then reheating to 400 °C for 24 hr and following with a quench to room temperature.

The stability of the Pu-Zr alloy was determined using the change of density as a function of time at room temperature, pressure, and thermal cycle.

Pu-2 at.% Zr

200X

Pu-3 at.% Zr

200X

Pu-4 at.% Zr

200X

Pu-5 at.% Zr

200X

Pu-6 at.% Zr

200X

FIGURE 10. Etched Structures of Pu-Zr Alloy Fast Cooled Through the Delta-Epsilon Phase Field then Heated to 400 °C for 24 hr and Quenched to Room Temperature.

*Pu-6 at.% Zr
As-Polished*

200X

Pu-6 at.% Zr

200X

FIGURE 11. Evidence of the Lack of Coring Resulting from Cooling a Homogenized Alloy from 400 °C to Room Temperature at 30°/hr.

Beta phase plutonium is present in greater quantity in the 2 and 3 at.% Zr alloys after the above heat treatment so, the majority of tests were made with these alloys, except for some of the time studies.

STABILITY OF BETA PHASE WITH TIME

To determine the stability of the beta phase with time at room temperature, homogenized Pu-Zr alloy specimens in the form of discs 3/8 in. in diameter and approximately 5/32 in. in height were quenched from 400 °C to room temperature. The density

changes with time for the various alloys are shown in Figure 12. In general, the density change with time curve assumes a different shape depending on the zirconium content. Using the density values for the beta and delta plutonium as a function of zirconium composition (Table III), some knowledge of how much of what phase exists after the quench and at the end of transformation can be ascertained. Because it was necessary to transfer the alloy specimens from the heat-treat-quench facility to the density facility, the densities could not be taken immediately after the quench. This did not obscure the start of the transformation in the alloys containing 4 to 6 at.% Zr, but it was long enough to miss the start of the transformation in the 2 and 3 at.% Zr alloys.

After 30 min the transformation is almost complete in the 2 at.% Zr alloy. After 10 to 11 days (~15,000 min) the density does not change. The final density of 17.78 indicates the presence of alpha and beta phases. This mixture of phases (~19% alpha) is metastable at room temperature. It is difficult to retain the delta phase in the 2 at.% Zr alloy. It can be speculated from the above data that in the 2 at.% Zr alloy the delta phase is retained a very short time after quenching and then transforms to the beta phase. The beta phase then in turn transforms to the alpha phase.

The transformation of the delta phase to the beta phase is slower in the 3 at.% Zr alloy. The density 30 min after quenching is 16.52 g/cm³.

FIGURE 12. Density Change with Time of Several Homogenized Pu-Zr Alloy After Quenching from 400 °C to Room Temperature.

This indicates a mixture of about 45% delta and 55% beta phases. As the density increases with time more beta phase is formed. After approximately 28 days ($\approx 40,000$ min) the density levels off and a mixture of roughly 93% beta and 7% alpha phase exists.

As shown in Figure 12, different curves appear for the 4 at.% Zr alloy. These curves are the result of quenching different size alloy specimens. The smaller size specimen was cooled faster and retained more delta phase plutonium at room temperature. The larger size specimen had less delta phase after the quench and, because of this and a different stress condition, the transformation kinetics differed from the smaller specimens. The density increases with time (approximately 70 days) until it levels off at a 16.75 g/cm^3 density. This density indicates that 85% of the delta phase has transformed to the beta phase. An X-ray diffraction pattern of the alloys showed strong beta and weak delta lines. This mixture of beta and delta phases appears to be metastable at room temperature.

In the 6 at.% Zr alloy the delta phase transforms slowly to the beta phase. After 3 days the density levels off. This density increase of 0.6% indicates that approximately 6% of the delta phase has transformed to the beta phase. This mixture is metastable and the density remains unchanged with time at room temperature. As the zirconium concentration decreases the delta phase becomes more unstable.

THERMAL CYCLING STUDIES

The next study undertaken to learn more about the stability of the beta phase was thermal cycling. Alloys used for this study were quenched from the delta field and held at least 11 days at room temperature or until the density no longer changed.

