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THE LOW TEMPERATURE ALLOTROPIC
TRANSFORMATIONS IN PLUTONIUM

April, 1965

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THE LOW TEMPERATURE ALLOTROPIC TRANSFORMATIONS
IN PLUTONIUM

By

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April, 1965

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ABSTRACT

Transformation kinetics, phase transformation damage, steady-state creep, and effects of applied stress on phase transformations of plutonium were investigated. These related phenomena are discussed and are correlated with similar information about more common metals. There are several characteristics of these phase changes that are consistent with either diffusional or martensitic transformations, but these data alone are insufficient to characterize them. Data for the $\beta \rightarrow \alpha$ and $\alpha \rightarrow \beta$ phase changes indicate martensitic transformations; data for the $\beta \rightarrow \gamma$ and $\gamma \rightarrow \beta$ phase changes are consistent with diffusional transformations.

The kinetic data show conclusively that the $\beta \rightarrow \alpha$, $\alpha \rightarrow \beta$, $\beta \rightarrow \gamma$, and $\gamma \rightarrow \beta$ phase changes in high purity plutonium can proceed isothermally to completion with no athermal component. The most significant characteristics of the $\beta \rightarrow \alpha$ transformation kinetics are 1) the $\beta \rightarrow \alpha$ TTT curve is a simple C curve with the maximum rate of transformation at -20 to -40°C; 2) several percent of retained high temperature phases may exist in pure plutonium at room temperature; 3) alpha grains form in disk shaped volumes at high alpha formation temperatures; 4) plastic deformation of the stable beta phase retards the subsequent $\beta \rightarrow \alpha$ transformation; and 5) plastic deformation of stable alpha accelerates the $\alpha \rightarrow \beta$ transformation.

Significant characteristics of the transformation of the gamma phase are 1) transformation of the gamma phase is depicted by a double C curve consisting of a $\gamma \rightarrow \beta$ transformation curve; a $\gamma \rightarrow \alpha$ transformation curve; and a complex region where the gamma, beta, and alpha phases can temporarily exist simultaneously; 2) the $\gamma \rightarrow \alpha$ transformation is a skip transformation; 3) plastic deformation of stable beta accelerates the $\beta \rightarrow \gamma$ transformation rate.

High purity as-cast plutonium may contain a large volume of microcracks that form during the $\beta \rightarrow \alpha$ transformation. The volume of microcracks increases with increasing transformation temperature, higher metal

purity, increased specimen size, and $\alpha \rightleftharpoons \beta$ transformation cycling. Transformation cycling produces growth in all directions, general distortion, and extensive surface rumpling. Plutonium free of microcracks can be produced by quenching from the beta phase to -75 to -115°C during casting. In metal that initially contains no microcracks, no physical damage has been observed after either $\gamma \rightleftharpoons \beta$, $\delta \rightleftharpoons \gamma$, or $\delta \rightleftharpoons \beta$ transformation cycling.

At a common temperature the creep rate of the phase normally stable at higher temperatures is greater than the creep rate of the phase normally stable at the lower temperatures except for beta formed from alpha. The creep rate of beta formed from alpha is 200 to 500 times greater than the creep rate of beta formed from gamma. As a consequence, the creep rate of beta that is formed from gamma is less than the creep rate of the gamma phase under the same temperature and stress conditions. The activation energies for creep of the six allotropes were 26, 30, 35, 31, 28, and 25 kcal/g-atom, respectively, for the α , β , γ , δ , δ' , and ϵ phases. The creep activation energies were related to the activation energies for self-diffusion.

Application of uniaxial compressive and tensile stresses markedly affect the total strain during $\beta \rightarrow \alpha$, $\alpha \rightarrow \beta$, $\beta \rightarrow \gamma$, and $\gamma \rightarrow \beta$ transformations in plutonium. The following conclusions were made: 1) both applied uniaxial tensile stresses and compressive stresses raise the temperature for the beginning of the $\beta \rightarrow \alpha$ transformation; 2) stresses applied during transformation produce pronounced crystallographic texturing and microstructural shape texturing due to anisotropic phase changes; 3) the (010) plane of the alpha phase formed under uniaxial stress becomes parallel to the applied tensile stresses and perpendicular to applied compressive stresses; 4) the $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ transformations occur anisotropically in textured plutonium; 5) there is an apparent crystallographic relationship between the parent and product phases of the $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ transformations; and 6) some excess creep occurs when plutonium is subjected to an external stress during transformation.

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CHAPTER I

INTRODUCTION

This dissertation describes a study of the low temperature allotropic transformations of plutonium. The primary objectives were to provide kinetic and creep data, to investigate the physical damage in plutonium, to provide transformation creep data, and to provide information concerning the mechanisms that might be responsible for these transformations.

Allotropic transformations in pure metals are not well understood; this is particularly true of plutonium. No data have been published concerning the mechanisms of any of the low temperature transformations. Several reasons for this lack of basic information on the mechanisms of the allotropic transformations of plutonium are:

- (1) Relatively pure plutonium did not become available until recent years.
- (2) Plutonium is a very complex metal.
- (3) It is impossible to retain any of the high temperature phases at room temperature for either microscopic or crystallographic studies.
- (4) Single crystals have not been made for any of the allotropes.
- (5) Experiments with plutonium are more difficult and proceed more slowly than for most metals.

These factors, collectively, make a determination of the phase transformation mechanisms very difficult for plutonium.

The many variables that influence transformation kinetics were investigated in detail. The effect they have on the transformation kinetics are discussed and related to mechanisms. The physical damage associated with the $\beta \rightarrow \alpha$ transformation was studied and is discussed. In addition, research was performed on the effect of applied stress on the low

temperature transformations. The results of these experiments are also related to mechanisms of phase transformation. The single phase, steady-state creep data, which were necessary to analyze the transformation creep data, are compared with the creep behavior of other metals.

A. CHARACTERISTICS OF THE METAL PLUTONIUM

1. Nuclear Characteristics

Plutonium has many remarkable features, peculiarities, and anomalies that present challenges and opportunities to the theoretical and experimental metallurgists to enhance our understanding of metals in the solid state.⁽¹⁻⁶⁾ Dr. Glen C. Seaborg referred to plutonium as "that ornery metal".⁽⁷⁾

Plutonium is the 94th element in the periodic table and it is the only synthetic element that has been produced in large amounts. It is used as a source of nuclear energy, either as an explosive or as a nuclear fuel. The principal isotope in plutonium is Pu^{239} , which is produced by bombardment of U^{238} with neutrons:

Pu^{239} is fissionable and is an alpha-emitter. It has a fission rate of 1.0×10^{-2} spontaneous fissions per second per gram and it has a half-life of 24,300 years. Approximately three neutrons form from spontaneous fission; the average energy of each neutron is 2 mev/neutron. Other isotopes, Pu^{238} , Pu^{240} , Pu^{241} , and Pu^{242} are present in various amounts depending on the neutron flux level. The isotopes above Pu^{239} are formed by successive neutron captures; Pu^{240} may vary between a few percent and 30% whereas Pu^{241} is generally less than 1%. Negligible amounts of plutonium isotopes are present above Pu^{242} because of the very short half-life of Pu^{243} . Pu^{238} and Pu^{240} are principally alpha emitters with half lives of 90 and 16,000 years respectively. The spontaneous fission rate of Pu^{240} is 4.52×10^2 fissions per second per gram. Pu^{241} is a beta and gamma emitter having a half-life of 13 years; radioactive decay by alpha emission is negligible since its alpha half-life is 560,000 years.⁽⁸⁾

Due to these nuclear properties, self-irradiation damage of plutonium occurs. There will be an accumulation of impurities; namely uranium, americium, and helium. Uranium and helium are produced by the decay of Pu^{239} whereas americium is produced by the decay of Pu^{241} . As a result, plutonium samples may contain several hundred parts per million of americium and uranium; for example, if the metal initially contains 0.5% Pu^{241} the amount of americium will increase approximately 250 ppm/year. Helium accumulates at a rate of approximately $0.0025 \text{ cm}^3/\text{yr/g}$ of plutonium. These impurities can affect the metallurgical properties of plutonium.

Because plutonium is a fissionable metal, criticality considerations must be made when handling plutonium. The minimum critical mass of a sphere of metallic Pu^{239} can be 5.6 kilograms if a thick water reflector is present. The minimum critical mass of plutonium can be 510 grams in a water reflected solution.

Criticality is not of as much concern to those performing research as is the health hazard created by the plutonium's radioactivity. This hazard is due to the alpha emission of Pu^{239} , which is neither a strong beta nor a strong gamma emitter. The alpha particles cause severe biological damage to body tissue immediately surrounding any point at which a particle of plutonium may be deposited. The toxic effect is such that the maximum permissible body-burden has been set at approximately 0.6 microgram; although only a small percent of the quantity inhaled or ingested is retained. Thus it is imperative that entry of plutonium into the body be prevented by containing it in gloveboxes while working with it. A typical glovebox is shown in Figure 1. Since the penetrating power of alpha particles is very low, only 3.68 cm in air, even though their maximum energy is 5.15 Mev, they will not penetrate either the walls of the glovebox or the neoprene gloves.^(1,2)

Alpha radioactivity will also produce internal warming of plutonium. For example, the temperature of a 100-gram spherical specimen will be 5 to 10°C warmer than the glovebox temperature. This heating is referred to as self-heating; the self-heating coefficient is

Figure 1

Glovebox for plutonium physical metallurgy research

1.9×10^{-3} watts/gram.⁽²⁾ Gamma activity of plutonium is not a serious problem in physical metallurgy research because small quantities of plutonium are used and the primary isotope Pu^{239} emits relatively weak gamma radiation.

2. Physical Metallurgy

The free plutonium atom has many nearly identical energy levels indicated by the multiple valencies. The electron state is readily affected by temperature, pressure, the atoms' neighbors, and by the electrical and magnetic environment. The valence electrons are $5f^6 6d^0 7s^2$ for the free plutonium atoms.^(2,3)

The most notable of the remarkable features in the physical metallurgy of plutonium are the six allotropic modifications. The temperature dependency of the thermal expansion of plutonium is shown in Figure 2. The crystal structure, some physical properties, and

Figure 2
Temperature dependency
of the thermal expansion
of plutonium

some thermodynamic properties are listed in Tables I and II. The alpha, beta, and gamma phases have crystal structures having low symmetry.

TABLE I
CRYSTAL STRUCTURES, SOME PHYSICAL PROPERTIES,
AND SPECIFIC HEAT DATA OF THE ALLOTROPES OF PLUTONIUM

<u>Phase</u>	<u>Crystal Structure</u>	<u>Number of Atoms per Structure Cell</u>	<u>Calculated Density g/cm³</u>	<u>Thermal Expansion Coefficient X 10⁶/°C</u>	<u>Resistivity μ-ohm-Cm</u>	<u>Specific Heat Cal/g-atom</u>
α 25°C	Simple Monoclinic	16	19.82	55	145.2	8.6
β 150°C	Body-centered Monoclinic	34	17.8	40	108.5	8.3
γ 235°C	Face-centered Orthorhombic	8	17.14	35	107.8	8.7
δ 320°C	Face-centered Cubic	4	15.92	-9	-100.4	9.0
δ' 470°C	Body-centered Tetragonal	2	16.00	-65	-102.1	13.2
ϵ 410°C	Body-centered	2	16.51	36	110.6	8.4
Liquid 670°C			16.6			

TABLE II
TRANSFORMATION TEMPERATURES, VOLUME CHANGE OF TRANSFORMATION
AND HEATS OF TRANSFORMATION OF THE PLUTONIUM ALLOTROPES

<u>Phase Change</u>	<u>Transformation Temperature °C</u>	<u>Volume Change Percent</u>	<u>$\Delta H^{(9)}$ Cal/g-atom</u>	<u>$\Delta S^{(9)}$ Cal/g-atom</u>
$\alpha \rightarrow \beta$	112	10	900	2.28
$\beta \rightarrow \gamma$	185	3.5	160	0.33
$\gamma \rightarrow \delta$	310	7	148	0.25
$\delta \rightarrow \delta'$	451	-0.5	10	0.01
$\delta' \rightarrow \epsilon$	480	-3	444	0.59
$\epsilon \rightarrow \text{Liquid}$	640	-3	676	0.74

The unit cell dimensions of the monoclinic alpha phase at 25°C are: $a = 6.183 \text{ \AA}$, $b = 4.82 \text{ \AA}$, $c = 10.963 \text{ \AA}$, $\beta = 101.79^\circ$. The space group is $P2_1/m$ with all the atoms having coordinates $\pm(x, 1/4, z)$. The coordinate values for the eight types of atomic positions and the bond lengths are given in Tables III and IV. The short bonds are all between 2.52 and 2.73 $\text{\AA}$, whereas all other bond lengths are between 3.09 and 3.30 $\text{\AA}$. Zachariasen believed these bonds to be covalent.^(10,11)

TABLE III

COORDINATE VALUES $\pm(x, y, z)$
FOR ALPHA PLUTONIUM, $y = 1/4$ ^(12,13)

<u>Atom</u>	<u>x</u>	<u>z</u>
I	0.345	0.162
II	0.767	0.168
III	0.128	0.340
IV	0.657	0.457
V	0.025	0.618
VI	0.473	0.653
VII	0.328	0.926
VIII	0.869	0.894

TABLE IV

BOND LENGTHS OF ALPHA PLUTONIUM AT 25°C

<u>Atom</u>	<u>Coordination Number</u>	<u>Short Bonds ($\text{\AA}$)</u>		<u>All Bonds ($\text{\AA}$)</u>		
		<u>Range</u>	<u>Mean</u>	<u>Number</u>	<u>Range</u>	<u>Mean</u>
I	5	2.52 - 2.69	2.62	12	2.52 - 3.51	3.01
II	4	2.62 - 2.69	2.68	14	2.62 - 3.62	3.00
III	4	2.54 - 2.67	2.63	14	2.54 - 3.67	3.11
IV	4	2.54 - 2.70	2.63	14	2.54 - 3.51	3.02
V	4	2.54 - 2.73	2.65	14	2.54 - 3.56	3.01
VI	4	2.58 - 2.73	2.68	14	2.58 - 3.62	3.02
VII	4	2.52 - 2.70	2.65	14	2.62 - 3.56	3.03
VIII	3	2.68 - 2.70	2.69	16	2.65 - 3.67	3.01

Zacharisen and Ellinger also determined the structure of the beta phase.^(11,14,15) The unit-cell dimensions are $a = 9.284 \text{ \AA}$, $b = 10.463 \text{ \AA}$, $c = 7.859 \text{ \AA}$, and $\beta = 92.13^\circ$. There are seven different types of atomic positions in the beta structure. The coordinates of all the atoms are $\pm(x, y, z)$ and $[(x + 1/2)(y + 1/2)(z + 1/2)]$ where values for x , y , and z are listed in Table V.

TABLE V
THE COORDINATES OF ATOMS FOR BETA PLUTONIUM

<u>Atom</u>	<u>Number of Atoms</u>	<u>Coordinates</u>	<u>x</u>	<u>y</u>	<u>z</u>
I	2	(000)	0	0	0
II	4	$\pm(x, 0, z)$	0.146	0	0.387
III	4	$\pm(x, 0, z)$	0.377	0	0.082
IV	4	$\pm(x, 0, z)$	0.434	0	0.672
V	4	$\pm(1/2, y, 0)$	0.500	0.220	0
VI	8	$\pm(x, y, z)(x, y, z)$	0.145	0.268	0.108
VII	8	$\pm(x, y, z)(x, y, z)$	0.167	0.150	0.753

The face-centered orthorhombic gamma phase has the lattice parameters: $a = 3.159 \text{ \AA}$, $b = 5.768 \text{ \AA}$, $c = 10.162 \text{ \AA}$.^(11,16,17) The space group is Fddd with the 8 equivalent plutonium atoms at: (000); $(1/2, 1/2, 0)$; $(1/2, 0, 1/2)$; $(0, 1/2, 1/2)$; $(1/4, 1/4, 1/4)$; $(3/4, 1/4, 3/4)$; $(3/4, 3/4, 1/4)$; $(1/4, 3/4, 3/4)$. Each atom has four neighbors at $3.026 \text{ \AA}$, two at $3.159 \text{ \AA}$, and four at $3.288 \text{ \AA}$.

The delta and epsilon phases have face-centered cubic and body-centered cubic atomic arrangements respectively. The lattice parameters of the delta and epsilon phases are $4.637 \text{ \AA}$ and $3.636 \text{ \AA}$ respectively. The distance of closest approach is $3.279 \text{ \AA}$ and $3.149 \text{ \AA}$ respectively for the delta and epsilon phases.⁽¹¹⁾

The delta prime phase can be described as having a body-centered tetragonal structure with the lattice dimensions: $a = 3.327 \text{ \AA}$, $c = 4.482 \text{ \AA}$ with eight neighbors at $3.249 \text{ \AA}$ and four neighbors at $3.327 \text{ \AA}$.⁽¹¹⁾

Some of the other peculiarities that have been reported for plutonium are:

- (1) The average coefficients of thermal expansion are high for the alpha, beta, gamma, and epsilon phases.
- (2) The coefficient of thermal expansion is negative for the delta and delta prime phases.
- (3) The volumetric changes are large for all the transformations except the $\delta \rightarrow \delta'$ transformation.
- (4) The close-packed, face-centered cubic delta allotrope has the lowest density of the allotropes.
- (5) The body-centered cubic epsilon phase contracts upon melting.
- (6) Extensive physical damage occurs during the $\beta \rightarrow \alpha$ transformation.
- (7) The electrical resistivities are high for all of the allotropes.
- (8) The thermal coefficient of resistivity is negative for the delta and delta-prime phases.
- (9) The ductility is high for the monoclinic beta phase formed from alpha phase whereas the monoclinic alpha phase has low ductility but can be rolled to 90% reduction in thickness at room temperature.

3. Phase Transformation in Plutonium

Dilatometry, resistivity, and thermal analysis have been used to study all of the phase transformations in plutonium. Of these techniques, dilatometry has been used the most extensively but it has provided very little information on the kinetics and mechanisms of the transformations, except for the $\delta \rightleftharpoons \gamma$ transformation. All the transformations, except the $\delta' \rightleftharpoons \epsilon$ and $\delta' \rightleftharpoons \delta$ transformations are quite sluggish near their transformation temperatures; i.e. there is a temperature hysteresis between the transformations upon heating and cooling.

The dilatometric curve of the $\delta \rightarrow \gamma$ transformation has a stepwise appearance upon continuous cooling of the metal. This phenomenon has been studied by Abramson,⁽¹⁸⁾ Pascard,^(19,20) Taylor,⁽²¹⁾ and Hill.⁽²²⁾ Pascard found that the $\delta \rightarrow \gamma$ transformation consists of three distinct temperature regions.

- (1) In region I, between 280°C and 310°C, the transformation is time-dependent at a fixed temperature. Hill observed that the transformation can go to completion in this temperature region.
- (2) In region II, between 220°C and 286°C the transformation proceeds as a series of discrete steps upon continuous cooling. The transformation is time-dependent at a fixed temperature.
- (3) In region III, below 220°C, most of the $\delta \rightarrow \gamma$ transformation occurs in large steps upon continuous cooling.

The proposed mechanism for the $\delta \rightarrow \gamma$ transformation is that it is diffusional in region I and martensitic in regions II and III.^(20,22)

Most of the $\gamma \rightleftharpoons \beta \rightleftharpoons \alpha$ transformation kinetics studies have been by Nelson.⁽²³⁻³¹⁾ The works of Nelson, Loasby, et al.,⁽³²⁾ and Rosen and Peterson⁽³³⁾ describe the kinetics of the $\beta \rightarrow \alpha$ transformation in detail, but they provide little indication of the type of transformation mechanism, i.e. they may be either diffusional, martensitic, or massive transformations. Since one of the purposes of this dissertation is to categorize the transformations according to type, it is necessary to define these three terms.

If a diffusional mechanism is operative then the atoms of the parent phase move to the product phase one, two, or a few atoms at a time by thermally activated jumps across the interface. The activation energies associated with diffusional transformations are quite large. The interface of diffusional transformations is incoherent. All transformations requiring partition of alloying elements, even trace elements, are diffusional.

Martensitic transformations are sometimes referred to as shear and diffusionless transformations. Growth occurs when a group of atoms in the parent phase undergo cooperative movement by shear. Individual atoms move less than an interatomic distance relative to their neighbors. The interface between the parent and the product phase moves semicoherently. Growth does not depend upon diffusion. Also a definite crystallographic orientation relationship and habit plane relate the parent and product phase.⁽³⁴⁾

A martensitic transformation may be either athermal or isothermal. In athermal martensitic transformations nucleation and growth are not thermally activated and the transformations are essentially time independent. In isothermal martensitic reactions, nucleation and perhaps growth occur by thermal activation. Isothermal martensitic transformations occur in U-Cr⁽³⁵⁾ and Fe-Ni-Cr⁽³⁶⁾ alloys.

The massive transformation consists of atomic re-arrangement at the interface with no partition of alloying elements and no long-range diffusion. That is, the transformation is thermally activated at the interface but macroscopically it is diffusionless. This mechanism has been proposed for transformation of the beta phase in Pu-Ti⁽³⁷⁾ alloys and for transformation of rapidly cooled beta in a Cu-38% Zn alloy.⁽³⁸⁾ One-component systems obviously do not require long-range diffusion since a composition change does not need to be accommodated.

B. PROGRAM OF INVESTIGATION

This investigation of the low temperature allotropic transformations in plutonium was performed to provide information that should be of practical use in the fabrication and heat treatment of plutonium and to advance our understanding of allotropic transformations in general. Plutonium having six allotropes offers a unique opportunity to study allotropic transformations. Because considerable conjecture exists on the mechanisms of the

transformations in plutonium, experiments were performed to provide indirect information concerning the mechanisms responsible for these transformations.

A definite crystallographic orientation relationship and a habit plane between the product phase and the parent phase are characteristic of a martensitic transformation. It is always desirable that these be established by X-ray diffraction before a transformation be categorized as martensitic. This is especially so if one wishes to deduce the atomic movements. Determinations of such relationships are yet unaccomplished for the low temperature transformations in plutonium because of the complexity of the crystal structure and because the elevated temperature phases neither can be retained at room temperature nor examined at temperatures above room temperature.

Transformation of a polished surface of the parent phase into a martensitic phase is generally characterized by a well-defined surface distortion that reveals the change in shape associated with the martensitic transformation. This is referred to as tilting. Bilby and Christian⁽³⁹⁾ pointed out that tilt on a metal surface is implicit in martensitic shear. This simple experimental test cannot be applied to plutonium for two reasons: 1) plutonium cannot be polished and examined satisfactorily at temperatures above room temperature and 2) the large volume changes cause surface rumpling and upheaval that cannot be attributed to tilting.

Although verification of any of the transformations in plutonium as martensitic is impossible by these experimental tests, basic information on the mechanisms of the allotropic transformations of plutonium can be obtained indirectly. First, the influence of certain variables; such as plastic deformation of the stable parent phase, preferred orientation of the parent phase, and applied uniaxial stresses on the transformation kinetics can be correlated to the mechanisms of transformation.

Second, the mechanism of phase transformation affects the manner in which the metal transforms under applied stress. Therefore the kinetics of $\gamma \rightleftharpoons \beta \rightleftharpoons \alpha$ transformations of unrestrained plutonium and the behavior of the transformations under applied stresses were investigated in detail to provide information that could be related to mechanisms of phase transformations.