The thermal cycle consisted of cooling an alloy specimen from room temperature to -54°C , heating it to 78°C , and then cooling it to room temperature. To complete an entire cycle required 8 hr. The temperature range chosen exceeded the temperature limits required for the engineering uses of the alloy. A 2 at.% Zr alloy specimen and a 3 at.% Zr specimen were thermal cycled three times. After each thermal cycle the density was taken. The density after 11 days was 17.68 g/cm^3 for the 2 at.% Zr alloy and 17.20 g/cm^3 for the 3 at.% Zr alloy. These densities indicated the presence of alpha and beta phase in the 2 at.% Zr alloy and beta and delta phases in the 3 at.% Zr alloy. Thermal cycling the alloys caused an increase in density (Figure 13). The density increase is greatest after the first cycle, then decreases with each succeeding cycle. In both the 2 and 3 at.% Zr alloy, alpha phase formation was the cause for the density increase. The alpha phase was detected in the alloys by X-ray analysis and metallography. The final density of 18.54 g/cm^3 for the 2 at.% Zr alloy indicated that approximately 58% alpha phase had formed during cycling. Formation of alpha

FIGURE 13. Effect of Thermal Cycle on the Density of Beta Stabilized Pu-Zr Alloys.

phase was much less in the 3 at.% Zr. A final density of 17.37 g/cm^3 indicates that approximately 10% alpha phase had formed.

Thermal cycling produced more alpha phase in the 2 at.% Zr alloy than was produced during the hold at room temperature. Thermal cycling had less effect on the 3 at.% Zr alloy. The final density of the 3 at.% Zr alloy after thermal cycling was nearly the same as it was after quenching from 400°C and holding at room temperature.

PRESSURE STUDIES

The response of a 2 and 3 at.% Zr alloy to pressure was studied at room temperature. The specimens used in the study had been quenched from the delta phase and held long enough at room temperature for the density to remain unchanged. Pressure studies were done with a series of specimens for both alloy compositions. Each specimen was isostatically pressed to a specific pressure and the density of the specimens was taken after they were compressed.

The change in density versus pressure curve has a different shape for the 2 and 3 at.% Zr alloys, (Figure 14). It is not clear why the density changes are less and start at a higher pressure for the 2 than for the 3 at.% Zr alloy below 80,000 psi. A possible explanation might be that the 2 at.% Zr alloy has more alpha phase before compression than the 3 at.% Zr alloy. Therefore, it transforms less per pressure change at the low pressures. The marked increase in density above 80,000 psi for the 2 at.% Zr alloy could be due to the zirconium atoms being rearranged to a position in the lattice that promoted the beta to alpha transformation. The same notable increase in density would be expected in the 3 at.% Zr alloy as in the 2 at.% Zr alloy only at a higher pressure. According to Figure 14 the pressure is in excess of 150,000 psi. The amount of alpha phase present after

FIGURE 14. Transformation of Retained Beta Phase with Pressure in a Pu-2 at.% Zr and a Pu-3 at.% Zr Alloy.

the 150,000 psi compression was 76% in the 2 at.% Zr and 30% in the 3 at.% Zr.

Annealing the specimens at 170 °C for times up to 2 hr after compression produced different results in the 2 and 3 at.% Zr alloys. The above heat treatment was sufficient to restore the 2 at.% Zr alloy to its original unpressed density. However, the density of the 3 at.% Zr alloy lowered very little after the same heat treatment. Extending the time to 7 hr at 170 °C for the 3 at.% Zr alloy did not restore the alloy to its original density. In fact, the extended time at temperature produced some zeta phase. Pressing annealed 2 at.% Zr specimens produced a different density change versus pressure curve (Figure 14) than obtained with the original alloy series. Obviously, the annealed specimens did not return to the same condition that existed in the specimens prior to the pressing studies.

HARDNESS OF RETAINED BETA PHASE

The beta hardness values were obtained using homogenized 2 and 3 at.% Zr alloys that were quenched from the delta phase and allowed to transform to the beta phase at room temperature. The hardness values appear in Table IX. It is interesting to note that the hardness for the beta retained 3 at.% Zr alloy is very near the hardness of the zeta phase shown in Table V. As the zirconium concentration increases the hardness of the beta retained Pu-Zr alloys increases.