Before analysis of the transformations under applied stress could be made, single-phase creep of each allotrope had to be evaluated. It has been demonstrated that the steady-state creep rate of pure metals depends upon self-diffusion. Accordingly, the temperature dependency of the creep data were used to obtain calculated activation energies for self-diffusion of the plutonium allotropes. The calculated values can be used as a very good approximation for the self-diffusion activation energies, which have been determined experimentally using radioactive tracer techniques for only the delta phase. These experiments were also the first opportunity to provide a comparison of creep data of six crystal structures, some simple and some complex, in the same metal.

Physical damage in the form of cracking during phase transformation can be quite severe. Since micro- and macrocracks are an integral part of the allotropic transformations it was imperative that this phenomenon be investigated. Thus the investigation of physical damage was undertaken for the primary purpose of determining its role in the allotropic transformations of plutonium. This was necessary before kinetic data could be interpreted and before a mechanism could be postulated for any of the transformations.

This dissertation provides information on the low temperature allotropic transformations in plutonium to learn more about this complex metal and to enhance our understanding of allotropic transformations in metals.

CHAPTER II

EXPERIMENTAL PROCEDURES AND TECHNIQUES

This chapter describes the procedures and techniques used to study the low temperature allotropic transformations in plutonium. Because plutonium is an alpha emitter of long half-life for which the maximum permissible body burden is 0.6 microgram,^(1,2) all of the experiments and their associated operations were conducted either in gloveboxes or in open-front hoods. This complicated most of the experiments. The large volumetric changes associated with the low temperature transformations; the very low, 112°C $\alpha \rightarrow \beta$ transformation; the high reactivity of plutonium with most liquids; and the high oxidation rates in air environments warrant special consideration. These are discussed in detail.

A. PREPARATION OF THE METAL

1. Source of the Metal

The metal used in these studies was from two sources:

- (1) Plutonium reduced to the metallic state during the bomb reduction of plutonium fluoride with calcium
- (2) Plutonium electrorefined by the fused salt electrorefining processes at the Los Alamos Scientific Laboratories.⁽⁴⁰⁾

Typical microstructures of the metal made by the two processes are shown in Figures 3 and 4.

The electrorefined plutonium was obtained in the form of rods 6 inches long and 0.38 inch diameter. Some of the rods were used in the as-received condition. Others, which contained excessive microcracks, were vacuum melted and vacuum cast with special procedures that minimized further microcracking due to subsequent $\beta \rightarrow \alpha$ transformation. Microcracking in plutonium is described in detail

Figure 3
Representative microstructure of alpha plutonium.
Polarized light illumination 200X

Cathodic vacuum etched,
45 minutes at 3 ma and 3500 volts
at a pressure of 1.5×10^{-2} torr

Electrolytically etched 60 sec
at 12 volts ac with a current density of 6 amps/cm^2
An electrolytic etchant was used consisting of
90% methyl alcohol and 10% nitric acid

Figure 4

Microstructure of electrorefined plutonium

100X

in Chapter IV. The chemical analysis of the as-received electro-refined plutonium is given in Table VI.

TABLE VI

CHEMICAL ANALYSES OF ELECTROREFINED PLUTONIUM
AND REPRESENTATIVE ANALYSES OF AS-REDUCED PLUTONIUM
BEFORE AND AFTER CASTING, ppm

	Electrorefined Plutonium	As-Reduced Plutonium	
		Before Casting	After Casting
Aluminum	10	40	30
Americium	40	170	190
Carbon	40	50-100	50-100
Calcium	5	100	10
Columbium	--	--	--
Hydrogen	2	2-10	2-5
Iron	30	50-100	50-100
Magnesium	--	100-500	10
Manganese	--	25	25
Nickel	5	25	25
Nitrogen	5	2-10	2-5
Oxygen	10	20	20
Silicon	--	20	20
Uranium	25	50-100	50-100
Others	50	100-200	100
Density, 25°C g/cm ³	19.58-19.76*	19.50-19.60	19.55-19.65

* The density variation was due to different casting procedures that caused a variation in the amount of microcracks.

The as-reduced plutonium was received in the form of buttons weighing two kilograms. These buttons were vacuum melted and vacuum cast into ingots, which were remelted and cast into the applicable shapes. That vacuum melting and vacuum casting improved the chemical purity of the as-reduced metal is evident in Table VI.

2. Vacuum Melting and Casting Techniques

The specimen geometry for all of the experiments was achieved by casting and machining. The metal used in the initial experiments was melted in a magnesium oxide crucible by heating to 900°C in a vacuum of 10^{-3} to 10^{-2} torr, and poured into a MgO-coated graphite mold.

Most of the experiments, though, were performed with high purity metal that was melted in a tantalum crucible by heating to 1000°C in a vacuum of 10^{-4} to 10^{-3} torr. The metal was then cast into preheated graphite molds coated with a ceramic paint that consisted of fused alumina and silica; the preheat temperature of the molds was 550°C.

After the ingots had cooled to approximately 140°C, which was in the beta phase region they were permitted to transform to the alpha phase by two basic techniques:

- (1) The ingots were taken from the molds in the beta phase and air-cooled to room temperature.
- (2) The ingots were taken from the molds at approximately 140 to 150°C, transferred to an oil bath at 110°C so that the metal could transform completely to beta, quenched to a low temperature of about -110°C to minimize microcracking that is introduced during $\beta \rightarrow \alpha$ transformation, and finally cycled between -80°C and +100°C to transform any retained phases to alpha.

The latter procedure produced ingots of electrorefined plutonium that had densities of 19.70 to 19.76 g/cm³.

The chemical analyses of specific heats are given in Table VII. The most prevalent impurity elements are iron, carbon, and uranium. The iron and carbon form compounds of Pu₆Fe and Pu₃C₂. The Pu₆Fe is present in a Pu-Pu₆Fe eutectic. Neither iron nor carbon has extensive solid solubility in plutonium; however, uranium forms a solid solution in the beta phase which transforms to the alpha phase by

means of a peritectoid reaction, $\beta(\sim 0.1\% \text{ U}) + \delta(25\% \text{ U}) \rightleftharpoons \alpha$ ($< 0.1\% \text{ U}$) + $\delta(25\% \text{ U})$ at approximately 125°C. Americium was also present in the amount of 50 to 150 ppm, although analysis was generally not made for it. This element is a delta stabilizer.

TABLE VII
DENSITY, g/cm^3 , AND CHEMICAL PURITY, ppm, OF THE
PLUTONIUM USED TO STUDY THE PHASE TRANSFORMATIONS

	Heat A	Heat B	Heat C	Heat D	Heat E	Heat F	Heat G
Aluminum	80	20	32	25	10	20	20
Americium	*	*	*	*	*	*	*
Carbon	130	110	100	120	60	90	100
Calcium	13	5	20	10	10	---	5
Chromium	100	16	20	20	---	---	10
Columbium	---	50	10	---	---	---	10
Hydrogen	*	5	8	*	*	*	*
Iron	726	130	260	60	50	50	50
Magnesium	<10	25	200	---	5	---	---
Manganese	40	25	20	20	20	20	20
Nickel	40	50	50	40	20	10	25
Nitrogen	*	1	1	*	*	*	*
Oxygen	*	180	180	*	*	*	*
Silicon	20	---	---	---	10	---	---
Uranium	*	50-100	50	50	50	50	50
Others	<50	<50	<50	<50	<50	<50	<50
Density	19.50	19.62	19.55	19.61	19.63	19.68	19.67

B. DENSITY DETERMINATION

1. Application of Density Determinations to Plutonium

The bulk density of a specimen determined according to Archimedes' principle is employed more frequently in studies on plutonium than on other metals. Moreover, in metallurgical studies of plutonium and its alloys either density or its reciprocal, specific volume, has become a useful index of the condition of the metal. Density values are important because they are sensitive to small changes within the metal. If density values are supplemented with metallography and chemical analysis, the "quality" of the metal can usually be established. Quality is defined here as an indication of the combination of impurities revealed by chemical analysis, and microcracks revealed by density and metallography.

The density of cast plutonium as determined by fluid displacement measurements is always lower than the X-ray value which is 19.84 g/cm^3 at 20°C . The lower density is due to the presence of vacancies and dislocations, lighter impurity atoms, retained phases of lower density, and cracks and voids.

Specific examples of the effect of prior treatment and composition on the density of plutonium metal can be cited:

- (1) Densities as high as 19.80 g/cm^3 at 25°C have been achieved by heating high-purity specimens to 170° to 200°C and cooling under pressures of 50,000 psi or more. This is a treatment that minimizes cracking and favors complete transformation to the alpha phase.
- (2) Metal with only 100 ppm impurities can, on the other hand, have a density as low as 19.4 g/cm^3 . The difference of 0.4 g/cm^3 from the theoretical density is primarily due to the presence of micro- and macrocracks.
- (3) Plutonium may have only a few microcracks and yet have a low density. Compounds such as Pu_3C_2 and Pu_6Fe can be responsible for the low density.

- (4) Plutonium may have few intermetallics and microcracks, and yet may have a density as low as 18.0 g/cm^3 . Such a low density is attributed to beta and delta phases that are retained as a result of the presence of certain stabilizing elements.

The previous examples illustrate some of the problems associated with the use of density alone as a measure of metal quality. They also indicate the need for accurate density values. As a general rule, accuracies better than $\pm 0.01 \text{ g/cm}^3$ (one part per 2000) are unwarranted since variations in the densities of castings obtained from the same melt and given identical treatment frequently exceed this range.

It is possible from density measurements alone to estimate with reasonable accuracy the volume of cracks and the amount of retained phases within alpha plutonium. In this instance, the metal must be subjected to subsequent heat treatments that promote transformation of the retained phases but do not influence the extent of cracking present in the specimen.

Density measurements contributed greatly to the study of the transformation of phases and physical damage in plutonium. For example, a 0.03% change in the density of a specimen ($\Delta\rho = 0.006 \text{ g/cm}^3$) can correspond either to 0.3% of the metal undergoing a $\beta \rightarrow \alpha$ transformation or to 0.03% change in the volume of the specimen due to elimination of void space. Such a change can be detected by fluid displacement measurements. If the transformation of small amounts of retained phases over periods of time as long as a year was to be detected, it was desirable that the precision of density measurements should be at least $\pm 0.005 \text{ g/cm}^3$.

Computation of the density of plutonium is based on the equation $\rho_{\text{Pu}} = m/V$, where ρ_{Pu} is the density of the plutonium in g/cm^3 , m is the true weight in g, and V is the volume of the metal in cm^3 . Since $V = (m - m_L)/\rho_L$, where m_L is the true weight of the plutonium in the fluid and ρ_L is the density of the liquid, substitution yields

$$\rho_{Pu} = \frac{m \rho_L}{m - m_L} \quad (II-1)$$

Although this equation is simple, several factors that are unique for plutonium must be carefully considered:

- (1) The large coefficient of thermal expansion of the alpha phase which results in a density decrease of $0.0028 \text{ g/cm}^3/\text{°C}$,
- (2) Self-heating characteristics ($1.9 \times 10^{-3} \text{ w/g}$),
- (3) Self-irradiation damage,
- (4) Chemical reactivity with most liquids,
- (5) High density,
- (6) Radioactivity and contamination problems that require glovebox operation, and
- (7) High oxidation rates in normal air environments.

These factors, collectively, make accurate density determinations quite difficult.

Although calculation of the density of plutonium is simple, the determination to better than 3 parts per 10,000 requires careful attention to technique. This is about the limit of reproducibility for density determinations of plutonium. Many factors such as air buoyancy, temperature differences, surface tension, chemical changes, and calibration of the density of the displacement fluid contribute significantly to the precision of the results.

2. Room Temperature Density Measurements

The density of a material is defined as mass per unit volume at a given temperature and pressure. The mass or weight is always determined by direct weighing and must be corrected to an equivalent weight in vacuum to compensate for air buoyancy effects. The volume can be found either directly from the dimensions or from the weight loss due to the buoyant effect of a liquid of known density. Unless the metal is machined with a high precision to a given simple

geometry, its volume can be determined more accurately by the fluid displacement technique.

Distilled water is a suitable fluid for density measurements of most light metals, but it is unsatisfactory for density determinations of plutonium because it reacts rapidly with plutonium. Bromobenzene, C_6H_5Br , is commonly used as a displacement fluid,^(41,42) because 1) it is inexpensive and readily available, 2) it does not corrode plutonium, 3) it is nonhygroscopic, 4) it is readily purified, 5) it has a sufficient vapor pressure to permit specimens to be readily cleaned and dried after immersion, 6) it has a volume coefficient of expansion of only $1.6 \times 10^{-4} \text{ cm}^3/\text{cm}^3 \text{ } ^\circ\text{C}^{-1}$, 7) it has a low viscosity, 8) it has a surface tension at room temperature of 36 dynes/cm, and 9) it has a density of 1.45 g/cm^3 at 20°C . The primary disadvantages of bromobenzene are its flash point of 50°C and its instability on exposure to air. Blumenthal⁽⁴¹⁾ found that the density may decrease as much as 0.004 g/cm^3 in a 12-day period and that it may increase or decrease during short periods.

An inert fluorochemical designated FC-75* was used extensively in the present investigation. This liquid offers most of the advantages of bromobenzene. Although it is more expensive and has a higher volume coefficient of expansion ($1.4 \times 10^{-3} \text{ cm}^3/\text{cm}^3/^\circ\text{C}$) than to bromobenzene it has advantages of 1) a higher density (1.78 g/cm^3), 2) a wider temperature range of fluidity ($< -100^\circ\text{C}$ to about $+100^\circ\text{C}$, 3) a lower surface tension (18 dynes/cm at room temperature), 4) a lower viscosity (1 centistoke at room temperature), 5) greater stability over long periods of time, and 6) no flash point.

Another displacement liquid also used for room temperature density determinations of plutonium and for density determinations between -50 and $+150^\circ\text{C}$ is perfluorotributylamine, $(C_4F_9)_3N$, designated FC-43.* It has a vapor pressure at room temperature of only 0.3 mm, which is significantly less than that of either water, FC-75, or

* FC-75 and FC-43 are manufactured by Minnesota Mining and Manufacturing Company.

bromobenzene. Its boiling point is approximately 170°C. Its inertness and density are slightly better than the fluorochemical previously mentioned. Its coefficient of volume expansion is $1.2 \times 10^{-3} \text{ } ^\circ\text{C}^{-1}$ at room temperature. Its major disadvantage is its high cost.

The density of the displacement liquid was determined from its buoyancy on a precision machined standard. Invar was used because it has a negligible thermal coefficient of expansion at room temperature. The density of the standard calculated from its weight and its dimensions, was found to be $8.0559 \pm 0.0007 \text{ g/cm}^3$ in the liquid. Accuracy greater than this was usually unnecessary because the variations in density rather than its absolute value were required.

A one-pan analytical substitution type balance (Figure 5), modified to allow the samples to be weighed beneath the balance case, was enclosed in a glovebox having an air atmosphere. The fluid was placed below the balance case rather than within to simplify correction of all weight measurements for air buoyancy effects. If the fluid were within the balance case the buoyancy effect of the heavier fluorochemical vapors would have been significantly greater than that of air.

The density of either of the immersion liquids can be approximated over a range of temperatures by the general equation:

$$(\rho_f)_t = (\rho_f)_{20C} + C_1 (T-20) + C_2 (T-20)^2 + C_3 (T-20)^3 \quad (\text{II-2})$$

where C_1 , C_2 , and C_3 are constant coefficients and T is the actual temperature in $^\circ\text{C}$. The value of C_1 is -2.56×10^{-3} for the FC-75, -1.35×10^{-3} for the $\text{C}_6\text{H}_5\text{Br}$, and -2.25×10^{-3} for the FC-43. The terms with exponents higher than 1 were neglected for room temperature density measurements since the temperature measurement was $24 \pm 2^\circ\text{C}$.

If the density is being considered in the range -100°C to $+100^\circ\text{C}$ then the deviation from linearity can be appreciable. If a degree of accuracy greater than $\pm 0.01 \text{ g/cm}^3$ is desired, higher order terms of T must be included.

Figure 5

Glovebox for density determination of plutonium

The density of different batches of the inert fluorochemical examined over a period of three years varied from 1.770 to 1.777 g/cm³ at 23°C. Accordingly, the density of each batch had to be measured accurately to obtain the value of $(\rho_L)_{20^\circ\text{C}}$. The densities of a representative batch measured daily at different temperatures during a four-month period are given in Figure 6. The degree of stability of this liquid with time is extremely high. The maximum deviation from linearity was ± 0.0001 g/cm³ in four months.

Figure 6
Linear relationship between
density and temperature of fluorochemical FC-75

The volume of an unknown specimen was calculated from the relationship

$$m/\rho_{Pu} = V = \frac{m - m_L}{\rho_L} \quad (II-3)$$

The value of m was determined by direct weighing with corrections being made for the air buoyancy of the plutonium and the balance weights. A value of $1.16 \times 10^{-3} \text{ g/cm}^3$ was taken as the average air density. The variation in density of air with time over the last ten-year period at Hanford, where the work was done, was $\pm 0.00004 \text{ g/cm}^3$. Neglecting this variation introduces an error in the measured value of the density of plutonium by an amount no greater than 0.0004 g/cm^3 . Corrections due to normal variations in air density caused by changes in temperature and pressure could therefore be neglected.

A 0.13 mm diameter tantalum wire supported the specimen in the liquid located beneath the balance case. The buoyancy of the wire could be calculated from the density of the liquid, the density of the tantalum, and its weight, i.e.,

$$\Delta m = \frac{m\rho_L}{\rho_{Ta}} \quad (II-4)$$

where m = the true weight of the wire, Δm = the difference between the dry weight and the weight in the liquid and ρ_{Ta} 16.6 g/cm^3 . The length of wire in the liquid was measured and hence the buoyancy per unit length could be calculated.

Thermal gradients in the specimen, liquid, and glovebox atmosphere can be responsible for large errors in determining the density of plutonium. A 0.1°C error in the temperature of the liquid will result in an error of 0.0026 g/cm^3 in the density of the specimen. The temperature gradient in the specimen and its effect on the temperature of the liquid can be quite large because of the self-heating of plutonium, $1.9 \times 10^{-3} \text{ w/g}$. This is especially true in the case of large specimens. Agitation of the displacement liquid for 15 minutes prior to weighing minimized this error. The volume of the liquid was at least two liters to provide an adequate heat

sink. Agitation under these conditions promoted a reproducible semi-equilibrium state with a negligible temperature difference between the specimen, the bath, and the glovebox. Temperatures were measured with mercury and resistance thermometers that were calibrated periodically. The sample immersed in the liquid was weighed within 15 to 30 seconds after agitation.

On any given day when the density of plutonium was determined, an additional check of the reproducibility of the procedures and reliability of results was made. This check involved an independent determination of the density of a gold standard that had none of the perturbing characteristics of plutonium but had an invariant density and weight that closely approximated those of plutonium. The density of the gold standard as a function of time is plotted in Figure 7. Because the variation from the mean of any given

Figure 7
Variation of the density of
a gold standard specimen with time

determination is less than $\pm 0.0027 \text{ g/cm}^3$ (1.5 parts per 10,000), the procedures used were considered satisfactory. A metal such as gold had to be used as a standard since the density of plutonium varies with time.

The density variations of a number of plutonium specimens with different thermal and mechanical treatments were determined periodically over a period of two and one-half years. The effect of different mechanical and thermal treatments on the density variation with time is reported in detail in Chapters III and IV. Errors due to measurement were greater for these specimens than for gold. The density variation with time of two representative samples is reported here. One sample was stored in vacuum between measurements and the other was stored in a refrigerator at 0°C between measurements. The latter required wire brushing prior to each density measurement. Both samples were hydrostatically pressed at 180°C (beta phase) and 90,000 psi and then cooled and transformed under pressure to yield dense plutonium.

The sample stored in the refrigerator between measurements exhibited apparent changes in density (Figure 8). The density variation over a long period of time, one and one-half years, was -0.013 g/cm^3 . The density variation over shorter periods of time, such as 30 days, was generally less than $\pm 0.006 \text{ g/cm}^3$. The observed fluctuations and variations in the data in Figure 8 can be attributed to 1) small errors in the density determinations, 2) differences in surface state arising from different specimen preparation, and 3) a gradual decrease in density associated with damage resulting from self-irradiation.

The large density variation was absent in the sample stored in vacuum between measurements, Figure 9. The density appears to decrease linearly with time, -0.006 g/cm^3 per 100 days. The variation from linearity is less than $\pm 0.003 \text{ g/cm}^3$. It is obvious that a specimen of plutonium cannot be used as a known standard in the determination of densities of unknown plutonium specimens.

Figure 8

Influence of aging time on the density change of alpha plutonium

Figure 9

Influence of aging time on the density change of alpha plutonium

3. Density Determinations Above and Below Room Temperature

The density determinations above and below room temperature were performed in a glovebox that could be evacuated and back-filled with either nitrogen or argon (Figure 10). It was possible to out-gas liquids and maintain a satisfactory inert atmosphere in this glovebox. The glovebox had two compartments, an upper compartment which contained an automatic recording balance and a lower compartment in which samples were weighed either dry or in a liquid (Figure 11). A diagram of the glovebox arrangement is given in Figure 12.

The average densities of nitrogen and argon used in the glovebox have been calculated to be 0.00112 and 0.00160 g/cm³, respectively. Actual deviations from these values due to variations in pressure and temperature were not great and could be neglected within the temperature range $24 \pm 3^{\circ}\text{C}$.

At temperatures below room temperature the inert fluorochemicals FC-75 and FC-43 were used as the displacement medium. The fluorochemical was placed within an inner chamber, and a suitable liquid at its freezing point was placed in the outer chamber of a double container. The atmosphere had to have a very low dew point to prevent freezing of moisture on the wire supporting the sample. FC-43 could not be used below about -30°C whereas FC-75 could be used to about -100°C .

The displacement liquid used primarily from room temperature to 250°C was a high temperature silicone fluid. Its density has been expressed by the relationship $\rho = 1.0640 - 7.6 \times 10^{-4}(T - 20)$, where T is temperature in $^{\circ}\text{C}$. The density-temperature dependency, however, was determined experimentally over the entire range of temperatures for each batch of fluid prior to use.

The temperature of the silicone fluid in a heating mantle was controlled within $\pm 0.02^{\circ}\text{C}$ by a precision temperature controller. This temperature variation caused a variation in the density of the liquid of 1.5×10^{-4} g/cm³ which in turn caused an error of

Figure 10

Facility for continuously recording the density change
(or specific volume) of plutonium undergoing phase transformation

Figure 11

Equipment arrangement in an evacuable glovebox for density determinations of plutonium between -120°C and 250°C

Figure 12
Schematic diagram of the evacuable glovebox facility

approximately $2.7 \times 10^{-3} \text{ g/cm}^3$ (1.5 parts per 10,000) in the density of plutonium. This was independently confirmed by determining the immersed weight variation of a 150-g Invar standard. The variation was $\pm 0.002\%$ over a 6-day period at $95^\circ\text{C} \pm 0.02^\circ\text{C}$. The immersed weight variation of a 25-g plutonium sample was less than $\pm 0.5 \text{ mg}$ over a 10-day period at $90^\circ\text{C} \pm 0.2^\circ\text{C}$.