TABLE IX. *Hardness of Retained Beta Phase Pu-Zr Alloys*

Zr Composition, at.%	Hardness, (a) DPHN
2	98
3	112

(a) 50 g load

ACKNOWLEDGMENTS

The author wishes to express his appreciation to R. D. Nelson and H. R. Gardner for the help and advice given during the course of this work.

I should like also to acknowledge the fine work done by J. H. Hammer in performing all the laboratory work associated with this project.

REFERENCES

1. J. A. C. Marples. *The Plutonium-Zirconium Alloy System*, AERE-R-3110. Atomic Energy Research Establishment, Harwell, Berks, England, 1959.
2. M. B. Waldron and A. E. Kay. *Plutonium 1965*, Chapman and Hall, London, England, 1967. pp. 423-424.
3. A. A. Bochvar, S. T. Konobeevski, V. I. Kutaitsev, P. S. Menshikova, and N. T. Chebatorev. *Proceedings of the 2nd International Conference on Peaceful Uses of Atomic Energy*, vol. 6, p. 184, Geneva, United Nations, 1958.
4. E. Grison, W. B. H. Lord, and R. D. Fowler. *Plutonium 1960*, Cleaver-Hume Press Ltd., London, England, 1961. pp. 318-319.

5. R. D. Nelson, C. R. Becker,
T. K. Bierlein, and F. E. Bowman.
Density Determinations of Plutonium,
HW-80841. Available from Clearing-
house for Federal Scientific and
Technical Information, Springfield,
Virginia. 1964.
6. F. H. Ellinger. Unpublished Data.
Los Alamos Scientific Laboratory,
University of California, Los
Alamos, New Mexico. November
1966. (Personal Communication).

DISTRIBUTION

No. of
Copies

2	<u>AEC Albuquerque Operations Office</u> D. Johnston Lt. Col. D. Overton	14	<u>Lawrence Radiation Laboratory, Livermore (AEC)</u> C. T. Brockett J. P. Diacanoff F. S. Eby E. H. Fleming J. Hadley C. R. Henry J. O. Jenson W. M. Miller/ D. E. Loewe D. C. Oakley H. N. Perl T. Perlman W. J. Ramsey J. L. Robbins R. G. Stone
2	<u>AEC, Chicago Patent Group</u> G. H. Lee R. K. Sharp (Richland)		
266	<u>AEC Division of Technical Information Extension</u>		
1	<u>AEC Library, Washington</u> Col. I. L. Williams Div. Military Application		
2	<u>AEC RDT Site Representative - PNL</u> P. G. Holsted	2	<u>Los Alamos Scientific Laboratory (AEC)</u> R. D. Baker F. W. Schonfeld
1	<u>AEC Richland Operations Office</u> C. L. Robinson/J. L. Rhoades	1	<u>Mound Laboratory (AEC)</u> L. J. Wittenburg
1	<u>AEC Rocky Flats Area Office</u> S. R. Woodruff, Jr.	29	<u>Battelle-Northwest</u> V. C. Asmund R. F. Burch, Jr. R. A. Busch J. J. Cadwell G. M. Dalen S. D. Dahlgren R. E. Falkoski H. P. Gardner G. P. Hanneman W. S. Hartnett D. D. Hayes Y. B. Katayama R. R. King, Jr. E. D. McClanahan R. W. Moss R. D. Nelson C. S. Powers J. C. Spanner R. W. Stewart J. M. Taylor W. B. Weihermiller O. J. Wick Technical Information (5) Technical Publications (2)
1	<u>Argonne National Laboratory</u> M. B. Brodsky		
3	<u>Battelle Memorial Institute</u>		
8	<u>Dow Chemical Company (AEC)</u> F. L. Collins/ W. H. Hauschildt R. D. Forest M. O. Johnson B. L. Kelchner L. A. Matheson J. E. Pavlick L. W. Pribila T. VanVorous		
1	<u>Lawrence Radiation Laboratory, Berkeley (AEC)</u> R. P. Connell		