The major problem of elevated temperature density determinations was the oxidation of samples. The oxidation of a plutonium sample was negligible only if the silicone fluid had been outgassed. Outgassing at temperature at a pressure of 5×10^{-2} torr generally required 30-60 minutes.

4. Specific Volume Measurements During Phase Transformation

The automatic recording balance enclosed in the glovebox shown in Figure 10 was used for continuous monitoring of the $\beta \rightarrow \alpha$, $\alpha \rightarrow \beta$, $\gamma \rightarrow \beta$, and $\beta \rightarrow \gamma$ transformations by measuring the time dependency of the specific volume change during transformation. This technique provided a simple and accurate means for determining the kinetics of the low temperature transformations. Since the samples were suspended below the balance case and since the plutonium was contained in an inert glovebox, the specimens could be rapidly transferred from one medium to another.

Continuous monitoring was possible for transformations that required days for completion. Continuous monitoring also was possible for transformations that were more rapid than this. One of the primary advantages of this technique is that very thin specimens, 0.012 centimeter or less, could be used.

The specific volume change for any percentage transformation was assumed to be proportional to the fraction transformed. For example, the fraction of beta transformed to alpha at any percentage of alpha is:

$$f = \frac{v_\beta - v_f}{v_\beta - v_\alpha} \quad (\text{II-5})$$

where v_{β} is the specific volume of beta,
 v_{α} is the specific volume of alpha, and
 v_f is the specific volume for the
 partially transformed metal;

or

$$f = \frac{[(m - m_L)/m\rho_L]_{\beta} - [(m - m_L)/m\rho_L]_f}{[(m - m_L)/m\rho_L]_{\beta} - [(m - m_L)/m\rho_L]_{\alpha}} \quad (\text{II-6})$$

Simplifying this equation yields

$$f = \frac{(m_L)_f - (m_L)_{\beta}}{(m_L)_{\alpha} - (m_L)_{\beta}} \quad (\text{II-7})$$

Thus the fraction transformed for any percentage of two phases can be computed directly from the immersed weights of a sample containing, 1) the parent phase, 2) a mixture of the parent phase and the product phase, and 3) the product phase. The liquid temperature was maintained constant within $\pm 0.2^{\circ}\text{C}$ so that the density of the liquid would be essentially constant. This simple calculation was complicated by the formation of microcracks during $\beta \rightarrow \alpha$ transformation.

For transformation kinetics studies the specimens were usually wafers with a diameter of 2.5 to 3.5 centimeter. The chosen thickness was usually between 0.012 and 0.025 centimeter for the very rapid transformations; whereas the thickness was usually between 0.05 and 0.10 centimeter for the slow transformations. The weight gain during the $\beta \rightarrow \alpha$ transformation (weight loss during the $\alpha \rightarrow \beta$ transformation) of a 3 centimeter diameter and 0.05 centimeter thick specimen in FC-43 is approximately 57 milligrams. The corresponding weight change of the buoyed specimen in silicone oil is 32 milligrams. The sample volume and weight of a specimen this size are approximately 0.35 cm^3 and 7 grams.

During the $\gamma \rightarrow \beta$ and $\beta \rightarrow \gamma$ transformations the weight change of a 0.35 cm^3 specimen buoyed in silicone oil is 12 to 14 milligrams. Thus a larger specimen was generally used to study these transformations. Generally, a specimen having a volume of approximately 1 cm^3 was found to be the most satisfactory. Thin samples, less than 0.03 cm thick, were used to study the $\gamma \rightarrow \alpha$ transformation because 1) the volume change is 13 to 15 percent, 2) the $\gamma \rightarrow \alpha$ transformation is very rapid, and 3) the temperature difference between the gamma heat-treating temperature and the $\gamma \rightarrow \alpha$ transformation temperature is 120°C or more.

C. METALLOGRAPHY

All specimens were mounted in Thalco polyester resin which sets up slightly above room temperature. This kept the specimen temperature below the 112°C $\beta \rightarrow \alpha$ transformation temperature during mounting. The mounted specimens were rough-polished by hand on wet-or-dry emery paper of 180 through 600 grit. A liberal amount of carbon tetrachloride was used as a lubricant and coolant during this operation.

Fine polishing was accomplished in a two-step process on Syntron vibratory polishers. The first step consisted of a 1-hour polish on silk cloth with Linde A emulsion in carbon tetrachloride. The second step, on a different Syntron, consisted of a 10 to 30 minute polishing period on microcloth with Linde A and carbon tetrachloride. This procedure resulted in a nonoxidized scratch-free surface which is termed "as-polished."

Electrolytic etching for inclusion studies and for grain structure was done in a solution of 25 parts tetraphosphoric acid, 15 parts water, and 60 parts 2-ethoxy ethanol. The specimens were generally prepared for grain structure examination by electrolytically etching 60 seconds at approximately 50 volts and 1 amp/cm^2 . Grain structure photomicrographs of specimens prepared with this etchant were taken under polarized illumination. Electrolytic

etching times for inclusion studies varied between 1 and 10 seconds at 15-23 volts.

The grain structure observed under polarized illumination was essentially the same as the grain structures revealed both by vacuum cathodic etching and by a grain structure, bright field etchant consisting of 10% nitric acid in methyl alcohol.

All of the metallography was conducted in gloveboxes. This complicated most of the metallographic operations and tended to lower the over-all quality of the surface finish. In addition, most of the metallographic samples were viewed through a sealed 0.015-inch thick clear plastic bag for polarized light examination since a glovebox enclosed metallograph was not available for polarized light illumination. Imperfections in the plastic frequently lowered the quality of the photomicrographs, especially at magnifications greater than 250X.

D. X-RAY DIFFRACTION

X-ray diffraction was used to observe the kinetics and degree of completion of the $\alpha \rightleftharpoons \beta \rightleftharpoons \gamma$ transformations using an elevated temperature goniometer attachment. X-ray diffraction was also used to study the texturing of the alpha phase that was formed under applied compressive and tensile stresses. The only difference between the procedures used for X-ray diffraction of plutonium and the conventional procedures used for most metals is that the X-ray goniometer was enclosed in a glovebox (Figure 13) containing an inert nitrogen atmosphere.

E. HEAT TREATING AND QUENCHING PROCEDURES

The heat treating and quenching procedures for plutonium are somewhat involved due to the six allotropes. The phase to which the metal is heated influences subsequent mechanical properties and transformation kinetics. Thus in heat treating plutonium it is important that the phase, temperature, and time of heat treatment be specified. When the metal is heated into the beta phase temperature range the metal is said to be beta heat treated. Correspondingly, when the

Figure 13
X-ray diffractometer and glovebox

metal is heat treated in the equilibrium temperature ranges of either the gamma, delta, or epsilon phases the metal is said to be either gamma, delta, or epsilon heat treated.

Beta heat treatment was done in either a vacuum, an inert atmosphere, or in a fluid that had previously been outgassed at a pressure of approximately 5×10^{-2} torr. The most common fluids were a high temperature silicone fluid and inert fluorochemicals, particularly FC-43. Gamma, delta, and epsilon heat treatments were in an inert atmosphere or in a vacuum. The fluids were heated by a heating mantle shown in Figure 11. Small resistance furnaces were used to heat samples in either vacuum or in nitrogen and argon atmospheres. Heat treatment in inert atmospheres was generally in a glovebox shown in Figure 10.

Quenching was performed simply by transferring the samples from their heat treating environment to an appropriate liquid. The fluid used most frequently was FC-75 because of its wide range of fluidity ($\approx -100^{\circ}\text{C}$ to about 100°C) and its low corrosive action on plutonium. Other fluids used between 25°C and $+150^{\circ}\text{C}$ were the high temperature silicone fluid and the FC-43. Alcohol was used between -80°C and -115°C , which is its pour temperature. Liquid nitrogen was used at -196°C .

F. COMPRESSION CREEP APPARATUS AND PROCEDURES

The metal used in this investigation was high-purity as-reduced plutonium that had been vacuum melted and vacuum cast. Typical impurity contents were: 50 ppm Fe, 60-100 ppm C, 50 ppm U, 20 ppm Ni, 10 ppm Al, 5 ppm Mg, and 10 ppm Si; the americium content was estimated to be 100 ppm. The concentration of all other impurities was considered to be less than 100 ppm. The high value for the density of the metal, greater than 19.60 g/cm^3 , was considered to be a necessary confirmation of metal quality and purity.

The compressive creep experiments were performed on solid cylindrical rod specimens. The specimens were prepared by casting and machining. The metal was melted in a tantalum crucible by

heating to 1000°C in a vacuum of 10^{-4} torr and then cast into preheated graphite molds coated with a fused alumina and silica paint. The preheat temperature of the molds was 550°C. After the ingots had cooled to approximately 150°C, they were transferred to an oil bath at 110°C and held at temperature for 2 hours so that the metal could transform completely to beta. Transformation of beta to alpha was accomplished by a procedure that minimized microcracking introduced during the $\beta \rightarrow \alpha$ transformation. This procedure consisted in quenching to a temperature of -80°C or lower followed by cycling between -80°C and +100°C to transform any retained phases.

The rods were machined to a final diameter of either 0.200, 0.250, 0.375, or 0.500 inch and cut to a length equal to one and one-half times the diameter. The 0.200 and 0.250-inch specimens were used for alpha, beta, and gamma creep studies. Because the delta, delta-prime, and epsilon phases have creep rates which are high compared to those of the low temperature allotropes, larger 0.375 and 0.500-inch diameter specimens were used. Barrelling and total strain for a given load was less in specimens with a large cross section. The crystal structures of the allotropes of plutonium, temperature ranges of stability, and densities are given in Tables I and II.

Creep testing was performed at a pressure of 10^{-3} torr in the apparatus shown in Figure 14. Tantalum sheet, 0.07 mm thick, was placed between the sample and the steel platens to prevent alloying of the plutonium and steel. Alloying occurs quite readily above 415°C due to the formation of a low melting Pu-Pu₆Fe eutectic.

The experiments were performed in the glovebox shown in Figure 15. The flange of the vacuum tube of the furnace located below the glovebox was welded directly to the floor of the glovebox. Power to the tube furnace heater equipped with a control thermocouple was supplied by a controller-variatic combination. A thermocouple attached to the specimen showed that the temperature during an experiment was maintained within $\pm 1^\circ\text{C}$. Relative displacement of the two platens was used as a measure of the creep strain of the specimen.

Figure 14
Apparatus for
compression creep studies
of plutonium

Two externally positioned differential transformers sensitive to 0.0001 inch changes and two dial indicators graduated in units of 0.0001 inch were used. The engineering strain, e , was determined as a function of time and then converted to true creep strain, ϵ , by the relationship $\epsilon = \ln(1 + e)$.

The experiments were performed at constant stress under isothermal as well as under variable temperature conditions. The stress was maintained constant by increasing the load on the platen in direct proportion to the increase in the cross-sectional area of the specimens. The actual stress deviated from the prescribed stress by an amount less than 0.5 percent. The determination of the cross-sectional area was based on the assumptions that the volume of the specimen remained constant and that barrelling of the specimen did not occur during the test. Experimentally, the latter assumption was true for strains up to 0.20. Thus the experiments were generally terminated before that strain was reached.

Figure 15

Glovebox and instrumentation for the plutonium creep experiments

CHAPTER III

THE KINETICS OF THE LOW TEMPERATURE ALLOTROPIC TRANSFORMATIONS IN PLUTONIUM

Research studies were performed on the kinetics of the low temperature allotropic transformations of plutonium. The primary objective of this activity was threefold:

- (1) Determine the transformation rates of the $\beta \rightarrow \gamma$, $\gamma \rightarrow \beta$, $\alpha \rightarrow \beta$, and $\beta \rightarrow \alpha$ transformations.
- (2) Investigate the factors and variables influencing the kinetics of these transformations.
- (3) Provide indirect information on the mechanisms of the transformations.

This chapter presents isothermal reaction curves and Time-Temperature-Transformation (TTT) curves of the $\beta \rightarrow \gamma$, $\gamma \rightarrow \beta$, $\alpha \rightarrow \beta$, and $\beta \rightarrow \alpha$ transformations. The influence of some variables on the transformation kinetics and the microstructure of the alpha phase are related to the mechanisms of transformation.

A. ISOTHERMAL REACTION CURVES AND TTT CURVES OF THE $\beta \rightarrow \alpha$ TRANSFORMATION

Martin and Selmanoff,^(43,44) first indicated that the $\beta \rightarrow \alpha$ isothermal transformation might proceed according to a C curve similar to the TTT curves of many transformations. They reported that the maximum rate of transformation was attained in 1-1/2 minutes at room temperature, whereas at -75°C the maximum rate was reached in 4 minutes.

The first extensive quantitative work on the transformation rates of the $\beta \rightarrow \alpha$ transformation was performed by the author.^(24,26,27,31) This work showed the TTT curve (Figure 16) of the $\beta \rightarrow \alpha$ transformation to have the form of a simple C curve with the maximum rate of transformation at -20°C to -40°C. The isothermal reaction curves of this early work showed that there was appreciable retained phase at 50°C to 70°C after apparent completion

Figure 16

First reported $\beta \rightarrow \alpha$ TTT curve by Nelson⁽²⁶⁾

of the $\beta \rightarrow \alpha$ isothermal transformation (Figure 17). Decreasing the transformation temperature to room temperature decreased the amount of retained phase. This is apparent from the curves but will be discussed in more detail in a later section.

Loasby and Lowe also performed extensive work on the $\beta \rightarrow \alpha$ transformation using a resistivity and volume dilatometric technique.⁽³²⁾ They found rates of transformation comparable to the author's initial results with the maximum rate occurring at -20°C to -30°C as shown in Figure 18. Peterson and Rosen studied the $\beta \rightarrow \alpha$ transformation by ultrasonic methods.⁽³³⁾ They reported a double C curve for the start of the transformation and for 50% transformation but a simple C curve for the completion of the transformation. The nose of the upper C curve was observed at about -10°C . The incubation times they reported for the transformation at the noses of the upper and lower curves were approximately 4 and 0.7 seconds, respectively. Detailed investigation by the author revealed no double C curve.

Figure 17

Representative isothermal reaction curves of the initial studies of the $\beta \rightarrow \alpha$ transformation in plutonium showing incomplete transformation at high alpha temperatures

Figure 18

The plutonium $\beta \rightarrow \alpha$ curve of Loasby and Lowe

[From R. G. Loasby and J. N. Lowe, in E. Grison, W. B. H. Lord, and R. D. Fowler (Eds.), Plutonium 1960, p. 13, Cleaver-Hume Press Ltd., London, 1961]

The isothermal $\beta \rightarrow \alpha$ transformation rates (Figure 19) of either electrorefined or high-purity as-reduced and vacuum-cast plutonium are more than five times faster than the rates of the lower quality metal used in the early work. Thin wafers having a 1-inch diameter and 0.005-inch thickness were used to establish the TTT curve by the fluid displacement technique so that isothermal conditions could be approached. Utilization of thin wafers is particularly important below the nose of the TTT curve so that the metal may reach the isothermal transformation temperature rapidly enough to prevent any of the beta phase from transforming to alpha at the nose of the curve. The difference in rates can be attributed to differences in metal quality. The high-purity plutonium depicted in Figure 19 had a density of 19.62 to 19.70 g/cm³ and contained less than 200 ppm total impurities. The metal initially used by Nelson had a density of 19.45 to 19.55 g/cm³ and contained 1000-1200 ppm total impurities, predominantly iron and carbon (Table VII).

The density of the metal is frequently taken as a criterion of metal quality. However, because of differences in casting, density alone is not satisfactory for determining the quality of high-purity metal; yet density with the aid of metallography will give a very good indication whether or not unalloyed plutonium is of reasonably high quality. Metal having a density greater than 19.65 g/cm³ is considered to be of very high quality. The difference between this value and the theoretical value of 19.83 g/cm³ is primarily due to the presence of vacancies, microcracks, and retained phases. The chemical analyses and densities of the different metals used in the investigation are given in Table VII.

TTT curves showing the times for 50% transformation from the results of Loasby and Lowe, Rosen and Peterson, and the author are given in Figure 20. Little meaning can be obtained from a comparison of the positions of the TTT curves because a number of variables retard or accelerate the rate of transformation at any given temperature. For example, the rate of transformation decreases with increasing beta heat-treating temperature, impurity content, and internal stresses.

Figure 19

Representative TTT curve of the $\beta \rightarrow \alpha$ and $\alpha \rightarrow \beta$ transformations of electrorefined plutonium

Figure 20

TTT curves of Loasby and Lowe,⁽³²⁾ Peterson and Rosen,⁽³³⁾ and Nelson showing the time for 50% $\beta \rightarrow \alpha$ transformation in plutonium

Anderson, et al,⁽⁴⁵⁾ state that the $\beta \rightarrow \alpha$ transformation of plutonium appears to be very rapid, and that the transformation rate is primarily related to the rate at which energy can be removed. They imply that the $\beta \rightarrow \alpha$ TTT curve is not a C curve. There is some truth to this for large specimens, since more than a few seconds are necessary to remove the heat, but this is not characteristic of the kinetics of the $\beta \rightarrow \alpha$ transformation.

Experiments were performed utilizing specimens in the form of wafers 0.005-inch thick that were beta heat-treated 45 minutes at 170°C, cooled to 110°C, quenched into ethyl alcohol at -115°C, held

for 2 to 3 seconds, and then quenched into liquid nitrogen at -196°C . Incubation times for beginning of transformation exceeded 6 hours. Specimens treated in this manner transformed within seconds when they were warmed to temperatures between -20°C and -80°C . These experiments confirm that the $\beta \rightarrow \alpha$ TTT curve is a C curve with the nose of the curve being at -20°C to -40°C .

The isothermal reaction curves in Figure 21 of the $\beta \rightarrow \alpha$ transformation have the shape of typical sigmoidal curves characteristic of nucleation and growth reactions to which the Avrami equation has been applied.

$$(1 - f) = \exp(-kt^n)$$

or

$$\ln \ln \frac{1}{1-f} = \ln k + n \ln t \quad (\text{III-1})$$

where

f = fraction transformed,

t = time,

n = constant, and

k = temperature dependent constant

Figure 21

Isothermal reaction curves of $\beta \rightarrow \alpha$ transformation in plutonium

The verification of a transformation obeying the Avrami relationship can be obtained by plotting $\ln \ln \frac{1}{1-f}$ as a function of $\ln t$ to confirm the linear relationship. For the $\beta \rightarrow \alpha$ transformation of plutonium, such a plot shows that the curve is linear for the early portion of the transformation as shown in Figure 22. The

Figure 22

Avrami plot of $\beta \rightarrow \alpha$ transformation in plutonium

linear portion of the curve has a slope of 4. This value of n is greater than the value of 2 to 3 reported by Loasby and Lowe.⁽³²⁾ The value of $n = 4$ is completely consistent with a transformation proceeding with time independent rates of nucleation and growth.^(47,48) This is to be expected for a transformation with thermally activated nucleation and growth processes not requiring alloy partition. Loasby's and Lowe's reported value for n appears surprisingly low

since it is impossible to account for values of n less than 3 in a pure metal where growth rates are not diffusion limited and therefore should be time independent. Anisotropic growth, as occurs during the $\beta \rightarrow \alpha$ transformation, does not influence the value of n since the growth rate is part of the constant k ; however, the growth rate must be time independent. Deviations from linearity may result from the large stresses generated during transformation. Particular evidence of the influence of internal stresses on the value of n is revealed by observations that n decreases slightly with increasing sample size.

B. KINETICS OF THE $\alpha \rightarrow \beta$ TRANSFORMATION

The isothermal reaction curves of the $\alpha \rightarrow \beta$ transformation between 115°C and 150°C also have the shape of typical sigmoidal curves, as shown in Figure 23. These particular curves were determined using a fluid displacement technique. The value of n was calculated from the Avrami relationship to be 4, which was the same as the $\beta \rightarrow \alpha$ transformation value.

Figure 23

Isothermal curves of the $\alpha \rightarrow \beta$ transformation in plutonium

These data were supplemented by work in which the decomposition of the alpha phase was investigated at temperatures up to 650°C using metallographic techniques, for the purpose of determining approximate isothermal reaction curves of the decomposition of alpha at very high temperatures. Transformation of the alpha phase is quite complex at temperatures higher than the stable phase since more than one product phase may be involved. The intermediate allotropes that form would be metastable and may even not form at all. For example, when plutonium in the alpha phase is immersed into molten metal at 600°C, the stable product phase is epsilon. If any of the intermediate phases, α , β , γ , δ , and δ' , form they would be in a metastable state.

The TTT curves in Figure 19 obtained from these isothermal reaction curves show that above 150°C the alpha completely transforms very rapidly. At 140°C, alpha is completely transformed after 2.5 minutes, and at 300°C, alpha is at least 90% transformed in less than 1 second. Below 120°C the transformation becomes somewhat sluggish with the transformation not starting until after 2 days at 116°C; however, the impurity content has been the only variable examined and this in only a cursory manner. All plutonium metal having either an as-cast density greater than 19.5 g/cm³ or a total impurity content less than 500 ppm will produce a TTT curve that closely corresponds to the one shown in Figure 19. The solution of impurities may take considerably longer than the $\alpha \rightarrow \beta$ transformation indicated by the TTT curve. The shape and volume of metal also influences the rate of transformation. (25)

C. KINETICS OF THE $\alpha \rightarrow \beta \rightarrow \gamma$ TRANSFORMATIONS

Isothermal reaction data shown in the TTT curve of Figure 24 for the $\alpha \rightarrow \beta \rightarrow \gamma$ transformations were also determined. The metal was transformed to the gamma phase from the alpha phase after holding at 100°C. The rate of $\alpha \rightarrow \beta$ transformations at temperatures between 200°C and 250°C was too rapid to be accurately measured by fluid displacement techniques. The $\alpha \rightarrow \beta$ transformation starts in less than 0.5 second and is completed in less than 10 seconds above 200°C. (25)

Figure 24

TTT curves of the $\alpha \rightarrow \beta \rightarrow \gamma$ transformations in plutonium

The $\beta \rightarrow \gamma$ transformation behaves in a manner similar to the $\alpha \rightarrow \beta$ transformation. The isothermal reaction curves are similar to those of the $\alpha \rightarrow \beta$ transformation. The reaction starts after only 1 or 2 seconds and is completed in 20 seconds at 250°C, whereas transformation is quite sluggish at 195°C. At this temperature reaction does not start until after 15 minutes and is not completed until approximately 1 day.

D. KINETICS OF THE $\gamma \rightarrow \beta \rightarrow \alpha$ TRANSFORMATIONS

The $\gamma \rightarrow \beta \rightarrow \alpha$ transformations have been studied in a similar manner as the $\beta \rightarrow \alpha$ and $\alpha \rightarrow \beta$ transformations. The isothermal reaction curves in Figure 25 represent the transformation of the gamma phase when held at temperatures below the $\gamma \rightarrow \beta$ equilibrium transformation temperature after gamma heat treating for 30 minutes at 260°C. The curves have a shape similar to the isothermal reaction curves of the $\beta \rightarrow \alpha$ transformation, except in the temperature range of 85°C to 112°C for plutonium containing less than 500 ppm impurities. Each of the curves in this range show a plateau that lengthens with increasing temperature. The plateau represents a transition period of no reaction following the end of the $\gamma \rightarrow \beta$ transformation and preceding the beginning of the $\beta \rightarrow \alpha$ transformation at the same temperature. At approximately 85°C, the plateau appears only as a change of slope of the isothermal reaction curve. The temperature at which this occurs depends on the impurities in the metal.

The shape of the isothermal curves in the range of -80°C to 160°C is reflected in the shape of the TTT curves for the $\gamma \rightarrow \beta \rightarrow \alpha$ transformations, as shown in Figure 26. The kinetics of the start of the transformation of gamma as revealed by the TTT curves is simple but the completion of the transformation can be somewhat complicated. The TTT curve of the $\gamma \rightarrow \beta \rightarrow \alpha$ transformations is a double C curve. The upper C curve represents the $\gamma \rightarrow \beta$ transformation and the lower portion of the TTT curve represents the beginning and completion of the alpha formation. There exists a temperature region where alpha, beta, and gamma phases can exist simultaneously for a brief time. Above this temperature range gamma transforms

Figure 25

Isothermal reaction curves of the $\gamma \rightarrow \beta \rightarrow \alpha$ transformations in plutonium

Figure 26

TTT curves of the $\gamma \rightarrow \beta \rightarrow \alpha$ transformations in plutonium

directly to beta; whereas it appears that below this range the gamma phase transforms directly to alpha and skipping the beta phase.

The rate of alpha formation when plutonium metal transforms directly to the alpha phase from the gamma phase is five times faster than when the metal is quenched from the beta range. The difference in rate becomes increasingly greater below the nose of the $\beta \rightarrow \alpha$ TTT curve, since it appears from the $\gamma \rightarrow \beta \rightarrow \alpha$ TTT curve that the rate of formation of the alpha phase from the gamma phase does not pass through a maximum. The rate of transformation to alpha is greater even at temperatures of 85°C to 112°C, where the gamma transforms completely to the beta phase before the appearance of alpha.

These data show that in relatively pure plutonium the appearance and retention of the beta phase can be avoided by rapid cooling from the gamma phase. The gamma phase does not seem to be retained, although careful experimental work is needed to determine if a small amount of gamma retention does occur.

Higher gamma heat-treating temperatures result in lower $\gamma \rightarrow \beta$ transformation rates, whereas variation of the gamma heat-treating temperature causes essentially no change in the $\gamma \rightarrow \alpha$ transformation rate. Varying the gamma heat-treating time has essentially no significant effect on either transformation rate.

E. EFFECT OF PHASE TRANSFORMATION ON THE MICROSTRUCTURE OF ALPHA PLUTONIUM

A variation in the heat-treating temperature and a variation in the rate of formation of the alpha phase can markedly influence the final grain size. Metal with an average grain size of less than 0.001 mm can be obtained by quenching from either the epsilon or delta phases to subzero temperatures. Increasing the heat-treating temperature from 160°C in the beta phase to 550°C in the epsilon phase decreases the quenched alpha grain size from approximately 0.05 mm to less than 0.001 mm. On the other hand, metal having an

average grain size of 0.1 to 0.2 mm can be obtained by epsilon or delta heat treating followed by slow cooling through the gamma and beta phases and transformation to the alpha phase at 70°C to 90°C. However plutonium heat treated in this manner will contain micro- and macrocracks, as discussed in Chapter IV. Figures 27 through 32 show the different grain sizes after different heat treating conditions and final rates of alpha formation.

The higher the heat treating phase the more uniform is the final grain size. Heat treating in the epsilon phase produces a microstructure having a fairly uniform alpha grain size whereas heat treating in the beta phase produces a microstructure having very irregular and nonuniform grains.

Gardner⁽⁴⁹⁾ studied the heat treatment of plutonium by the Jominy end-quenching technique. He found that the final alpha grain size after epsilon heat treating increased by a factor of 10 when the cooling rate was decreased one order of magnitude, i.e., the average grain size was 0.002 and 0.02 mm after cooling from the epsilon phase at 5000°C and 500°C per minute, respectively. On the other hand, the final alpha grain size after beta heat treating increased by only a factor of 2, when the cooling rate was decreased one order of magnitude.

Plutonium wafers, one-half inch diameter and 0.10 inch thick, were beta heat treated 30 minutes at 170°C and allowed to partially transform at 79°C. The transformation was interrupted after different amounts of transformation by quenching the specimens to -75°C so that untransformed beta would transform to a fine-grained alpha. The alpha formed during quenching was readily distinguishable by metallography from the alpha formed isothermally at 79°C. Metallographic observations of specimens with different percentages of transformed alpha at 79°C and the remainder transformed during quenching show that:

Figure 27

Typical microstructure of as-cast plutonium.
 The average grain size is 0.03 - 0.05 mm.
 Polarized light illumination 100X

Figure 28

Microstructure of plutonium that was beta heat treated
 1 hour at 175°C and isothermally transformed at 65°C
 The average grain size is 0.02 mm.
 Polarized light illumination 100X

Figure 29

Microstructure of plutonium that was beta heat treated 1 hour at 175°C and isothermally transformed at 85°C

The average grain size is 0.04 to 0.06 mm.

Note the very irregular grain size

Polarized light illumination

100X

Figure 30

Microstructure of plutonium that was delta heat treated 1 hour at 400°C, quenched to 90°C and isothermally transformed at 90°C. The average grain size is 0.01 mm. Note that this grain size is less than that of metal beta heat treated and transformed at the lower temperatures of 65 - 85°C. Also the microstructure consisted of more uniform grains

Polarized light illumination

100X

Figure 31

Microstructure of plutonium that was delta heat treated
1 hour at 400°C and quenched to -40°C

The average grain size is less than 0.005 mm.

Polarized light illumination

100X

Figure 32

Microstructure of plutonium that was epsilon heat treated
1 hour at 550°C, cooled to 90°C at 5°C/hr, and cooled to 50°C
at 1 - 2°C/hr. The average grain size is 0.1 to 0.3 mm.

Polarized light illumination

100X

- (1) Alpha grains initially form in bands, evident in Figure 33, that are randomly oriented in the absence of applied stress or thermal gradients.
- (2) The interface between the transformed and untransformed metal is well defined (Figure 34).
- (3) The grain size increases very slightly with time from the start of the transformation (Figure 35).

F. TRANSFORMATION OF RETAINED PHASES

1. Athermal Behavior of the $\beta \rightarrow \alpha$ Transformation

The initial work of the author^(26,31) and the work of Loasby and Lowe⁽³²⁾ showed that between 15°C and 70°C the $\beta \rightarrow \alpha$ transformation went to apparent completion. That is, the transformation ceased isothermally but the metal contained retained phases. Decreasing the temperature caused further transformation, indicating that the transformation was at least partially athermal in the metal used in these investigations. Subsequent lowering of the transformation temperature reduced the amount of retained phase at any given temperature. This phenomenon is not reversible. This is readily apparent from the isothermal reaction curves of Figure 17. Peterson and Rosen in later work verified this apparent athermal behavior in their study of the $\beta \rightarrow \alpha$ transformation.⁽³³⁾ The amount of retained phase observed in the author's work was significantly less than reported by Loasby and Lowe. This is shown in Figure 36, in which the fraction of untransformed beta as a function of transformation temperature for the two works is compared. Rosen and Peterson did not report the amount of retained beta as a function of the transformation temperature.

The difference between the author's and Loasby and Lowe's work was attributed to a difference in the amount of impurities, primarily the amount of aluminum. Loasby and Lowe showed a linear relationship between the fraction transformed and the isothermal transformation temperature but the author's data indicated that the transformation approached 100% completion asymptotically. The detection and analysis

Figure 33

Microstructure of a plutonium specimen that had been beta heat treated 20 hours at 185°C, isothermally transformed to yield 30% of the alpha phase at 79°C, and then completely transformed by quenching to -75°C. The bands are the alpha phase that formed at 79°C; the smaller grains are the alpha that formed during the quench to -75°C. These bands observed in metallographic sections are the veins observed visually on the free surface of specimens undergoing transformation.

Polarized light illumination

75X

Figure 34

Microstructure of a specimen that had been 35% transformed from the beta phase to the alpha phase at 79°C and then quenched to -75°C. The columnar grains formed isothermally at 79°C and the fine grains at the upper right formed upon quenching to -75°C. Note the interface between the transformed and the untransformed metal at 79°C.

Polarized light illumination

250X

2.5% Transformed

10% Transformed

60% Transformed

Figure 35

Photomicrographs showing partial $\beta \rightarrow \alpha$ transformation at 79°C.
 The transformation at 79°C was interrupted by quenching to -75°C.
 The bands formed at 79°C whereas the small grains formed during quenching
 Polarized light illumination 100X

Figure 36

Fraction of the plutonium $\beta \rightarrow \alpha$ transformation
that is complete versus transformation temperature

of 99% transformation compared to 100% transformation is very difficult. Retention of phases are attributed to the presence of impurities. The amount of retained beta or delta depends upon the amount and type of impurity element. The gamma phase is not believed to be retained in the alpha phase region since it has not been detected in any amount below 80°C, whereas retained beta and delta are common.

Additional work has demonstrated that the transformation of the beta phase of high quality plutonium (less than 300 ppm total impurities and less than 100 ppm of the beta or delta stabilizers) will go to completion if the metal is held at a high alpha transformation temperature long enough. Up to 4% retained beta (or possibly delta) has been observed in high purity plutonium after subzero transformation (Figure 37). Retained phases in high purity plutonium result

Figure 37

Amount of retained beta in high quality plutonium
as a function of the transformation temperature

from the large stresses introduced during $\beta \rightarrow \alpha$ transformation, particularly in plutonium that contains appreciable amounts of impurities.

This athermal behavior is accentuated by alloying additions. For example, the completion of the transformation of plutonium-uranium alloys containing up to 7% uranium is extremely sluggish above room temperature.⁽⁵⁰⁾ That is, the isothermal reaction curves appear to level off before completion of the transformation in a manner similar to that shown in the author's original studies of somewhat impure plutonium, but showing a much larger amount of

retained phase at a corresponding isothermal transformation temperature. This effect is also quite pronounced in plutonium-zirconium alloys containing 0.5% to 2% zirconium.⁽⁵¹⁾

2. Transformation Rates of Retained Phases

The transformation of these retained phases at room temperature can readily be detected and determined with precision density determination. If, for example, 1% of the metal consists of retained beta that transforms to alpha, the density will increase approximately 0.02 g/cm^3 . This small amount of transformation can be followed quite easily by volume change whereas the amount of the phase responsible for the density change has not been observed directly by any technique. The transformation of retained phases in some specimens has been observed for periods up to 2 years. Typical results of the density increases of different quality as-cast specimens are given in Figure 38. A significant density increase, 0.02 g/cm^3 or more, from the time of casting has been observed in all plutonium metal examined except that which has been transformed very slowly through the $\beta \rightarrow \alpha$ transformation.

The room temperature density changes, to reveal transformation of retained phases, were determined of specimens supposedly containing no retained phases and of specimens containing retained phases according to the data depicted in Figure 37. Isothermal $\beta \rightarrow \alpha$ transformation of high-purity plutonium at 70°C to 75°C results in essentially no retained beta, whereas transformation at subzero temperature results in appreciable retained beta. Accordingly a plutonium rod, 0.38 inch diameter and 4 inches long was furnace cooled to the beta phase and held at 120°C for 1 hour. One-half of the rod was transformed to alpha at 73°C and one-half of the rod was transformed to alpha at -80°C . The portion of the rod transformed at 73°C showed no subsequent transformation at room temperature after 2 years while plutonium transformed at -80°C had a further density increase of 0.06 g/cm^3 , Figure 39. Most of the density increase of the specimen transformed at -80°C occurred during the first 100 days. The lower density of specimens transformed at the higher temperature

Figure 38

Room temperature density increases
of four as-cast plutonium specimens of varying quality

Figure 39

Density increases at 25°C of plutonium isothermally transformed at 73°C and -80°C after interrupting the casting cycle in the beta phase

can be explained by the larger volume of microcracks which form at the higher $\beta \rightarrow \alpha$ transformation temperatures.

Figure 40 indicates that the retained phases can be made to transform by thermal cycling within the alpha phase region. The cycling range must be from a temperature high in the alpha phase, preferably near the $\beta \rightarrow \alpha$ transformation temperature, to a subzero temperature such as -80°C . Five to ten cycles are sufficient to transform all of the retained phases in plutonium having less than 300 ppm total impurities and an as-cast density greater than 19.60 g/cm^3 . General observations have shown qualitatively that the number of cycles necessary to transform the retained phases increases with decreasing purity.

Figure 40

Effect of alpha thermal cycling (-80°C to $+100^{\circ}\text{C}$)
on the room temperature density of high quality plutonium

G. VARIABLES INFLUENCING THE RATE OF $\beta \rightarrow \alpha$ TRANSFORMATION

In addition to impurities and stresses, the variables that influence $\beta \rightarrow \alpha$ transformation rate of plutonium are prior heat-treating time and temperature, plastic deformation, previous transformation, and specimen size.

The metal used in this part of the investigation was 99.95% pure and contained 0.02% Fe, 0.01% C, and 0.01% U, 0.01% Am, 0.005% Al, and the remainder totaled less than 0.01%. Also some electrorefined plutonium was used to determine the effect of beta heat-treating times and temperatures on the subsequent $\beta \rightarrow \alpha$ transformation.

Increasing the beta heat-treating temperature decreased the rate of transformation. This was indicated by a shift of the TTT curve to the right. The time for 50% transformation at 74.8°C as a function of the beta heat-treating temperature is plotted in Figure 41. The specimens were heated to the beta phase region by

Figure 41

Effect of beta heat-treating temperature ($\pm 2^\circ\text{C}$) on the plutonium $\beta \rightarrow \alpha$ transformation rates

direct immersion into a high temperature silicone fluid, held at the beta temperature for 1 hour, cooled to 110°C, and quenched to the $\beta \rightarrow \alpha$ transformation temperature.

Increasing the beta heat-treating time significantly slows the subsequent $\beta \rightarrow \alpha$ transformation. Table VIII compares the $\beta \rightarrow \alpha$ incubation times of electrorefined plutonium after beta heat treating 1 hour and 70 hours at 135°C and 180°C. The incubation time is defined as the time required for the first observable amount of transformed phase to appear.

TABLE VIII

INFLUENCE OF THE $\alpha \rightarrow \beta$ TRANSFORMATION TEMPERATURE AND THE BETA HEAT-TREATING TIME ON THE $\beta \rightarrow \alpha$ INCUBATION TIME AT $87.0 \pm 0.02^\circ\text{C}$ OF ELECTROREFINED PLUTONIUM

$\alpha \rightarrow \beta$ Transformation Temperature	Beta Heat-Treating Time	$\beta \rightarrow \alpha$ Incubation Time (Sec)	Maximum $\beta \rightarrow \alpha$ Transformation Rate (%/Sec)
135°C	1 hour	200	0.091
135	70 hours	1300	0.54
180	1 hour	1040	0.040
180	70 hours	4000	0.025

The incubation period remained the same regardless of the specimen size. Larger sample sizes caused a decreased rate of transformation as shown in Figure 42. The divergence increased as the transformation proceeded and as the sample size became larger. This is primarily associated with stresses in the metal. The same was true of wafers with different thicknesses or of rods with different diameters.

Transformation cycling between the alpha and beta phases initially increased the incubation for the $\beta \rightarrow \alpha$ transformation and decreased the maximum rate of transformation. The largest change occurred during the first four cycles and affected the kinetics most strongly at the nose of the TTT curve and below. The longest

Figure 42

Effect of specimen size on the plutonium $\beta \rightarrow \alpha$ transformation at $74.5 \pm 0.2^\circ\text{C}$

incubation time and the least maximum rate of transformation were reached at eight to ten cycles. Continued cycling caused the incubation time to decrease and the maximum rate of transformation to increase.

H. INFLUENCE OF BETA PLASTIC DEFORMATION ON THE $\beta \rightarrow \alpha$ TRANSFORMATION KINETICS

1. Beta Deformation by Compression

The influence of the plastic deformation of beta plutonium on a subsequent transformation to the alpha phase was investigated. A series of specimens from the same melt were compressed from zero to 95 percent reduction in thickness in the beta phase after transforming from the alpha phase. The beta phase formed from alpha is designated β_α . The specimens were allowed to transform to the alpha phase at 80°C . This transformation temperature yielded reasonable

times for the start of the $\beta \rightarrow \alpha$ transformation of specimens that were:

- (1) Either gamma or delta heat treated.
- (2) Only beta heat treated after casting; i.e., without plastic deformation.
- (3) Plastically deformed in the beta phase.

The deformation temperature was usually the same as the beta formation temperature.

For purposes of comparing the $\beta \rightarrow \alpha$ incubation times, specimens of the same melt were subjected to varying heat treatments in the beta, gamma, and delta phases and varying amounts of deformation in the beta phase at 150°C. The starting times of the $\beta \rightarrow \alpha$ transformation of specimens heat treated and deformed in these different ways are given in Table IX. Typical isothermal reaction curves of undeformed and deformed metal are given in Figure 43. Density measurements at 80°C gave the data for the isothermal reaction process.

TABLE IX
INCUBATION TIMES FOR THE PLUTONIUM $\beta \rightarrow \alpha$ TRANSFORMATION AT 80°C
THAT HAD THE INDICATED MECHANICAL AND THERMAL TREATMENTS

<u>Reduction in Thickness Percent at 150°C</u>	<u>Heat Treatment</u>	<u>Incubation Time Seconds</u>
0	30 min at 150°C	200
0	30 min at 150°C	200
60	30 min at 150°C	2000
70	30 min at 150°C	5400
75	30 min at 150°C	5000
75	30 min at 150°C	6000
93	30 min at 150°C	3000
95	30 min at 150°C	2800
0	48 hr at 180°C	2400
0	30 min at 450°C	70
	1 hr at 190°C	
	1 hr at 110°C	
0	30 min at 450°C	400
	19 hr at 150°C	
60	30 min at 450°C	1400
	19 hr at 150°C

Figure 43

Effect of beta plastic deformation on the plutonium $\beta_{\alpha} \rightarrow \alpha$ transformation at 80°C

These data clearly show that beta plastic deformation increased the $\beta_{\alpha} \rightarrow \alpha$ incubation time and decreased the $\beta_{\alpha} \rightarrow \alpha$ transformation rate. In addition to retarding the $\beta_{\alpha} \rightarrow \alpha$ transformation, plastic deformation in the beta phase followed by a high alpha temperature transformation produced a metal having a very nonuniform grain structure. Typical microstructures are shown in Figure 44. Note that the banding in deformed metal is more pronounced than banding observed in the undeformed metal shown in Figure 45.

A similar study was performed with plastically deformed beta that was formed from gamma. Beta formed from gamma is designated β_{γ} . Because the $\beta_{\gamma} \rightarrow \alpha$ transformation rate is greater than the $\beta_{\alpha} \rightarrow \alpha$ transformation rate, specimens were transformed to alpha at different temperatures to yield approximately equal transformation rates for the undeformed beta phase. The maximum $\beta_{\gamma} \rightarrow \alpha$ transformation rate and incubation time at 90°C equalled the maximum $\beta_{\alpha} \rightarrow \alpha$ transformation rate and time at 80°C. Undeformed beta was formed from either alpha or gamma at 140°C to 150°C to provide these comparable transformation conditions.

Plastic deformation of beta formed from gamma also decreased the $\beta_{\gamma} \rightarrow \alpha$ transformation rate very markedly, evident in Table X.

TABLE X

EFFECT OF BETA PLASTIC DEFORMATION BY COMPRESSION ON THE
 $\beta_{\gamma} \rightarrow \alpha$ TRANSFORMATION RATE AT 90.0 $\pm$ 0.2°C

<u>Deformation Temperature °C</u>	<u>Reduction in Thickness Percent</u>	<u>Incubation Time (min)</u>	<u>Maximum Rate of Transformation Percent/min</u>
	0	2.5	6.0
120	75	Not well defined	0.30
135	80		0.16
150	80	120.0	0.10
165	80		0.09
180	80	300.0	0.08

Figure 44

Typical microstructure of plutonium plastically deformed in the beta phase by compression at 150°C to a reduction of 60% in thickness and then isothermally transformed at 80°C. Note the bands of columnar grains and the very irregular grain structure.

Polarized light illumination

75X

Figure 45

Microstructure of alpha plutonium transformed from undeformed beta at 80°C. Polarized light illumination 75X

Typical $\beta_{\gamma} \rightarrow \alpha$ isothermal reaction curves of undeformed and deformed beta are shown in Figure 46. Note that the $\beta_{\gamma} \rightarrow \alpha$ incubation time is not sharply defined after plastic deformation.

The study of the effect of deformation temperature on the $\beta_{\gamma} \rightarrow \alpha$ and $\beta_{\alpha} \rightarrow \alpha$ transformations after 75% to 85% reduction in thickness showed very little difference between the two transformations (Figure 47); in all cases higher deformation temperatures resulted in slower transformation rates. Increasing the amount of deformation beyond 20% reduction in thickness had little effect on the $\beta_{\alpha} \rightarrow \alpha$ transformation rate; however increasing the amount of beta deformation up to about 40 percent decreased the $\beta_{\gamma} \rightarrow \alpha$ transformation rate (Figure 48).

Because the rates of nucleation and growth processes are increased rather than decreased by plastic deformation, it is inferred that diffusion of individual atoms is not a major part of the $\beta \rightarrow \alpha$

Figure 46

Typical plutonium $\beta \rightarrow \alpha$ isothermal reaction curves showing the effect of beta plastic deformation on the transformation to alpha of beta formed from gamma

Figure 47
 Effect of beta deformation temperature on the plutonium
 $\beta_{\alpha} \rightarrow \alpha$ and $\beta_{\gamma} \rightarrow \alpha$ transformation rates.
 The specimens were compressed 75% in thickness

Figure 48

Effect of beta plastic deformation by compression on the $\beta_{\gamma} \rightarrow \alpha$ maximum transformation rate

transformation. The observed effects of plastic deformation appear to be explainable as the mechanical stabilization of a martensitic transformation.

2. Beta Deformation by Tension

Plastic deformation of the beta phase in tension decreased the $\beta_{\alpha} \rightarrow \alpha$ transformation rate similarly to plastic deformation by compression. Tensile specimens were transformed to beta from alpha at 150°C and elongated 50 percent in tension. The subsequent $\beta_{\alpha} \rightarrow \alpha$ incubation time was increased; consequently the $\beta_{\alpha} \rightarrow \alpha$ maximum transformation rate was decreased. A comparison of the isothermal reaction curves clearly showed that plastic deformation of the beta phase by tension decreased the $\beta \rightarrow \alpha$ transformation rate. Beta formed from gamma could not be deformed in tension because of its very low ductility.

I. INFLUENCE OF BETA PLASTIC DEFORMATION ON THE $\beta \rightarrow \gamma$ TRANSFORMATION KINETICS

Plastic deformation of the beta phase increased both the $\beta_{\alpha} \rightarrow \gamma$ and $\beta_{\gamma} \rightarrow \gamma$ transformation rates. This is the opposite effect of beta plastic deformation on the $\beta_{\alpha} \rightarrow \alpha$ and $\beta_{\gamma} \rightarrow \alpha$ transformation rates. The increase in the $\beta_{\alpha} \rightarrow \gamma$ transformation rate was essentially the same as the $\beta_{\gamma} \rightarrow \gamma$ transformation rate. Again the beta phase formed from gamma was deformed only by compression since the ductility of β_{γ} is very low. The influence of deformation by compression on the $\beta_{\alpha} \rightarrow \gamma$ transformation rate was nearly the same as the influence of deformation by tension; both tension and compression increased the transformation rate by about the same amount for a given deformation. The effect of the deformation temperature and the effect of the amount of deformation on the transformation rate were not determined. Representative isothermal reaction curves depicting the effect of beta plastic deformation on the $\beta_{\alpha} \rightarrow \gamma$ transformation rate are shown in Figure 49. The results clearly show that plastic deformation of the beta phase accelerated the $\beta \rightarrow \gamma$ transformation.

Figure 49

Typical plutonium $\beta_{\alpha} \rightarrow \gamma$ isothermal reaction curves showing the effect of beta plastic deformation on the subsequent $\beta \rightarrow \gamma$ transformation

J. INFLUENCE OF ALPHA PLASTIC DEFORMATION
ON THE $\alpha \rightarrow \beta$ TRANSFORMATION KINETICS

Plastic deformation of the stable alpha phase accelerated the $\alpha \rightarrow \beta$ transformation at slow transformation rates similarly to the effect of beta plastic deformation on the $\beta \rightarrow \gamma$ transformation. Since alpha plutonium could not be plastically deformed by tension because of its negligible ductility it was deformed only by compression. The specimens were compressed 30 to 50% in thickness at 70°C to 90°C. Representative $\alpha \rightarrow \beta$ isothermal reaction curves of the deformed and the undeformed alpha phase are shown in Figure 50. They clearly show the accelerating effect of the $\alpha \rightarrow \beta$ transformation rate by prior plastic deformation of the parent alpha phase.

Figure 50

Typical plutonium $\alpha \rightarrow \beta$ isothermal reaction curves showing the effect of alpha plastic deformation on the subsequent $\alpha \rightarrow \beta$ transformation

L. DISCUSSION OF RESULTS

The kinetic data show conclusively that the $\beta \rightarrow \alpha$, $\alpha \rightarrow \beta$, $\gamma \rightarrow \beta$, and $\beta \rightarrow \gamma$ transformations in high purity plutonium can proceed isothermally to completion with no athermal component. Kinetic data alone are insufficient to characterize the transformations as diffusional or martensitic. The main difference between diffusional and martensitic transformations is in the type of growth and in the type of interface. In martensitic transformations the interface is semi-coherent and growth occurs by a glide process, whereas in diffusional transformations the interface may be either incoherent, semicoherent, or coherent. Also in diffusional transformations growth is always thermally activated and proceeds by an atom by atom migration across the interface. In martensitic transformations the interface moves into the parent phase leaving the atoms rearranged on the product phase lattice and the atomic rearrangement involves the cooperative movement of all the atoms. Usually there is no alloy partition between the parent and the product phases in a martensite transformation. The reaction kinetics of martensite transformations are controlled either by nucleation, or by growth, or by both nucleation and growth. Nucleation may or may not be thermally activated; similarly growth may or may not be thermally activated.

There are several characteristics of these transformations that are consistent with either diffusional or martensitic transformations. The most significant characteristics of the $\beta \rightarrow \alpha$ transformations are:

- (1) The $\beta \rightarrow \alpha$ TTT curve has a simple C curve with the maximum rate of transformation at -20°C to -40°C . The rate of $\beta \rightarrow \alpha$ transformation is very nearly zero above 95°C and at -175°C to -196°C .
- (2) Several percent of retained phases may be in plutonium at room temperature.

- (3) The completion of the $\beta \rightarrow \alpha$ transformation is very sluggish in impure plutonium; therefore the transformation appears to be partially athermal.
- (4) Microstructural studies revealed that alpha grains initially form in bands at high alpha temperatures.
- (5) Microstructural studies also revealed that the grain size increases very little from the start of the transformation to the completion of the transformation, i.e., grain size is not a function of time.
- (6) Beta plastic deformation by either compression or tension decreases the $\beta \rightarrow \alpha$ transformation rate, but does not alter the general form of the temperature dependence of the transformation rate as revealed by the isothermal reaction curves.

The most significant characteristics of the transformation of the gamma phase are:

- (1) Transformation kinetics of the gamma phase can be depicted by a double C curve consisting of a $\gamma \rightarrow \beta$ transformation curve, a $\gamma \rightarrow \alpha$ transformation curve, and a complex temperature region where the gamma, beta, and alpha phases can temporarily exist simultaneously.
- (2) The $\gamma \rightarrow \alpha$ is a skip transformation.
- (3) Gamma plastic deformation increases the $\gamma \rightarrow \beta$ transformation rate.

Diffusionless transformations may display either athermal-kinetic behavior or isothermal-kinetic behavior. Although most diffusionless transformations are athermal, there are a number of isothermal transformations. The most notable of these are in iron-nickel⁽³⁶⁾ and uranium⁽³⁵⁾ alloys. Isothermal, diffusionless transformations are suppressible by rapid cooling similar to diffusional type transformations; whereas many athermal transformations are not suppressible by rapid heating or cooling.

A diffusionless transformation may not start immediately when cooling is resumed after having been interrupted. This phenomenon is referred to as thermal stabilization. The cause of thermal stabilization may be different for different transformations. Kaufman and Cohen⁽⁵²⁾ give a number of possibilities for thermal stabilization. These are:

- (1) Solute or impurity atoms undergo short-range diffusion to the strain centers in the parent phase, and thereby lower the driving force for the transformation in regions that might otherwise serve as preferred nucleation sites.
- (2) The interface of an embryo or plate of martensite may become immobilized by a slight concentration buildup in a manner analogous to dislocation pinning.
- (3) Close coupling between austenite and martensite, which confers high mobility upon the interface, may be partially destroyed by time-dependent plastic yielding or relaxation.
- (4) Cottrell atmospheres or precipitation strengthens the parent phase and causes the matrix to be more resistant to the displacements attending martensitic transformations.

The parent phase of a diffusionless transformation may also be stabilized by plastic deformation. This is referred to as mechanical stabilization and has been observed in an 18-8 austenitic stainless steel alloy by Fiedler, Averbach, and Cohen.⁽⁵³⁾ It has also been observed in other iron-nickel alloys.⁽⁵⁴⁻⁵⁷⁾ Plastic deformation of the stable parent phase may depress the M_s temperature.⁽⁵⁸⁾

Fiedler, Averbach, and Cohen⁽⁵³⁾ found that plastic strains up to 2 percent elongation favored the austenite to martensite transformation, whereas plastic strains above 2 percent elongation hindered the subsequent transformation. They suggested that mechanical stabilization of this alloy was due to the distorted or sub-grain structure of the deformed austenite. The high dislocation density and deformed lattice of the cold-worked austenite may

interfere with the propagation of martensite. Kurdjumov^(59,60) observed similar mechanical stabilization in a steel containing 0.954% C and 3.5% Mn.

Mechanical stabilization by plastic deformation of the stable parent phase is to be differentiated from plastic deformation of the unstable parent phase. The transformation rate is accelerated by plastic deformation of the unstable phase;⁽⁶¹⁻⁶⁴⁾ the extent of the effect depends upon the sluggishness of the transformation.

The allotropic transformations in some metals may occur only by a martensitic mechanism and some transformations may occur by only a diffusional mechanism. Some allotropic transformations may occur by both types depending on the transformation conditions. Cobalt,⁽⁶⁵⁻⁶⁷⁾ cerium,⁽⁶⁸⁾ and titanium⁽⁶⁹⁾ are believed to be of the martensitic type. The type of transformation is still questionable in metals such as tin^(70,71) and uranium.⁽⁷²⁻⁷⁴⁾ The $\beta \rightarrow \alpha$ transformation in uranium is considered to be both diffusional and diffusionless.⁽⁷⁴⁾

The inhibiting effect of plastic deformation of the parent phase on martensitic transformations has been observed in cerium and cobalt in addition to the Fe-Ni alloys. The inhibiting effect of plastic deformation of the stable parent phase has not been observed in diffusional transformations; on the contrary plastic deformation always accelerates diffusional transformations because it promotes nucleation and growth.⁽⁷⁵⁾ Accordingly, any or all of the low temperature allotropic transformations in plutonium can be martensitic transformations; however, the $\beta \rightarrow \alpha$ transformation, which is retarded by plastic deformation is a martensitic transformation. The influence of cold worked structures on the other transformations, which are accelerated by plastic deformation, may be counterbalanced by increased nucleation and growth rates.

The retained phases in plutonium can be either delta or beta. The delta phase can be retained since americium is generally present in the amount of 100 ppm or more. Americium is a common delta

stabilizer but has essentially zero solubility in the beta phase. There is a very good correspondence relation between the delta phase and the alpha phase.⁽⁷⁶⁾ All the atom movements and angular rotations are very small for translation from the delta lattice to the alpha lattice. This could explain the athermal behavior of the $\beta \rightarrow \alpha$ transformation in impure plutonium. It could also explain the decreased $\beta \rightarrow \alpha$ transformation rate due to prolonged beta heat treating at 180°C, which probably increases the amount of solute in solid solution.

Solute elements such as zirconium⁽⁵¹⁾ and uranium⁽⁵⁰⁾ have a pronounced effect on the athermal behavior of the completion of the $\beta \rightarrow \alpha$ transformation. One percent of either element will cause retention up to 25% beta at room temperature. The retained beta transforms only upon cooling below room temperature or upon applying pressure. This athermal behavior makes it difficult to explain the $\beta \rightarrow \alpha$ transformation on the basis of a diffusional process.

There is no comprehensive understanding of the means by which impurities and alloying elements affect the kinetics of phase transformations. Certainly substitutional solute atoms markedly affect the movement of a transformation front if partition of alloying elements is involved. The retarding influence of solutes on nucleation is much more striking than it is on the growth. For example, 0.0003 wt% boron in steel retards the rate of transformation to ferrite and pearlite by a factor of 1/10. This can only be explained as a retardation of the nucleation rate.⁽⁷⁷⁾ The retarding influence of solute impurities on the various transformations in plutonium can be best explained as a retardation of the rate of thermally activated nucleation, regardless of whether the transformations are martensitic or diffusional.

CHAPTER IV

PHASE TRANSFORMATION DAMAGE IN PLUTONIUM

When plutonium is transformed from beta to alpha, it sustains extensive physical damage as indicated by cracks. These cracks vary in size from below detectability by microscopy to a size comparable to the specimen dimensions depending upon the previous mechanical and thermal history of the metal. The most significant variables that influence the amount, size, and distribution of these cracks are the temperature of the $\beta \rightarrow \alpha$ transformation, the metal quality, the specimen size and shape, and the number of previous $\beta \rightarrow \alpha$ transformations.

The physical damage in plutonium after repeated $\beta \rightarrow \alpha$ transformations may be quite pronounced.^(24,29,31) Large macrocracks, or even fracture of the metal may occur after only one $\beta \rightarrow \alpha$ transformation. Coffinberry and Waldron⁽¹⁾ reported that in early work at Los Alamos thermal cycling of plutonium between phases resulted in a progressive decrease in density and increase in surface distortion similar to that found in uranium subjected to transformation cycling. It has been suggested that the microcracks formed primarily during the $\beta \rightarrow \alpha$ transformation because this was the first transformation between two complex crystal structures on cooling from elevated temperatures.^(1,6)

A. MICROCRACKING IN AS-CAST PLUTONIUM

Metallography and ultrasonic testing reveal that as-cast plutonium may contain a large volume of microcracks. The volume of these microcracks varies from less than 0.1% to as high as 2% of the total specimen volume depending upon the impurity content and the rate of $\beta \rightarrow \alpha$ transformation. High-purity plutonium cooled through the $\beta \rightarrow \alpha$ transformation at 1 to 20°C/min will contain a distribution of microcracks similar to that revealed by the microstructure in Figure 52. These microcracks appear predominantly at the final alpha grain boundaries as indicated in Figure 53.

Figure 52
Microcracks in electrorefined plutonium
As-polished 100X

The size, distribution, and concentration of microcracks generally vary considerably within a given piece of metal. The dependency of microcracks on the $\beta \rightarrow \alpha$ transformation rate and impurity level is discussed in greater detail in the section on thermal cycling damage. In general, a higher $\beta \rightarrow \alpha$ transformation temperature and higher purity will result in more extensive microcracking. Electrorefined plutonium specimens having a density of 19.77 g/cm^3 were obtained by direct quenching the beta phase to subzero temperatures during casting and then by thermally cycling the alpha metal between -80°C and $+100^\circ\text{C}$ to transform the retained beta to alpha. The high density indicates that the alpha metal was formed essentially free of cracks by rapid $\beta \rightarrow \alpha$ transformation; the theoretical density is 19.83 g/cm^3 . The microstructure of plutonium quenched in this manner was very fine-grained and was extremely brittle.

Figure 53
Microstructure of electrorefined plutonium showing
microcracks at the grain boundaries
Polarized light illumination 150X

The microcracking appears to occur after the $\beta \rightarrow \alpha$ transformation is 50% to 60% complete. Loasby and Lowe⁽³²⁾ have plotted the percent of void formation against the percent of beta that had transformed into alpha and obtained a linear relationship in the range 50 and 100% beta transformed. Nelson⁽²⁴⁾ found this relationship to be a nonlinear as shown in Figure 54. The deviation from the data shown depends upon such factors as specimen size, isothermal transformation temperature, and impurity content.

Figure 54
Void formation in
plutonium as a
function of percent
 $\beta \rightarrow \alpha$ transformation
at 73°C

The volume associated with microcracks in as-cast plutonium decreased only slightly by hydrostatic compression at 6000 atmospheres at a temperature of 90°C, which is within the alpha phase stability range. The metal was subjected to pressure for only 2 to 5 minutes. Accordingly, the metal density increased only slightly, 0 to 0.05 g/cm³. The major portion of the observed density change was probably the volume decrease due to transformation of retained phases. Hydrostatic pressing at the same pressure but at 180°C followed by slow cooling to the alpha phase under pressure resulted in larger density increases, 0.10 g/cm³ or more. The amount of

increase depended upon the temperature of pressing and the extent of microcracks, inclusions, and other imperfections in the metal. If microcracks comprise 1% of the volume of the metal and they are eliminated during compression, the density will increase 0.2 g/cm^3 . Densities up to 19.80 g/cm^3 at 25°C have been obtained by hydrostatic pressing. Microcracks were not discernible at 250X after this treatment.

The slight density increase of high quality plutonium after pressing at 90°C can be attributed primarily to transformation of a small amount of retained beta phase and not to decreasing the volume of microcracks. The density increase after pressing beta plutonium at 180°C was probably due primarily to decreasing the volume of microcracks and only a small percentage of the density increase resulted from transformation of retained phases. The volume decrease associated with the transformation of retained phases was the same in either pressing operation; however, in beta pressing the volume decrease associated with compressing the microcracks was much greater than in alpha pressing. The amount of density increase brought about by pressing depends upon the previous history of the metal because the volume of retained phases and the volume of cracks depends on the thermal history.

B. PHYSICAL DAMAGE AFTER REPEATED $\alpha \rightleftharpoons \beta$ TRANSFORMATIONS

Repeated $\alpha \rightleftharpoons \beta$ transformations resulted in an increase in the extent of internal cracking. The size of the cracks increased progressively with continued thermal cycling (Figure 55). The extent of thermal cycling damage depended upon the metal quality, sample size, and $\beta \rightarrow \alpha$ transformation temperature during thermal cycling.

Plutonium that was thermally cycled through the $\beta \rightarrow \alpha$ transformation by heating and cooling at 2°C/min formed voids up to 3 percent per cycle (0.6 g/cm^3 density decrease per cycle), resulting in growth, general distortion, and extensive surface rumpling (Figure 56). Growth was always observed in both the radial and longitudinal directions. Occasionally one to four very slow $\beta \rightarrow \alpha$ transformations

As-Cast

One-Cycle

Four Cycles

Figure 55

Representative Photomicrographs of Plutonium Specimens
Cycled Between the Alpha and Beta Phases 50X

0 Cycles

50 Cycles

150 Cycles

Transverse section after 125 cycles

Figure 56

Effect of $\alpha \rightleftharpoons \beta$ transformation cycling
on the dimensions of plutonium specimens
that were cycled at 2 to 10°C/min

were sufficient to cause fracture of a specimen. Densities of certain specimens decreased from 19.7 to 6 g/cm³ after 100 thermal cycles.

Transforming plutonium into one of the high temperature phases and cooling very slowly into the alpha phase region caused macrocracks and even fracture after only one transformation cycle. Transforming plutonium into the epsilon phase region and slow cooling produced the most damage. For example, a high-purity plutonium specimen, 1 centimeter in diameter and 1 centimeter long that had been epsilon heat treated at 600°C, cooled to 95°C at 10°C/hr and then cooled to 60°C at 1°C/hr contained a macrocrack 1/2 centimeter long and 1/16 centimeter wide. The cooling rate was changed at 90°C to permit a very slow $\beta \rightarrow \alpha$ transformation. The $\beta \rightarrow \alpha$ transformation was presumed complete at 60°C.

The transformation damage was greater for metal transformed from the beta phase at high alpha temperatures, e.g., 70°C, than at subzero temperatures. Samples from the same melt were allowed to transform isothermally to the alpha phase at -80°C, -23°C, 25°C, 60°C, and 73°C after beta heat treating 30 minutes at 180°C. Each specimen was allowed to transform at the appropriate alpha temperature until apparent completion of the transformation was observed. The densities after each transformation were then determined at room temperature (Figure 57).

After the first cycle the decreases in density of the specimens transformed isothermally at -23°C and -80°C were essentially identical, 0.12 g/cm³. This density decrease was due to both the retention of the lower density beta and the development of microcracks in the specimens. Further cycling to six cycles in the subzero range resulted in a very small density change and hence very little physical damage. Increasing the transformation temperature above -23°C resulted in more extensive physical damage and less retained beta. The amount of damage was greatest in the metal transformed at 73°C with the density decrease being 0.40 g/cm³ per cycle. The amount

Figure 57

Influence of the $\beta \rightarrow \alpha$ transformation temperature
on the physical damage in plutonium as a result
of $\alpha \leftrightarrow \beta$ transformation cycling

of damage was slightly less, 0.30 g/cm^3 per cycle in the specimen transformed at 60°C .

Plutonium rods 1 centimeter in diameter or less that did not initially contain microcracks did not form microcracks upon repeated $\beta \rightleftharpoons \alpha$ transformations by direct quenching from the beta phase to subzero temperatures. Microcracks initially present within the metal, however, were enlarged by such thermal cycling treatment. Microcracks were formed in plutonium rods during the casting process by permitting the beta to transform to alpha slowly (high alpha temperatures). Such rods containing microcracks were thermally cycled 17 times by direct quenching into the beta phase at 180°C and into the alpha phase, at a subzero temperature of -80°C . Such an $\alpha \rightleftharpoons \beta$ cycling was followed by cycling within the alpha phase (100°C to -80°C) to transform any retained phase which was present to alpha. The rods were 1 centimeter long and 1 centimeter in diameter. That the $\alpha \rightleftharpoons \beta$ transformation cycling enlarged microcracks was confirmed by metallography and density measurements. Plutonium that was quenched from the beta phase during casting to avoid formation of microcracks and then thermally cycled in the same manner sustained no microcracking and therefore less physical damage. The microstructure and the density of the rods after the thermal cycling treatments were essentially the same as before the cycling treatments. Pertinent density data from these experiments are shown in Table XI.

TABLE XI

EFFECT OF $\alpha \rightleftharpoons \beta$ TRANSFORMATION CYCLING
($-80^\circ\text{C} \rightleftharpoons +180^\circ\text{C}$) ON THE DENSITY OF PLUTONIUM

	<u>Metal X</u>	<u>Metal Y</u>	<u>Metal X</u>	<u>Metal Y</u>
Density before cycling	19.60 g/cm^3^*	19.55 g/cm^3^*	19.60^{**}	19.72^{**}
Density after 17 $\alpha \rightleftharpoons \beta$ cycles	18.98	19.24	19.56	19.68
Density after 5 subse- quent cycles within the alpha phase	19.04	19.35	19.61	19.72

* Contained microcracks

** Contained no microcracks

The temperature dependence of physical damage in cylindrical 1 centimeter rod specimens is presented in Figure 58. The data were obtained by two methods. First, the percent microcracking per cycle was determined from the average slope of the curves between cycles 2 and 6 in Figure 57. Second, the density change was observed in metal that had been beta-pressed after casting, transformed to alpha under pressure, beta heat-treated 30 minutes at 160°C, quenched and isothermally transformed to alpha at different temperatures, and then finally thermally cycled between -75°C and 100°C to transform retained beta to alpha. A schematic of this procedure is shown in Figure 59.

Although microcracking in high-purity plutonium was pronounced at high alpha transformation temperatures, the amount of retained phases in metal cycled between the beta phase and the high alpha temperatures was quite small. The retention of beta, however, was quite significant below room temperature.

The voids and microcracks, after repeated $\alpha \rightleftharpoons \beta$ transformations, were somewhat uniformly distributed throughout specimens, but large macrocracks were observed at or near the center of specimens. For example, spheres approximately 4 centimeters in diameter, thermally cycled at 2°C/min between 175°C and 25°C contained voids 1 to 1-1/2 centimeter in diameter at the center. Large macrocracks have also been observed at the center of thermally cycled rods.

Increasing the specimen size generally increased the amount of void formation (Figure 60). However, 1/4 inch diameter rods have been shown to have nearly as large a density decrease as 1 inch diameter rods when thermally cycled at a rate of 2°C/minute.⁽²⁹⁾ Similar data have been obtained for spheres of varying diameter. This indicates specimen size is not as important as the metal quality or the $\beta \rightarrow \alpha$ transformation conditions at this slow transformation rate. The amount of microcracking was not great at subzero temperatures in small specimens, but rods or spheres greater than 1-1/2 inch in diameter readily fractured when quenched from the beta phase to subzero temperatures where the $\beta \rightarrow \alpha$ transformation rate is a

Figure 58
Microcracking in plutonium as a function
of the transformation temperature

Figure 59

Schematic diagram showing the procedure for determining the volume percent of microcracks and retained phases in plutonium by density measurements

Figure 60

Effect of specimen size on density decrease of plutonium
when thermally cycled through $\alpha \rightleftharpoons \beta$ transformation
at a cooling rate of 2°C/min

maximum. This was due to large temperature differences within the metal that lead to the formation of the more dense and less ductile alpha phase at the exterior of the specimens, while the interior consists of the lower density beta phase that subsequently transforms, develops tensile stresses, and opens up voids, leading to fracture.

The physical damage associated with thermal cycling between the beta and alpha phases depends upon the amount and type of impurities present in the metal. Elements such as iron and nickel, which have little solubility in solid plutonium, and elements such as aluminum, which have extensive solubility in the delta phase mitigated the cyclic thermal damage. Some elements such as carbon may possibly enhance microcracking; however, no detailed investigation of this was performed. Nickel or iron in the amount of 1000 ppm decreased

the amount of microcracks to 1/4 that of unalloyed plutonium containing less than 250 ppm total impurities. Addition of 600 ppm aluminum decreased the amount of physical damage to 1/10 that of the same unalloyed plutonium. However, this amount of aluminum significantly increased the amount of the retained delta and beta phases.

C. PHYSICAL DAMAGE AFTER $\gamma \rightleftharpoons \alpha$ CYCLING

Density measurements revealed that the physical damage associated with thermal cycling between the gamma and alpha phases increased with decreasing $\gamma \rightarrow \alpha$ transformation temperature (Figure 61).

Figure 61

Influence of the $\gamma \rightarrow \alpha$ transformation temperature on the physical damage in plutonium as a result of $\gamma \rightleftharpoons \alpha$ transformation cycling

This temperature dependence was in the reverse direction and the absolute magnitude was not as great as after repeated $\beta \rightarrow \alpha$ thermal transformation. However, the change in transformation rate between -75°C and $+73^{\circ}\text{C}$ of the $\gamma \rightarrow \alpha$ transformation is not as great as that for the $\beta \rightarrow \alpha$ transformation. This temperature interval is where the gamma phase transforms directly to the alpha phase. Fracture generally occurred after the first few cycles during either $\delta \rightleftharpoons \alpha$ or $\gamma \rightleftharpoons \alpha$ cycling in which the quenching medium was at -75°C . Fracture resulted from the large volume changes between phases. These volume changes are approximately 25 and 15% respectively.

The physical damage at temperatures where the gamma phase first transforms to the beta phase and then to alpha was not measured, but is quite large. The least amount of damage occurs when the gamma phase is transformed to the beta phase before the metal is quenched to subzero temperatures.

D. PHYSICAL DAMAGE AFTER $\gamma \rightleftharpoons \beta$, $\delta \rightleftharpoons \gamma$, AND $\delta \rightleftharpoons \beta$ CYCLING

No physical damage was observed during either $\gamma \rightleftharpoons \beta$, $\delta \rightleftharpoons \gamma$, or $\delta \rightleftharpoons \beta$ transformation cycling in metal that initially contained no microcracks; however, any microcracking that was initially present in the metal was increased by these transformations. A 0.08 g/cm^3 density decrease was observed after the first $\beta \rightleftharpoons \gamma$ cycle. This can be attributed to a retention of a small percentage of the delta phase at 190°C . A comparison of the physical damage associated with $\delta \rightleftharpoons \gamma \rightleftharpoons \beta \rightleftharpoons \alpha$ thermal cycling as revealed by density measurements is given in Figure 62. The data were obtained from metal that had been cooled only to the beta phase during casting. This metal supposedly contained no microcracks initially. Similar data were obtained from plutonium which had initially been hydrostatically pressed at 180°C and cooled under pressure.

E. DISCUSSION OF RESULTS

High purity as-cast plutonium may contain a large volume of microcracks that form during the $\beta \rightarrow \alpha$ transformation. The volume of microcracks increases with increasing transformation temperature,

Figure 62

Physical damage in plutonium due to phase transformation cycling

higher metal purity, increased specimen size, and $\alpha \rightleftharpoons \beta$ transformation cycling. Transformation cycling produced growth in all directions, general distortion, and extensive surface rumpling. Plutonium containing essentially no microcracks can be produced by quenching from the beta phase to -75°C during casting. No physical damage has been observed in metal that initially contains no microcracks after either $\gamma \rightleftharpoons \beta$, $\delta \rightleftharpoons \gamma$, or $\delta \rightleftharpoons \beta$ transformation cycling.

The explanation offered by Buckley,⁽⁷⁸⁾ and supported by Stobo⁽⁷⁹⁾ for transformation cycling damage in uranium appears to be applicable to the $\beta \rightarrow \alpha$ transformation of plutonium. Lehr,⁽⁷³⁾ de Jong and Rathenau,⁽⁸⁰⁾ and Clinard⁽⁸¹⁾ further support this explanation with results of studies of phase transformation in iron. Stobo⁽⁷⁹⁾ gives a general statement of this explanation as: "When a phase transformation boundary moves through a specimen there is a tendency for the specimen to retain the dimensions of the stronger phase in the directions tangential to the boundary." This statement assumes that there is continuity at the phase boundary and to maintain this continuity, plastic deformation occurs on both sides of the phase boundary to relieve the transformation stresses. More plastic deformation occurs in the weaker phase.

Accordingly, transformation damage during the $\beta \rightarrow \alpha$ transformation can be explained in the following manner. During transformation the weaker beta phase is forced to deform plastically to conform to the geometry of the stronger alpha phase. If the beta grains are randomly oriented, cracking will occur at the randomly oriented $\beta \rightarrow \alpha$ interfaces and thus resulting in isotropic swelling. In textured samples growth caused by transformation damage is probably anisotropic because of the non-random orientation of the $\beta \rightarrow \alpha$ transformation interfaces. This has been confirmed experimentally. Transformation cycling of textured plutonium will be discussed in more detail in Chapter VI.

De Jong and Rathenau⁽⁸²⁾ correlated the average tensile yield strength of the parent and the product phases, S_0 , the average modulus of elasticity, E ; and transformation volumetric change,

$\Delta V/V_0$, to provide a parameter, Q_c , for establishing whether plastic deformations or elastic deformations will occur during transformation. This correlation is:

$$Q_c = \frac{S_0}{\frac{2}{3} E \frac{\Delta V}{V_0}} \quad (IV-1)$$

Only elastic deformations will occur if Q_c is greater than 1, whereas plastic deformations will occur if Q_c is less than 1. Plastic deformations, but not elastic deformations, lead to transformation cracks.

Approximate calculated values of Q_c for the $\beta \rightarrow \alpha$, $\gamma \rightarrow \beta$, and $\delta \rightarrow \gamma$ transformations of plutonium are approximately 0.04, 0.08, and 0.02 at 85°C, 160°C, and 220°C, respectively. Q_c is approximately 0.1 for the $\beta \rightarrow \alpha$ transformation at -80°C. The larger value of Q_c at -80°C compared to the value at 85°C is due primarily to the much larger yield stress at -80°C. All the values of Q_c being less than 1 indicate that transformation damage should occur for all $\beta \rightarrow \alpha$ transformation temperatures and for the $\delta \rightarrow \gamma$ and $\gamma \rightarrow \beta$ transformations. Since transformation damage was not observed during the $\delta \rightarrow \gamma$, $\gamma \rightarrow \beta$, $\delta \rightarrow \beta$, and subzero $\beta \rightarrow \alpha$ transformations, the cracking criterion of de Jong and Rathenau is questionable.

Although it is impossible to formulate a quantitative correlation for transformation cracking in plutonium it does seem logical to qualitatively explain $\beta \rightarrow \alpha$ transformation damage on the basis of the volume change accompanying transformation and on the relative strengths of the parent and product phases.

CHAPTER V

STEADY-STATE CREEP OF PLUTONIUM

Research was performed to provide information concerning the mechanisms by which specific transformations in plutonium proceed. In particular, the effect of compression stress on the low temperature transformations was studied. The primary objective of this activity was to provide indirect information on the type of mechanism that might be responsible for these transformations; one such study was the deformation of plutonium with concurrent phase transformation; this is discussed in Chapter VI. Steady-state creep data were needed for analysis of the transformation creep data. Thus, this chapter presents results of steady-state, compressive creep experiments on the six allotropes of plutonium.

A. STRESS DEPENDENCY OF THE STEADY-STATE CREEP RATES

Representative compression creep curves obtained at different stresses and temperatures for the different allotropes of plutonium are shown in Figures 63 and 64. The creep curves are typical in that they consist initially of primary creep followed by secondary or steady-state creep.

Sherby has derived an empirical expression relating strain rate to temperature and stress.⁽⁸³⁾ A more recent version of this equation has the form^(84,85)

$$\dot{\epsilon} = K\gamma^{3.5}D\left(\frac{\sigma}{E}\right)^n, \quad (V-1)$$

where K is a constant for all metals, γ is the stacking fault energy, σ is the applied stress, n is a constant equal to about 5, E is the modulus of elasticity, and $D = D_0 e^{-Q_{sd}/RT}$. In the expression for D , D_0 is a universal constant, Q_{sd} is the activation energy for self-diffusion, T is the test temperature in degrees Kelvin and R is the universal gas constant.

Figure 63
Compression creep curves of plutonium

Figure 64
Compression creep curves of plutonium

The original equation⁽⁸³⁾ contained a grain size term; the more recent equation is grain size independent. Because the grain size of the allotropes, excluding alpha, can be neither determined nor maintained constant, the new form of the equation has obvious advantages in analyzing creep data of several allotropes of the same metal. The stacking fault energies of the six allotropes of plutonium are not known but they were assumed to be constant during the creep tests. The values for the moduli of elasticity of the different allotropes over a range of temperatures are given in Table XII.

TABLE XII
VALUES FOR THE MODULUS OF ELASTICITY⁽⁸⁶⁾

<u>Temperature Phase</u>	<u>Temperature °C</u>	<u>Modulus of Elasticity psi</u>
α	115	12.3×10^6
β	115	6.2
β	185	5.5
γ	185	5.5
γ	305	4.6
δ	305	2.5
δ	450	2.4
δ'	450	*
ϵ	475	*
ϵ	475	*

*No modulus of elasticity values available.

Sufficient data were obtained for some of the allotropes to conclude that there was a range of strain rate values where n was a constant and is approximately equal to 5. For low values of $\dot{\epsilon}$, n was less than 5, and for high strain rates n was greater than 5. Most of the experimental work was performed at stresses where $\dot{\epsilon} \propto \left(\frac{\sigma}{E}\right)^5$. The applied stress was compensated for the modulus of elasticity according to equation V-1 so that the ratio $\frac{\sigma}{E}$ would remain constant at different temperatures. Representative data showing the dependency of the creep rates of the beta, gamma, and delta phases on the modulus compensated stress, i.e. $\frac{\sigma}{E}$, are shown in Figures 65 to 67. It is apparent from Figure 67 that n had a value of 6 for delta; no explanation for this can be offered at this time.

Because the creep rate of the alpha phase was low at stresses below 15,000 psi, and because the stable temperature ranges of the delta-prime and epsilon phases are relatively high, only a limited amount of data was obtained on the creep of the alpha, delta-prime, and epsilon phases.

Figure 65

Dependency of the creep rate of beta plutonium on the applied stress that was compensated for the modulus of elasticity

Figure 66

Dependency of the creep rate of gamma plutonium on the applied stress that was compensated for the modulus of elasticity

Figure 67

Dependency of the creep rate of delta plutonium on the applied stress that was compensated for the modulus of elasticity

B. TEMPERATURE DEPENDENCY OF THE STEADY-STATE CREEP RATE

Figure 68 permits a comparison of the logarithm of the steady-state creep rate versus reciprocal temperature for all plutonium allotropes. There was a very marked difference between the creep rates at the same stress of two, single phase allotropes, one stable and the other unstable, that could each exist at temperatures where transformation is extremely sluggish.

If the creep rate and temperature are related by the Arrhenius equation, $\dot{\epsilon} = Ae^{-Q_c/RT}$, then the creep activation energy can be determined from the slope of the plots in Figure 68,⁽⁸⁷⁾ i.e.:

$$Q_c = \frac{-2,3R \, d \log_{10} \dot{\epsilon}}{d(1/T)} \quad (V-2)$$

The average values for Q_c were 26, 30, 35, 31, 28, and 25 kcal/g-atom, respectively, for the α , β , γ , δ , δ' , and ϵ phases. The activation energy, Q_c , is related to the self-diffusion activation energy by the relationship:⁽⁸⁷⁾

$$Q_c = Q_{sd} - \frac{NRT^2}{E} \frac{dE}{dT} \quad (V-3)$$

At a common temperature the creep rate of the phase normally stable at higher temperatures was greater than the creep rate of the phase normally stable at the lower temperatures with but one exception -- the creep rate of gamma was less than the creep rate of the beta phase near the $\beta \rightleftharpoons \gamma$ equilibrium transformation temperature. It is to be noted that this exception applies only to beta that was formed from alpha. The creep rate of beta formed from alpha was two to three orders of magnitude greater than the creep rate of beta formed from gamma. As a consequence, the creep rate of beta that was formed from gamma was less than the creep rate of the gamma phase under the same temperature and stress conditions. This difference will be discussed in Section D of this chapter.

Figure 68
 Temperature dependency of the creep of plutonium.
 The creep stresses are indicated in lb/in.^2

Beta, gamma, and delta phase creep was investigated extensively. Because creep of the alpha phase was small unless the applied stress exceeded 15,000 psi and because the stable temperature ranges of the delta-prime and epsilon phases are relatively high (above 450°C), only a small amount of data was obtained on the creep of the alpha, delta-prime, and epsilon phases. In addition, extensive creep data of the delta-prime and epsilon phases are not directly applicable to the study of the mechanisms of the low temperature transformations.

C. ACTIVATION ENERGIES FOR SELF-DIFFUSION OF THE PLUTONIUM ALLOTROPES

The activation energy for self-diffusion can be calculated from the strain rates at two temperatures according to the relationship

$$\frac{\dot{\epsilon}_1}{\dot{\epsilon}_2} = \frac{K_Y^{3.5} (\sigma/E_1)^n D_o e^{-Q_{sd}/RT_1}}{K_Y^{3.5} (\sigma/E_2)^n D_o e^{-Q_{sd}/RT_2}} \quad (V-4)$$

If the ratio σ/E is held constant by experimentally changing σ to compensate for the temperature dependency of E , then the relationship becomes:

$$\frac{\dot{\epsilon}_1}{\dot{\epsilon}_2} = \frac{e^{-Q_{sd}/RT_1}}{e^{-Q_{sd}/RT_2}} \quad (V-5)$$

The activation energy, Q_{sd} , can also be calculated at constant stress using known values of E and n from the relationship:

$$\frac{\dot{\epsilon}_1 E_1^n}{\dot{\epsilon}_2 E_2^n} = \frac{e^{-Q_{sd}/RT_1}}{e^{-Q_{sd}/RT_2}} \quad (V-6)$$

In the present investigation the technique of holding the stress constant and compensating for the modulus was used rather than holding σ/E constant. Representative data of the temperature dependency of the modulus compensated strain rate are given in Figure 69. The moduli used for compensating the strains of the

Figure 69

Modulus compensated creep rate versus reciprocal temperature
for the six allotropes of plutonium

delta-prime and epsilon phases were extrapolated values. The difference between the modulus compensated strain rates of two phases at their mutual transformation temperature, apparent in Figure 69, is generally less than the difference between the noncompensated strain rates, Figure 68. This is because the modulus of elasticity of the stable phase above the transformation temperature is generally less than that of the stable phase below the transformation temperature; exceptions are the beta and gamma phases at the $\beta \rightleftharpoons \gamma$ transformation temperature, where $E_\gamma = E_\beta$. It is also apparent from Figure 69 that the strain rate of the higher temperature phase for a given stress is generally greater than the strain rate of the lower temperature phase; an exception to this generalization is that the strain rate of the gamma phase is less than the strain rate of the beta phase, if the beta phase is formed from alpha.

The activation energy for self-diffusion can be obtained from the slope of the curves shown in Figure 69. The average activation energies calculated for the alpha, beta, gamma, and delta phases are 23, 27, 31, and 30 kcal/g-atom respectively. These activation energies are for the stress range where $n = 5$ in the proportionality $\dot{\epsilon} \propto \sigma^n$. Additional data, not included, tend to show that the activation energies are higher at stresses when $n > 5$, and they are lower when $n < 5$.

With the calculated self-diffusion activation energies substituted into equation V-1, creep data obtained for the six allotropes can be presented in the form shown in Figure 70, where $\log \dot{\epsilon} e^{Q/RT}$ is plotted as a function of $\log \frac{\sigma}{E}$. The slopes of the curves correspond to the exponent n . The difference in the values of $\dot{\epsilon} e^{Q_{sd}/RT}$ at constant $\frac{\sigma}{E}$ for the allotropes other than alpha can be attributed to differences in stacking fault energies. These data imply that there is little difference in stacking fault energy of the beta, gamma, delta, delta-prime, and epsilon phases.

Figure 70

Creep data correlated according to the relationship^(84,85)

$$\dot{\epsilon} = k \gamma^{3.5} D_0 e^{-Q_{sd}/RT} \left(\frac{\sigma}{E} \right)^n$$

For the data of the alpha phase to correspond to this model the stacking fault energy would have to be one-tenth the stacking fault energy of the higher temperature phase. More detailed experiments on creep of alpha plutonium may reveal that the activation energy, Q_{sd} , of alpha is greater than 23 kcal/g-atom. It should be borne in mind that creep of the alpha phase may not be described by equation V-1.

Using tracer techniques, Tate and Cramer⁽⁸⁸⁾ obtained an activation energy of 23.8 kcal/g-atom for self-diffusion of the delta phase of plutonium between 350°C and 440°C. Their value is somewhat lower than the value of 30 kcal/g-atom derived from the creep data. No diffusion data are available to make similar comparisons between activation energies for creep and self-diffusion for the other allotropes.

Sherby and Simnad⁽⁸⁹⁾ derived an expression for the activation energy for self diffusion, Q_{sd} , in terms of the effect of absolute melting temperature, T_m , the valence, V , and a crystal structure parameter, K_o . Their relationship is:

$$Q_{sd} = RT_m (K_o + V) \quad (V-7)$$

The effective melting temperature is essentially the theoretical melting temperature of an allotrope. If the liquid, epsilon, delta-prime, delta, gamma, beta, and alpha phases are designated 0, 1, 2, 3, 4, 5, and 6, respectively, then the effective melting temperature of each phase can be calculated according to the method derived by Ardell.⁽⁹⁰⁾

$$T_m^i = \frac{\sum_{i=1}^n \Delta H^{i \neq (i+1)}}{\sum_{i=1}^n \Delta S^{i \neq (i+1)}} \quad (V-8)$$

In this expression $\Delta H^{i \neq (i+1)}$ and $\Delta S^{i \neq (i+1)}$ are the enthalpy and entropy changes associated with the transformation of a

particular phase to the next higher temperature phase. The effective melting temperatures of all six allotropes calculated in this manner are tabulated in Table XIII. The enthalpy and entropy changes associated with each transformation used in these calculations are also listed in Table XIII. Ianniello,⁽⁹¹⁾ calculated the effective melting temperature to be 622°K, which is slightly higher than the value calculated by Ardell's method. The fact that every transformation temperature is greater than 0.5 T_m is worthy of note.

TABLE XIII

NORMAL TRANSFORMATION ENTHALPY AND ENTROPY CHANGES, EFFECTIVE MELTING TEMPERATURES, ACTIVATION ENERGIES FOR CREEP AND SELF-DIFFUSION, AND STRUCTURE FACTORS, FOR THE SIX ALLOTROPES OF PLUTONIUM

Phase	Enthalpy and Entropy Changes for Normal Transformation cal/g-atom ⁽⁹⁾		Effective Melting Temperature T_m		Activation Energy cal/g-atom		Structure Factor
	$\Delta H^{i \rightarrow (i+1)}$	$\Delta S^{i \rightarrow (i+1)}$			Q_c^i	Q_{sd}^{ii}	$(K_o + V) = \frac{Q_{sd}}{RT_m}$
			°K	°C			
α	900	2.28	557	284	26,000	23,000	21
β	160	0.33	748	475	30,000	27,000	18
γ	148	0.25	804	531	35,000	31,000	19.5
δ	10	0.01	843	570	31,000	30,000	18
δ'	444	0.59	842	569	28,000		17
ϵ	676	0.74	913	640	25,000		14

i - Derived from Figure 68

ii - Derived from Figure 69

Plutonium offers a unique opportunity to determine the values of six crystal structure factors for a single metal. From the activation energies and the effective melting temperatures in Table XIII, values for $(K_o + V)$ can readily be calculated from the expression

$$(K_o + V) = \frac{Q_{sd}}{RT_m} \quad (V-9)$$

The values calculated for $(K_o + V)$ of all six allotropes are also given in Table XIII.

Unfortunately, values for V in the above relationship have not been established. Sherby and Simnad⁽⁸⁹⁾ assigned zero to V for uranium. By analogy, zero for V may also be applicable to plutonium. However, the significance of such a value for the valency term would be doubtful. If V does equal zero, then values for K_o will be the same as the values given for $(K_o + V)$ in Table XIII.

Sherby and Simnad⁽⁸⁹⁾ determined K_o to be 14, 17, and 21 for the body-centered cubic, face-centered cubic, and diamond structures, respectively. If $V = 0$, then K_o for the body-centered cubic and face-centered cubic allotropes of plutonium are 14 and 18 which are essentially in agreement with Sherby's and Simnad's values derived from other metals.

D. PROPERTIES OF BETA PLUTONIUM RELATED TO PHASE TRANSFORMATION

The ultimate strength and yield strength of the beta phase of unalloyed plutonium have been reported to be very low.⁽⁹²⁾ The ductility of the beta phase is very high and tensile elongation values up to 600 percent have been reported. These reported values were obtained on beta that had been formed from alpha. No consideration was given to what effect that the prior phase might have on the properties of the final phase.

The ultimate strength and the yield strength of the beta phase were increased by a factor of 3 when the beta was formed

from gamma instead of from the alpha phase. For example, at 160°C and at a testing speed of 0.05 in./min the ultimate strength increased from 8,000 to 23,000 psi; the yield strength increased from 5,500 to 18000 psi; and the percent elongation decreased from 400 percent to less than 20 percent. The appearance of two fractured tensile specimens showing the large difference in ductility of the beta phase, which was formed from the alpha phase in one and then from the gamma phase in the other are given in Figure 71.

Top: As-cast
Middle: Beta formed from gamma
Bottom: Beta formed from alpha

Figure 71

Tensile specimen of plutonium fractured in the beta phase at 160°C and at a testing speed of 0.05 in./min

The compressive creep rates of beta phase specimens obtained by transformation from gamma was much less than the compressive creep rates of beta phase specimens obtained by transformation from alpha. The former creep rate was only 0.2 to 0.5 percent of the latter. For example, the steady-state creep rate of the beta phase formed directly from alpha is $1 \times 10^{-2} \text{ hr}^{-1}$ at 185°C and 2700 psi. At the same temperature and stress the creep rate of the beta formed directly from gamma is $6 \times 10^{-5} \text{ hr}^{-1}$. The times and temperatures at which

the samples were held in each phase are given in Figure 72. The steady-state creep rate of gamma at the same conditions is also given. Note that the creep rate of the gamma phase was between the creep rates of the beta phase formed from alpha and beta formed from gamma. Other examples are given in Table XIV.

TABLE XIV
EXAMPLES OF THE CREEP RATES OF BETA PHASE PLUTONIUM
FORMED FROM GAMMA AND FROM ALPHA

Applied Compressive Stress psi	Test Temperature °C	Steady-State Creep Rate of Beta Phase Plutonium Hr ⁻¹	
		Transformed from Alpha	Transformed from Gamma
2500	115	6×10^{-5}	2×10^{-7}
7500	115	1×10^{-2}	5×10^{-5}
15000	115	3×10^{-1}	9×10^{-4}
2500	150	4×10^{-4}	1×10^{-6}
7500	150	7×10^{-2}	2×10^{-4}
2700	185	2×10^{-2}	6×10^{-5}

A representative temperature-strain rate curve at a compressive stress of 7,200 psi for the beta phase formed from alpha and gamma is shown in Figure 73. Modulus compensated strain rates were calculated so that the activation energies may be determined from the relationship:

$$\dot{\epsilon}E^5 = K e^{-Q/RT} \quad (V-10)$$

for constant stress, Figure 74. The activation energy was computed as 27-28 kcal/g-atom for beta formed from either alpha or gamma. The densities of specimens of the comparable metal at 140°C after either the alpha to beta or gamma to beta transformation were $19.63 \pm 0.01 \text{ g/cm}^3$, implying that the transformation to beta was essentially complete after both transformations.

Figure 72

Schematic diagram showing the steady-state creep rate of beta at 2700 psi after $\alpha \rightarrow \beta$ and $\alpha \rightarrow \beta \rightarrow \gamma \rightarrow \beta$ transformation

Figure 73

Temperature dependency of the steady-state compressive creep rate of beta plutonium formed from alpha and from gamma plutonium

Figure 74

Modulus compensated creep rates of beta plutonium formed from alpha and gamma plutonium

The concept of apparent strengthening of beta phase specimens by transforming from the gamma phase instead of from the alpha phase was utilized in experiments which have provided information concerning the mechanism of the $\beta \rightarrow \alpha$ transformation.

CHAPTER VI

TRANSFORMATION OF PLUTONIUM UNDER APPLIED STRESSES

Research was undertaken to determine the effect of concurrent applied stress on the $\beta \rightarrow \alpha$, $\alpha \rightarrow \beta$, $\gamma \rightarrow \beta$, and $\beta \rightarrow \gamma$ transformations. The primary objective of this activity was to gain information about the mechanisms of these transformations and to compare the transformations in plutonium to transformations in more familiar metals. A secondary objective was to learn the effect of applied stress on the phase transformations of a metal that is unique because:

- (1) Volume changes of 9 and 3 percent are associated with the $\alpha \rightarrow \beta$ and $\beta \rightarrow \gamma$ transformations, respectively.
- (2) The transformations are between complex crystal structures.
- (3) The creep of the beta phase at a given stress and temperature can be varied between two and three orders of magnitude.
- (4) The ductility and the creep rate of the beta phase can be much greater than the ductility and creep rate of the alpha phase.
- (5) The ductility and creep rate of the beta phase can either be less than or greater than the corresponding properties of the gamma phase.
- (6) The $\beta \rightarrow \gamma$ and $\gamma \rightarrow \beta$ transformations take place at temperatures where diffusional processes should be operative; whereas the $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ transformations take place at temperatures where diffusional processes are not likely to be operative.

A number of investigators have found a marked influence of applied stress on the kinetics of phase transformations.^(56-65,93-101) The most extensive work has been done with iron alloys, although some information is available on other alloys such as tin alloys containing antimony,⁽⁹⁷⁾ gold-cadmium,⁽⁶²⁾ copper-zinc,⁽¹⁰²⁾ copper-aluminum,⁽¹⁰³⁾ indium-thallium,⁽⁶³⁾ and lithium-magnesium alloys.⁽¹⁰⁴⁾ An applied stress may markedly alter

the transformation kinetics of both diffusional and martensitic transformations, and it may introduce extra creep deformation with concurrent phase transformation.

The austenite $\rightarrow$ pearlite and austenite $\rightarrow$ bainite transformations can be accelerated by an applied stress.⁽⁶¹⁾ The austenite $\rightarrow$ martensite transformation can be induced by applied stresses and residual stresses. In iron-nickel-carbon alloys^(100,101) and indium-thallium alloys⁽⁶³⁾ the M_s temperature of the $\beta' \rightarrow \beta$ transformation of a Au-47.5 at.% Cd alloy was raised during cooling under applied stress but was lowered during heating under applied stress; that is, the reversible martensite transformation was always favored by applied uniaxial stresses.

The most extensive work on the deformation of metals with concurrent phase transformation has been performed by Clinard and Sherby,⁽⁹³⁾ de Jong and Rathenau,^(80,82) and Porter and Rosenthal⁽⁹⁴⁾ on iron and iron alloys.

The three strain components proposed by Sherby and Clinard to make up the observed deformation during phase transformation are 1) phase transformation strain [excess creep strain], 2) normal creep strain, and 3) strain due to volumetric change. Clinard's and Sherby's conclusions concerning deformation during the $\alpha \rightarrow \gamma$ and $\gamma \rightarrow \alpha$ phase transformations in iron are:

- (1) "Transformation strain [excess creep strain] is responsible for a significant portion of the total strain, both on heating and on cooling, up to the highest stress studied (1085 psi)."
- (2) "Transformation strain obtained on heating is significantly greater than that obtained on cooling."
- (3) "Transformation strain is a non-linear increasing function of applied stress."
- (4) "The amount of transformation strain is a function of transformation rate."

They proposed that excess point defects formed during transformation contribute to dislocation climb, by which mechanism the deformation rate

is increased. Vacancies form during the $\alpha \rightarrow \gamma$ transformation and interstitials form during the $\gamma \rightarrow \alpha$ transformation. They called the resulting excess creep strain "transformation strain".

De Jong and Rathenau⁽⁸⁰⁾ observed that in iron the $\alpha \rightarrow \gamma$ excess creep strain on heating was essentially the same as the $\gamma \rightarrow \alpha$ excess creep strain on cooling. They also observed that the excess creep strain is independent of transformation rate and is a linear function of applied stress. These observations disagree with the more recent results of Clinard and Sherby.⁽⁹³⁾ De Jong and Rathenau⁽⁸⁰⁾ concluded that excess creep strain is really not a kind of creep. They proposed that two processes might produce excess creep strain under applied stress:⁽⁸²⁾

- (1) "Owing to the difference in density of the parent and the product phases, internal stresses are thought to occur during transformation. The material yields to the superimposed external stress at a lower value because of the pre-existing internal stresses. Excess elongations are to be expected at even small external stresses if these stresses remove the equivalence of the slip systems which are activated by the change in volume."
- (2) "During transformation, especially in the martensitic case, out of the possible modes of transformation those are favored which allow the largest elongation in the direction of the external stress."

This chapter presents results of compressive and tensile creep experiments with concurrent phase transformation during isothermal transformation and upon continuous heating and cooling. The plutonium was 99.5% pure containing 0.005% Fe, 0.01% C, 0.005% U, 0.01% Am, and all others totaling less than 0.02%.

The total strain accompanying the various transformations in pure plutonium is most conveniently analyzed by considering three contributions to the total strain:

- (1) Normal creep strain. This has been discussed in Chapter V. Normal creep can occur significantly during transformation under stress.
- (2) Excess creep strain. As described above, excess creep is postulated to be caused by an excess concentration of point defects.
- (3) Transformation strain. Transformation strain is defined as the macroscopic shape change resulting from the summation of the shape change accompanying the formation of each grain of the product phase. In a perfectly random transformation this strain would be isotropic and equal to one-third the fractional volume change accompanying transformation. If the transformation occurs anisotropically the resulting transformation strain will be similarly anisotropic.

A. STRAIN OF THE $\beta \rightarrow \alpha$ TRANSFORMATION UNDER APPLIED STRESS

1. Strain with Applied Compressive Stresses

The strain during the $\beta \rightarrow \alpha$ transformation in plutonium was measured as a function of applied compressive stress from 200 to 20,000 psi. The parent beta phase was formed by transformation from either the alpha or the gamma phase. The beta phase was significantly strengthened by first transforming the metal to gamma and then transforming back to beta. This procedure for strengthening the beta phase was experimentally advantageous because the much lower creep rate of beta formed from gamma permitted tests at stresses up to 20,000 psi. When the beta was formed from alpha, tests could be performed at stresses no higher than 5000 psi without appreciable creep of the beta phase. More detailed creep data were given in Chapter V.

Specimens were heated to 260°C and held at temperature for 30 minutes to ensure complete transformation to gamma. They were

then cooled to 120°C to transform the gamma phase to the beta phase. The $\gamma \rightarrow \beta$ transformation was presumed complete after keeping the specimen one hour at 120°C. Specimens in which the beta was formed directly from alpha were heated to 180°C and maintained at that temperature for one hour to ensure complete $\alpha \rightarrow \beta$ transformation. All specimens were cooled to 110-115°C for the start of the tests.

Representative creep curves of the single phase alpha and beta phases as well as curves showing the strain associated with the $\beta \rightarrow \alpha$ transformation with no applied stress are shown in Figure 75.

Figure 75

Representative data of the strain accompanying the plutonium $\beta \rightarrow \alpha$ transformation and single phase creep of alpha and beta plutonium under applied compressive stresses at 110°C

The total, normal creep strain during continuous cooling and continuous heating at a given stress was obtained from steady-state creep data using graphical integration according to the relationship:

$$\epsilon = \int_0^t \dot{\epsilon} dt \quad (\text{VI-1})$$

The normal creep strain was small compared to the volumetric change and generally could be neglected. Because the heating and cooling rates were generally very slow, graphical integration was required over only a few degrees. In most cases the transformation proceeded under isothermal conditions.

The total strain during transformation was investigated as a function of the transformation rate. The total strain, $\Delta L/L_0$, was always measured in the direction of the applied stress. Representative total strains of the $\beta \rightarrow \alpha$ transformation under an applied stress of 5000 psi are shown in Figure 76 for three cooling rates. These curves show that the total strain during transformation was only slightly dependent on the $\beta \rightarrow \alpha$ transformation rate. This was in contrast to the behavior of iron as reported by Clinard and Sherby.⁽⁹³⁾ The strain during transformation was correlated with the approximated maximum transformation rate, because this was believed to be the best parameter to characterize the transformation rate. Increasing the maximum transformation rate from 0.15%/min to 50%/min by increasing the cooling rates resulted in only a 20% decrease in the total strain associated with the $\beta \rightarrow \alpha$ transformation, Figure 77. The transformation temperature was raised approximately 15°C when the maximum transformation rate was lowered from 50%/min to 0.15%/min. Note that the total strain accompanying transformation was nearly the same regardless of whether beta was formed from alpha or from gamma.

The total strain during transformation increased rapidly with increasing applied stress and reached a constant value at about 9000 psi, Figure 78. This constant value of 0.09 was equal to $\Delta V/V_0$ and was thus three times the linear change, 0.03, expected for the strain when transformation occurs with no applied stress. Therefore,

Figure 76

Total strain accompanying the plutonium $\beta \rightarrow \alpha$ transformation
with 5000 psi compressive stress

Figure 77

Effect of transformation rate on the total strain accompanying the $\beta \rightarrow \alpha$ transformation

the data led to the conclusion that the effect of applied stress was to cause all of the $\beta \rightarrow \alpha$ volumetric change to occur by contraction in the direction of the applied stress. If this were so, then the total strain accompanying the transformation consisted only of the anisotropic volume change and a small amount of normal creep.

Figure 78

Effect of applied compressive stress on the total strain accompanying the plutonium $\beta \rightarrow \alpha$ transformation at a cooling rate of 0.5-1.0°C/hr

2. Strain with Applied Tensile Stresses

The total strain during $\beta \rightarrow \alpha$ transformation was also investigated as a function of applied tensile stresses at different transformation rates. A tensile stress tends to oppose the contraction of the transformation in the direction of the applied stress. Representative total strains at stresses from 250 psi to 7000 psi at a cooling rate of 2°C/hr are shown in Figure 79. These curves show that the effect of applied tensile stresses was more pronounced and somewhat different from the effect of applied compressive stresses on the $\beta \rightarrow \alpha$ transformation. The total strain accompanying the transformation with very low stresses was negative but the contraction in the specimens was less than the strain with no applied stress.

Figure 79

The total strain accompanying the $\beta \rightarrow \alpha$ transformation under applied tensile stresses at a cooling rate of 2°C/minute

At 1500 psi the specimens elongated during the first stages of transformation. The positive rate of strain decreased as the transformation proceeded, became zero, and then became negative because of the contraction associated with the volumetric change. The effect was similar at 2900 psi with the elongation being greater and the contraction less than at 1500 psi. Some net elongation was observed in the direction of the applied tensile stress in specimens transformed with 7000 psi. It is reasonable to assume that the linear transformation strain is limited to values between zero and $\Delta V/V_0$, i.e., 0 to 0.09; this assumption will be discussed in connection with the observed microstructure. Therefore the elongation observed in specimens transformed in tension must be attributed to excess creep strain.

B. TEXTURING OF THE ALPHA PHASE FORMED UNDER APPLIED STRESSES

1. Metallographic and Crystallographic Relationships

The transformation of beta to alpha proceeded by the formation of thin disk shaped volumes, which consisted of many individual columnar grains of the alpha phase. The long axes of the grains were all perpendicular to the plane of the disk. In a polished and etched cross-section the disks appeared as bands, which were randomly oriented in the absence of stresses (Figure 33). When a compressive stress was applied to the metal, the disks formed at right angles to the compressive stress, while the grains within the disks were parallel to the applied stress (Figures 80-82). The alignment of the alpha disks was particularly evident from the appearance of the bands in specimens only partially transformed with 15,000 psi uniaxial compression (Figure 83).

During transformation the (010) alpha planes formed with their alignment predominantly in a direction perpendicular to the applied compressive stress. X-ray diffraction patterns of the transverse and longitudinal sections of a specimen transformed with an applied compressive stress of 16,000 psi are compared to the random structure in Figures 84-86. Although the (020) and (211) reflections

The applied compressive stress was perpendicular to the plane of the paper

The longitudinal axes of the grains were in the direction of the applied stress

Figure 80

Microstructure of a specimen completely transformed from the beta phase to the alpha phase with a compressive stress of 15,000
Polarized light illumination 250X

Figure 81

Microstructure of a plutonium specimen completely transformed from the
beta phase to the alpha phase under a compressive stress of 15,000 psi
Polarized light illumination 400X

(a)

(b)

(c)

(d)

Figure 82

Photomicrographs showing the texturing that occurs during the transformation under an applied compressive stress. The direction of the applied compressive stress was vertical

	(a)	(b)	(c)	(d)
Applied stress (psi)	2000	7200	5000	5000
Cooling rate ($^{\circ}\text{C}/\text{min}$)	0.005	0.005	0.005	0.5-1
Maximum transformation rate ($\%/ \text{min}$)	0.5	0.5	0.5	10

-146-

Direction of the applied
stress compressive

Specimen edge

20% transformed

90% transformed

Figure 83

Microstructure showing the bands in a plutonium specimen partially transformed under a compressive stress of 15,000 psi at 70-80°C and quenched to -75°C. (The columnar grains formed under the applied stress whereas the small grains formed during the quench. The bands of columnar grains were perpendicular to the direction of applied stress

Polarized light illumination

100X

Figure 84
X-ray diffraction pattern of an as-cast,
random structure of plutonium

Figure 85

X-ray diffraction pattern of plutonium transformed from the beta phase to the alpha phase at 15,000 psi.

The X-ray pattern was of a surface perpendicular to the direction of the applied compressive stress

Figure 86

X-ray diffraction pattern of plutonium transformed from the beta phase to the alpha phase at 15,000 psi.

The X-ray pattern was of a surface parallel to the direction of the applied compressive stress.

are superimposed, the presence or absence of the (010) planes parallel to the specimen surface can be determined by the relative intensities of the (040) reflection. The (040) reflection was very pronounced in the diffraction pattern from the transverse section, but it was not detected in the diffraction pattern obtained from the longitudinal section. Also reflections (201), (002), (20 $\bar{3}$), and others, where k of the (hkl) value was zero, were very weak in the section that was perpendicular to the applied stress. These reflections belonging to the [010] zone axis were strong in the section parallel to the applied stress. This verified that the (010) plane lies predominantly perpendicular to the direction of applied compressive stress.

When a tensile stress was applied to the metal, the disks formed parallel to the direction of the applied stress, while the grains within the bands were perpendicular with the applied stress (Figures 87-88). The (010) planes became aligned parallel with the direction of the applied stress, revealed by the very weak (040) reflection from a section perpendicular to the applied stress.

When plutonium transformed under compression the dimensions perpendicular to the plane of the disk depended only upon impingement, whereas the disk extended to the boundaries of the specimen in the direction parallel to the plane of the disk. When the plutonium transformed under no applied stress or under tension all dimensions of the disk were restricted by either impingement or the boundaries of the specimen.

2. Anisotropy of the $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ Transformations

A highly textured cylindrical rod specimen with the (010) planes perpendicular to the rod axis was cycled once through the $\alpha \rightarrow \beta$ and back through the $\beta \rightarrow \alpha$ transformation without applied stress. The specimen was heated to 115°C where the diameter and the length were measured in the alpha phase. The dimensions of a rod in the alpha phase can be readily compared to the corresponding dimensions in the beta phase at 115°C since both beta and alpha can exist at this

Tensile
applied
stress

Figure 87

Microstructure of a specimen transformed from the beta phase to the alpha phase with an applied uniaxial tensile stress of 7000 psi. The specimen surface was parallel to the direction of the applied stress
Polarized light illumination 100X

Figure 88

Microstructure of a specimen transformed from the beta phase to the alpha phase with an applied uniaxial tensile stress of 7000 psi. The specimen surface was perpendicular to the direction of the applied stress
Polarized light illumination 100X

temperature for long times. The specimen was heated to 160°C, held for one hour to transform the metal completely to beta, and then cooled to 115°C for measuring the length and diameter of the rod in the beta phase. Transformation of the beta phase to the alpha phase was accomplished by cooling to room temperature at a rate of 50°C/hr. The rod was then reheated to 115°C and the dimensions of the alpha phase rod were measured. The dimensions of the rod in the alpha phase before cycling, in the beta phase, and in the alpha phase after cycling could therefore be compared.

The length increased 7.9 percent and the diameter increased 0.8 percent during the $\alpha \rightarrow \beta$ transformation. This indicated that nearly all of the volume change during transformation occurred by expansion in a direction parallel to the length of the specimen. The length and the diameter decreased 1.2 and 4.3 percent, respectively, during the $\beta \rightarrow \alpha$ transformation. The sample after transformation cycling had increased in length by 6.5 percent and had decreased in diameter by 3.4 percent. From this it can be concluded that both the $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ transformations occurred anisotropically.

The anisotropic nature of the $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ transformations of the textured rod indicated that a texture should still be present in the alpha phase after an $\alpha \rightarrow \beta \rightarrow \alpha$ cycle with no applied stress. A texture after cycling was confirmed by X-ray diffraction and by metallography, but it was different from the texture that had been observed before cycling. After cycling, the disks were aligned predominantly parallel to the direction of the original applied compressive stress, (Figure 89), rather than 90 degrees to the applied stress as observed before cycling (Figure 80). The alignment of the elongated alpha grains in the radial direction is in accordance with the observation that strain accompanying transformation occurred primarily radially.

X-ray diffraction revealed that the (020) and (040) reflections were very weak from the transverse section and moderately strong from the longitudinal section after cycling. Before cycling the (020) and

Surface that was perpendicular to the
direction of the applied stress

Surface that was parallel to the
direction of the applied stress

Figure 89

Plutonium that was textured by $\beta \rightarrow \alpha$ transformation with
20,000 psi compressive stress and then cycled
into beta by heating and into alpha by cooling
Polarized light illumination 100X

(040) reflections were most pronounced in the transverse section. The X-ray diffraction pattern of the transverse section after cycling was similar to the X-ray diffraction pattern (Figure 86) of the longitudinal section before cycling. All of the reflections of planes belonging to the [010] zone axis were stronger than in the pattern from randomly oriented specimens and much stronger than reflections from these planes in either the longitudinal section after cycling or the transverse section before cycling. It should be noted that the degree of texture prior to cycling was not a perfect [010] texture. The degree of texture was less after cycling than it was before cycling.

The anisotropic $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ transformation strains and the 90° rotation of the crystallographic and microstructural textures imply that there is a specific crystallographic orientation relationship between the parent and the product phases of the $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ transformations. From the 90° rotation of the texture it can be concluded that there is more than one crystallographic variant of the orientation relationship in spite of the low symmetry of the two phases. These are characteristics to be expected of martensitic transformations.

The longitudinal section of a textured cylindrical rod specimen with the (010) plane essentially perpendicular to the surface and rod axis was polished metallographically and transformed through the $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ transformations. Very little surface distortion was observed after the $\alpha \rightarrow \beta$ transformation but considerable surface distortion occurred during the $\beta \rightarrow \alpha$ transformation (Figure 90). The surface rumpling may have been partly the result of martensitic shear; however, the distortion appeared to be so irregular that it could also have been attributed to plastic flow caused by transformation volumetric change. Quantitative observation of martensitic surface tilting was impossible.

An as-cast specimen having a random structure was polished in the beta phase and quenched to -80°C . The surface was also extensively rumpled and had no discernible linear surface upheavals (Figures 91-92) characteristic of many martensitic transformations.

Figure 90

Surface of a specimen that was polished and then $\alpha \rightarrow \beta \rightarrow \alpha$ cycled. The specimen was slowly cooled during the $\beta \rightarrow \alpha$ transformation. Texturing was accomplished by $\beta \rightarrow \alpha$ transformation under 20,000 psi compressive stress. The polished surface was parallel to the applied stress.

Bright field illumination 250X

Figure 91

Surface of a specimen that was polished
in the beta phase and quenched to -80°C
250X

Figure 92

Same surface as Figure 91 after polishing
and electrolytic etching for polarized
illumination. The direction of the original
applied stress was essentially parallel to the bands 100X

C. EFFECT OF APPLIED STRESS ON THE
 $\beta \rightarrow \alpha$ TRANSFORMATION TEMPERATURE

The temperature for the beginning of the $\beta \rightarrow \alpha$ transformation was determined as a function of applied uniaxial tensile and uniaxial compressive stresses. These temperatures were compared with those for the start of the transformation as a function of hydrostatic pressure (Figure 93).

Figure 93

Effect of applied uniaxial tensile and compressive stresses on the temperature of the start of the $\beta \rightarrow \alpha$ transformation at a cooling rate of 2°C/hr

The three methods of stressing the specimens produced virtually linear changes in the transformation temperature up to 7000 psi. The slopes of the curves were $+3^{\circ}\text{C}/1000$ psi for tension and compression and $+0.4^{\circ}\text{C}/1000$ psi for hydrostatic pressure.⁽¹⁰⁶⁾ These data clearly show that there was an appreciable difference between the three types of loading. Note that all three types of loading increased the transformation temperature. The very large temperature increase of the start of the transformation of specimens transformed in compression and the positive increase of the specimens transformed in tension are difficult to explain on the basis of a diffusional transformation, but can be explained on the basis of a martensitic type transformation.

D. STRAIN ACCOMPANYING THE PLUTONIUM
 $\alpha \rightarrow \beta$ TRANSFORMATION WITH APPLIED STRESSES

1. Strain with Applied Compressive Stresses

The maximum compressive stress that could be utilized in the study of the $\alpha \rightarrow \beta$ transformation was 2500 psi. The creep rate of beta formed from alpha was so high that above 2500 psi little strain was observed during transformation other than normal creep. The magnitude of the normal creep component is apparent in Figure 94, where representative creep of the alpha and beta phases at 125°C and 2500 psi are depicted along with the total strain accompanying the $\alpha \rightarrow \beta$ transformation when it is not subjected to an applied stress. The time dependency of the strain during $\alpha \rightarrow \beta$ transformation was investigated as a function of transformation rate. Typical curves are shown in Figure 95. A given applied stress influenced the $\alpha \rightarrow \beta$ transformation more than it did the $\beta \rightarrow \alpha$ transformation. The total strain during transformation was approximately zero for stresses between 1500 psi and 2000 psi; a variation in stress at this stress level caused little change in the total strain. This implies that most of the transformation volume change occurred in a direction perpendicular to the applied compressive stress. Accordingly, the specimens should have been highly textured, but this was impossible to establish since metallographic techniques for polishing and

Figure 94

Representative data of the strain accompanying the plutonium $\alpha \rightarrow \beta$ transformation and single phase creep of alpha and beta plutonium under applied compressive stresses at 125°C

Figure 95

Typical curves of the total strain accompanying the plutonium $\alpha + \beta$ transformation with applied compressive stresses

etching the beta phase in unalloyed plutonium have not been developed. Even so there appeared to be a small strain opposing the volumetric change that could not be attributed either to the microstructural shape texture or the single phase beta creep. In addition, the amount of total strain depended on the $\alpha \rightarrow \beta$ transformation rate (Figure 96). Thus the data indicate that there may have been some excess creep strain concurrent with $\alpha \rightarrow \beta$ transformation and that the excess creep strain of the stressed specimens was only slightly dependent on the transformation rate.

Figure 96

Effect of stress and transformation rate on the total strain accompanying the $\alpha \rightarrow \beta$ transformation

2. Strain with Applied Tensile Stresses

Extra creep deformation during $\alpha \rightarrow \beta$ transformation was more evident under applied uniaxial tensile stresses than it was under applied uniaxial compressive stresses. An applied tensile stress favors expansion in the direction of the applied stress during $\alpha \rightarrow \beta$ transformation. If all of the transformation were to occur in the direction of the applied stress without normal creep and without excess strain accompanying the transformation, then $\Delta L/L_0$ would equal $\Delta V/V_0 \approx 0.09$; this is equivalent to the $\beta \rightarrow \alpha$ transformation conducted under an applied uniaxial compressive stress. The total strain accompanying the $\alpha \rightarrow \beta$ transformation increased with applied stress and increased with decreasing transformation rate. Experiments showed that $\Delta L/L_0$ during $\alpha \rightarrow \beta$ transformation under an applied tensile stress exceeded 0.09, evident in Figure 97.

Since the formation of disks of beta during the $\alpha \rightarrow \beta$ transformation analogously to the formation of alpha disks observed to form during the $\beta \rightarrow \alpha$ transformation has not been verified, it is impossible to place limits on the range of transformation strain.

E. STRAIN ACCOMPANYING THE $\gamma \rightarrow \beta$ AND $\beta \rightarrow \gamma$ TRANSFORMATIONS WITH APPLIED STRESSES

The total strain accompanying the $\gamma \rightarrow \beta$ transformation was evaluated as a function of applied compressive stresses from 100 psi to 3000 psi. Representative data of the total strain associated with the $\gamma \rightarrow \beta$ and $\beta \rightarrow \gamma$ transformations with no applied stress and creep curves of the single phase beta and gamma phases are shown in Figure 98. Creep of the gamma phase at 190°C at stresses above 3000 psi was so great that it obscured the strain associated with the $\gamma \rightarrow \beta$ transformation. The volume change associated with this transformation is only 3 percent compared to 9 percent for the $\beta \rightarrow \gamma$ transformation.

For investigating the $\gamma \rightarrow \beta$ transformation the specimens, 0.30 inch diameter and 0.45 inch long, were heated to 260°C for 30 minutes to transform the metal to gamma and then cooled to 195°C

Figure 97

The total strain accompanying the $\alpha \rightarrow \beta$ transformation
with applied tensile stresses

Figure 98

Strain of plutonium transformed from gamma to beta and beta to gamma and of the beta and gamma phases under applied compressive stresses

where the tests were started. Prior to performing the $\beta \rightarrow \alpha$ transformation creep experiments, the beta phase was formed from the gamma phase so that stresses up to 2000 psi at 230°C could be applied to the specimen with negligible creep of the beta phase. Otherwise, stresses of only 1000 psi would cause extensive creep at 230°C of beta formed from alpha.

The strain during the $\gamma \rightarrow \beta$ transformation was investigated as a function of the transformation rate at 2000 psi (Figures 99 and 100) and as a function of the applied stress (Figure 101). These curves clearly show that the $\gamma \rightarrow \beta$ transformation was strongly dependent upon the transformation rate. This implies that excess creep may have been significant in the $\gamma \rightarrow \beta$ transformation; certainly more so than in the $\beta \rightarrow \alpha$ and $\alpha \rightarrow \beta$ transformations.

Figure 99

The total strain accompanying the plutonium $\gamma \rightarrow \beta$ transformation
with 2000 psi at different cooling rates

Figure 100

Effect of transformation rate on the total strain accompanying the $\gamma \rightarrow \beta$ transformation with applied compressive stresses

Figure 101

Effect of applied compressive stress on the total strain
accompanying the plutonium $\gamma \rightarrow \beta$ transformation
at a cooling rate of 0.5°C/hr

F. DISCUSSION OF RESULTS

1. Summary

Application of uniaxial compression and tensile stresses markedly affected the total strain accompanying the $\alpha \rightarrow \beta$, $\beta \rightarrow \alpha$, $\beta \rightarrow \gamma$, and $\gamma \rightarrow \beta$ transformations in plutonium. A number of conclusions can be made from the data.

- (1) Both applied uniaxial tensile stresses and compressive stresses raised the temperature for the beginning of the $\beta \rightarrow \alpha$ transformation at a constant cooling rate for stresses up to 7000 psi.
- (2) Applied stresses during $\beta \rightarrow \alpha$ transformation produced a microstructural shape texture. The alpha grains were elongated in a direction perpendicular to the applied compressive stresses. The elongated grains were aligned in disks which were perpendicular to compressive stresses and parallel to the direction of the applied tensile stresses.
- (3) Applied stresses during the $\beta \rightarrow \alpha$ transformation produced a crystallographic texture. The alpha (010) planes were aligned parallel to the applied tensile stresses and perpendicular to the applied compressive stresses.
- (4) The anisotropic strain accompanying transformation under uniaxial stress indicated that texture also occurred during $\alpha \rightarrow \beta$, $\gamma \rightarrow \beta$, and $\beta \rightarrow \gamma$ transformations under applied uniaxial stresses.
- (5) Some phase transformation excess creep occurred during the transformations in specimens subjected to an external stress.
- (6) More excess creep occurred under tension than it did under compression. Little or no excess creep occurred during the $\beta \rightarrow \alpha$ transformation under compression but some $\beta \rightarrow \alpha$ excess creep was observed under tension.

- (7) The effect of applied compressive stress above 9000 psi was to cause essentially all of the $\beta \rightarrow \alpha$ transformation strain to occur as contraction parallel to the applied stress, i.e., $\Delta L/L_0 = \Delta V/V_0$. The total strain during $\beta \rightarrow \alpha$ transformation under compression was almost completely independent of the transformation rate.
- (8) The effect of applied tensile stresses above about 4000 psi on the $\beta \rightarrow \alpha$ transformation was to cause all of the transformation strain to occur as contraction perpendicular to the applied stress, i.e., $\Delta L/L_0 = 0$.
- (9) In textured plutonium the $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ transformations resulted in anisotropic transformation strain in the absence of applied stress.

2. Excess Creep

Some excess transformation creep was observed with concurrent phase transformation but it was much less than the anisotropic transformation strain of the transformations under applied stress. Compressive stresses applied during the $\beta \rightarrow \alpha$ transformation produced essentially no excess creep with concurrent phase transformation.

The model proposed by de Jong and Rathenau⁽⁸⁰⁾ to explain deformation with concurrent phase transformation is based on 1) the generation of internal stresses during transformation because of the difference in specific volume of the parent and product phases and on 2) the average strength of the parent and product phases. According to this model the metal deforms at a lower applied stress during transformation because the internal stresses formed during transformation are superimposed on the applied stress.

De Jong and Rathenau⁽⁸²⁾ correlated strain during transformation with the strength of the metal. They showed that the net strain after one complete cycle through the transformation was directly proportional to the change in volume, directly proportional to the applied stress, and inversely proportional to the average hardness

of the two phases. They made the correlation for four iron alloys, cobalt, and a Cu-39.2 wt% zirconium alloy.

The data from the present investigation of the $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ transformations conducted under stress can be interpreted in a similar manner. However, the deformation in plutonium when cycled through the $\alpha \rightleftharpoons \beta$ transition was much higher than would be predicted from de Jong's and Rathenau's correlation. For example, the predicted strain upon transformation cycling at 2500 psi is between 0.02 and 0.04. The experimental value was 0.12 when the specimens were heated and cooled at rates of 2°C to 5°C/hr.

The model presented by Sherby and Clinard⁽⁹³⁾ to explain excess defects is that the excess point defects formed during transformation contribute to dislocation climb; this accelerates the deformation rate. Vacancies are formed during transformation from a less dense phase to the more dense phase, whereas, interstitials form during transformation from the more dense phase to the less dense phase. Accordingly, excess vacancies and excess interstitials should form during the $\beta \rightarrow \alpha$ and $\alpha \rightarrow \beta$ transformations of plutonium, respectively.

From this model it must be inferred that more excess creep should occur during the $\beta \rightarrow \alpha$ transformation than during the $\alpha \rightarrow \beta$ transformation. Experimentally, more excess creep was observed during the $\alpha \rightarrow \beta$ transformation. This can be explained on the basis of a higher creep rate of the beta phase during the $\alpha \rightarrow \beta$ transformation which was conducted at a temperature 40°C higher than the $\beta \rightarrow \alpha$ transformation. The excess creep occurred during the latter stages of the $\alpha \rightarrow \beta$ transformation and during the first stages of the $\beta \rightarrow \alpha$ transformation. The significance of this observation is that excess creep occurs in the weaker beta phase during both the $\alpha \rightarrow \beta$ and the $\beta \rightarrow \alpha$ transformations.

Both models are compatible with the experimental evidence for excess creep deformation during the low temperature allotropic transformations of plutonium under applied stress. In either of

the two models, the anisotropic transformation strain during $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ transformations is large compared to the sum of normal creep and extra transformation creep deformation.

3. Martensitic $\beta \rightarrow \alpha$ Transformation

Although the results of this investigation are not sufficient criteria for determining unequivocally whether the $\beta \rightarrow \alpha$ transformation is martensitic or diffusional, they do indicate that the transformation behaves in a manner consistent with known martensitic transformations. This conclusion is based on the following observations:

- (1) Both uniaxial tensile stresses and uniaxial compressive stresses raised the temperature for the beginning of the $\beta \rightarrow \alpha$ transformation at a fixed cooling rate.
- (2) Stresses applied during either the $\alpha \rightarrow \beta$ or the $\beta \rightarrow \alpha$ transformations produced pronounced crystallographic texturing and microstructural shape texturing.
- (3) There was an apparent crystallographic relationship between the alpha and the beta phases.

The alpha grains of plutonium are aligned during transformation under applied stress. Similarly, a marked alignment of bainite and martensite needles⁽⁹⁸⁾ has also been observed in the transformation of austenite under applied tensile stresses. The alpha grains of plutonium formed by transformation from beta under stress are also in the form of needles or rods. The grains transformed under compressive stresses are longer and thinner than those formed by transformation under no stress; the higher the stress the thinner are the alpha grains. More significantly, the elongated grains were aligned in disks which were random in the absence of applied stresses, perpendicular to applied compressive stresses, and parallel to applied tensile stresses.

Both applied uniaxial tensile and compressive stresses raised the temperature for the beginning of the $\beta \rightarrow \alpha$ transformation for

a given cooling rate. That is, all applied stresses favor the alpha nucleation process. This is completely in keeping with the hypothesis that the $\beta \rightarrow \alpha$ transformation is a martensitic transformation. Similar effects have been observed in the austenite-martensite transformation in steel⁽¹⁰¹⁾ and in martensitic transformations in gold-cadmium⁽⁶²⁾ and indium-thallium alloys.⁽⁶³⁾ The shear and normal components of a compressive stress favor the plutonium $\beta \rightarrow \alpha$ transformation; the shear component of tensile stresses also favors the $\beta \rightarrow \alpha$ transformation in plutonium; but the normal component of tensile stresses opposes the $\beta \rightarrow \alpha$ transformation. There are no shear components in hydrostatic compression:

Kaufman and Cohen⁽⁵²⁾ and Patel and Cohen⁽¹⁰¹⁾ explain this effect in steel on the basis that the resolved shear stress aids the austenite-martensite transformation, which is a shear plus expansion, to a greater extent than the normal compressive component opposes the transformation. Accordingly, the shear stress in the $\beta \rightarrow \alpha$ transformation in plutonium can be considered to aid the transformation more than the normal tensile stress opposes it; the metal contracts during transformation. For this explanation to be valid the shear strains would have to be larger than dilational strains. These strains are not known for the plutonium $\beta \rightarrow \alpha$ transformation but evidently the shear strain is much larger than the dilational strain.

Mechanical work done on the matrix undergoing transformation adds to the chemical free energy driving force but mechanical work done by the transforming region subtracts from the chemical driving force. Kaufman and Cohen⁽³⁰⁾ derived an expression relating this mechanical energy to the free energy change for martensite transformation:

$$\Delta G = \frac{1}{2} V_m S [\gamma_0 \sin 2\beta \pm \epsilon_0 (1 + \cos 2\beta)] \quad \text{VI-2}$$

where V_m is the molar volume, S is the applied stress, β is the angle between the stress axis and the normal to the habit plane,

γ_0 is the transformation shear strain, and ϵ_0 is the dilational transformation strain. The plus sign is used for uniaxial tension and the minus sign is used for uniaxial compression.

An applied compressive stress should raise the temperature for the beginning of the transformation more than an applied tensile stress equal in magnitude. Since this is not observed experimentally it can be concluded that the normal components are negligible compared to the shear stresses.

4. Formation of Disks of Alpha

The formation of large disk shaped volumes of alpha during the $\beta \rightarrow \alpha$ transformation is a most unusual microstructural feature. These disks with their columnar alpha grains are reminiscent of the internally twinned martensite plates that form in iron alloys, however, they differ in that they are much larger and that their component alpha grains appear to be columnar crystals and not simply twins.

A disk shaped transformed region gives the lowest strain energy for a given volume change.⁽¹⁰⁶⁾ For a particle having a high surface to volume ratio the strain energy term is a minimum and the surface energy term is a maximum, whereas a spherical particle has a maximum strain energy and a minimum surface energy. Thus for a large volume change the strain energy attendant to the volume change favors the formation of a disk.

In order for a thin disk shaped transformed region to grow in thickness while maintaining continuity with the parent phase across the approximately planar interfaces, the volume change must be accommodated almost entirely by expansion or contraction perpendicular to the plane of the disk. Thus, for a disk $\Delta L/L_0 = \Delta V/V_0$ in the direction perpendicular to the flat interface and $\Delta L/L_0 = 0$ in the plane of the interface. The anisotropic shape change of the individual disks determine the limits on the macroscopic transformation obtained in specimens textured by transformation under applied

stress. This is quite in keeping with the data for the $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ transformations.

The growth of individual crystals in disk shapes is common during transformations. The alpha plutonium disks are remarkable because they are polycrystalline. This calls for some speculation upon the process of their propagation. If the mode of transformation is martensitic, as the evidence indicates, the first grain or nucleus of alpha to form from the surrounding beta parent phase would undergo an anisotropic shape change. This would result in an anisotropic stress field in the beta matrix near the alpha nucleus. Subsequent nucleation would be favored by the stress in some regions of the stress field and inhibited in others. Also the orientation of subsequent nuclei would be influenced by the stress field of the first nucleus; those nuclei whose shape change was in the direction to relieve the stress would be favored. The disk shape of the transformed region suggests that the stress field surrounding the first nucleus may have cylindrical symmetry, secondary nucleation being favored in a plane. Thus the edgewise growth of the transformed region would be a continuing process of sympathetic nucleation resulting in a polycrystalline disk of increasing diameter. The growth of the individual alpha grains in the disk would be limited by impingement with their neighbors to growth in the direction perpendicular to the plane of the disk.

The observed texturing influence of applied stresses is consistent with this suggested explanation for the formation of the disks. Applied stresses would certainly favor the nucleation and growth of disks oriented so that their transformation strain would be in the direction of the applied stress.

CHAPTER VII

SUMMARY AND CONCLUSIONS

This dissertation provides information on the low temperature allotropic transformations in plutonium. The data are primarily about the transformation kinetics and transformation damage of the low temperature allotropes, about the steady-state creep of the six allotropes, and about the behavior of the low temperature transformations under applied stress. The results of these experiments indicated that the $\beta \rightarrow \alpha$ transformation is a martensitic transformation. The significant results were:

- (1) The $\beta \rightarrow \alpha$ TTT curve was a simple C curve with the maximum transformation rate at -20°C to -40°C , where the incubation time of electrorefined plutonium was about 3 seconds.
- (2) The beta phase transformed to the alpha phase according to the Avrami relationship,

$$f = 1 - \exp(-At^n), \quad (\text{VII-1})$$

during the earlier portion of the transformation. The time exponent, n , had a value of 4, which is consistent with an isothermal martensitic transformation.

- (3) The $\alpha \rightarrow \beta$ transformation kinetics proceeded according to the Avrami relationship, in which the time exponent also had a value of 4.
- (4) The $\beta \rightarrow \gamma$ transformation kinetics were similar to the $\alpha \rightarrow \beta$ transformation kinetics.
- (5) Transformation kinetic data of the gamma phase showed that the $\gamma \rightarrow \beta \rightarrow \alpha$ transformations can be depicted by a double C curve consisting of a $\gamma \rightarrow \beta$ transformation curve, a $\gamma \rightarrow \alpha$ transformation curve, and a complex temperature region where the gamma, beta, and alpha phases can temporarily exist simultaneously.

- (6) A variation in the heat-treating temperature and a variation in the rate of formation of the alpha phase markedly influenced the final grain size; the higher the temperature of the heat-treating phase the finer and more uniform was the final grain size, e.g. alpha formed upon quenching the gamma phase was finer than that formed upon quenching the beta phase.
- (7) Microstructural studies revealed that during slow $\beta \rightarrow \alpha$ transformations the alpha grains initially formed in disks that were randomly oriented in the absence of applied stress. The grain size increased very slightly with time from the start of the transformation.
- (8) The disks of alpha grains were aligned perpendicular to the direction of applied compressive stresses and parallel to the direction of applied tensile stresses.
- (9) The disks of columnar alpha grains were postulated to be analogous to internally twinned martensite plates that form in iron alloys, however, they differ in that they are much larger and that their component alpha grains appear to be columnar crystals and not simply twins.
- (10) The completion of the $\beta \rightarrow \alpha$ transformation was very sluggish in impure plutonium. Up to 4% retained beta (or possibly delta) was observed in high purity plutonium after subzero $\beta \rightarrow \alpha$ transformations.
- (11) Beta plastic deformation by either compression or tension decreased the subsequent $\beta \rightarrow \alpha$ transformation rate. Retardation of a transformation by plastic deformation is characteristic of a martensitic transformation.
- (12) The $\alpha \rightarrow \beta$, $\beta \rightarrow \gamma$, and $\gamma \rightarrow \beta$ transformations were accelerated by plastic deformation of the parent phase. Both martensitic and diffusional transformations can be accelerated by plastic deformation of the parent phase.

- (13) The microcracks observed in high purity as-cast plutonium form during the $\beta \rightarrow \alpha$ transformation. The transformation damage studies showed that the volume of microcracks increased with increasing transformation temperature, higher purity, increased specimen size, and $\alpha \rightleftharpoons \beta$ transformation cycling. The explanation offered by Buckley, et al,⁽⁷⁸⁾ and Stobo⁽⁷⁹⁾ for transformation cycling damage in uranium appears to be applicable to the $\beta \rightarrow \alpha$ transformation damage in plutonium. The correlation of de Jong and Rathenau⁽⁸²⁾ does not appear to apply.
- (14) Transformation damage occurred after the transformation was 50% to 60% complete.
- (15) Transformation cycling produced growth in all directions, general distortion, and extensive surface rumpling.
- (16) Plutonium containing essentially no microcracks was produced by quenching from the beta phase to -75°C during casting.
- (17) No physical damage was observed in metal that initially contained no microcracks after either $\delta \rightleftharpoons \gamma$, $\delta \rightleftharpoons \beta$, or $\gamma \rightleftharpoons \beta$ transformation cycling.
- (18) The compression creep curves of the six allotropes of plutonium were typical in that they consisted initially of primary creep followed by secondary or steady-state creep. The steady-state creep data could readily be analyzed according to the empirical expression

$$\dot{\epsilon} = D_0 e^{-Q_{sd}/RT} \left(\frac{\sigma}{E}\right)^n \quad (\text{VII-2})$$

- a) The value of n was approximately 6 for the delta phase and 5 for the beta and gamma phases.
- b) The average values for the creep activation energy, Q_c , calculated from the Arrhenius equation were 26, 30, 35, 31, 28, and 25 kcal/g-atom respectively for the α , β , γ , δ , δ' , and ϵ phases.

- c) Self-diffusion activation energies were calculated for the alpha, beta, gamma, and delta phases. The respective values were 23, 27, 31, and 30 kcal/g-atom.
 - d) At a common temperature the creep rate of the phase normally stable at higher temperatures was greater than the creep rate of the phase normally stable at the lower temperatures with but one exception -- the creep rate of gamma was less than the creep rate of the beta phase near the $\beta \rightleftharpoons \gamma$ equilibrium transformation temperature.
 - e) The creep rate of beta that was formed from gamma was less than the creep rate of the gamma phase under the same temperature and stress conditions.
- (19) Both applied uniaxial tensile stresses and compressive stresses raised the temperature for the beginning of the $\beta \rightarrow \alpha$ transformation at a constant cooling rate for stresses up to 7000 psi.
 - (20) Applied stresses during $\beta \rightarrow \alpha$ transformation produced a microstructural shape texture. The alpha grains were elongated in a direction perpendicular to applied tensile stresses and they were parallel to the applied compressive stresses. The elongated grains were aligned in disks which were perpendicular to compressive stresses and parallel to the direction of the applied tensile stresses.
 - (21) Applied stresses during the $\beta \rightarrow \alpha$ transformation produced a crystallographic texture. The alpha (010) planes were aligned parallel to the applied tensile stresses and perpendicular to the applied compressive stress.
 - (22) A 90° rotation of the crystallographic and metallographic texture was observed after an $\alpha \rightarrow \beta \rightarrow \alpha$ cycle. This implies that there is a specific crystallographic orientation relationship between the parent and the product phases of the $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ transformations. From the 90° rotation of the

texture it can be concluded that there is more than one crystallographic variant of the orientation relationship in spite of the low symmetry of the alpha and beta phases. These are characteristics to be expected of martensitic transformations.

- (23) The anisotropic strain accompanying transformation under uniaxial stress indicated that texture also occurred during $\alpha \rightarrow \beta$, $\beta \rightarrow \gamma$, and $\gamma \rightarrow \beta$ transformations under applied uniaxial stresses.
- (24) Some phase transformation excess creep occurred during the transformations in specimens subjected to an external stress.
- (25) More excess creep occurred under tension than it did under compression. Little or no excess creep occurred during the $\beta \rightarrow \alpha$ transformation with compression but some $\beta \rightarrow \alpha$ excess creep was observed with tension.
- (26) The effect of applied compressive stress above 9000 psi was to cause essentially all of the $\beta \rightarrow \alpha$ transformation strain to occur as contraction parallel to the applied stress, i.e. $\Delta L/L_0 = \Delta V/V_0$. The total strain during $\beta \rightarrow \alpha$ transformation under compression was almost completely independent of the transformation rate.
- (27) The effect of applied tensile stresses above about 4000 psi on the $\beta \rightarrow \alpha$ transformation was to cause all of the transformation strain to occur as contraction perpendicular to the applied stress, i.e. $\Delta L/L_0 = 0$.
- (28) In textured plutonium the $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ transformations resulted in anisotropic transformation strain in the absence of applied stress.

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