T-1642

A STUDY OF HOMOGENIZATION RATES IN PLUTONIUM-1 WT% GALLIUM ALLOY AS A FUNCTION OF PERCENT REDUCTION BY COLD ROLLING

BY

Richard Jack Erfurdt

March 6, 1974

A Thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science.

Signed: Richard J Erfurdt
Student

Golden, Colorado
Date: April 23, 1974

Approved: Walter L Bradley
Thesis Advisor

Head of Department

Golden, Colorado
Date: April 23, 1974

ABSTRACT

Isostatic pressing for 30 minutes at 85,000 psi was used to determine the effect of cold rolling on the homogenization rates of Pu-1 wt% Ga alloy. A curve of density versus gallium composition was determined for 10 homogenized and isostatically pressed Pu-Ga alloys between 0.1- and 1.0 wt% gallium. It was determined that delta phase Pu-Ga alloys below 0.7 wt% gallium are partially transformed to alpha phase when isostatically pressed at room temperature to 85,000 psi. Samples from a Pu-1 wt% Ga alloy ingot, rolled to 0-, 10-, 30-, 50-, 70-, and 90% reduction, were homogenized for various lengths of time at 450°C. Curves of isostatically pressed density versus homogenization time were generated for each percent reduction. Four levels of homogeneity, 25-, 50-, 75-, and 90% were evaluated. Each level of homogeneity was represented by an isostatically pressed density. Homogenization time as a function of percent reduction was generated for each degree of homogeneity. Initially, when the ingot was rolled to 10% reduction, the time required for partial homogenization (25%) was decreased more than 40%. For larger percent reductions the (25%) homogenization versus percent reduction curve approaches a one to one linear relationship. For example, a 70% rolling reduction reduced the homogenization time by 70%. This was explained by nonuniform deformation across a cored grain during rolling at the lower percent reductions. Strain hardening of the locally deformed areas equalized the mechanical properties across the grain such that more uniform deformation occurred across the grain when the ingot was rolled to larger percent reductions. Rolling seemed to effect the homogenization time less for more complete (90%) homogenization. This was attributed to the resistance of localized high strength, low gallium, areas such as triple points and/or grain boundaries, to deformation. The occurrence of localized areas of alpha phase material in a 90% rolled structure was verified metallographically.

TABLE OF CONTENTS

TABLE OF CONTENTS (continued)

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES (cont.)

LIST OF FIGURES (cont.)

ACKNOWLEDGMENTS

The author gratefully acknowledges the people whose efforts made this report possible. In particular the author would like to thank Dr. W. L. Bradley for the counseling and encouragement as thesis advisor; Mrs. P. Norton for the speed with which she typed and compiled the report; and Mr. R. L. Pratt and Mr. M. W. Maulfair for their outstanding experimental support.

INTRODUCTION

Unalloyed plutonium solidifies at 640°C. Upon cooling to room temperature, it undergoes six allotropic phase transformations. An idealized temperature-expansion curve[1] and some crystallographic data[1] for unalloyed plutonium are shown in Figure 1 and Table 1, respectively. Certain concentrations of gallium stabilize plutonium in the delta phase. A plutonium gallium phase diagram[2] is shown in Figure 2. Note from the diagram that Pu-1 wt% Ga alloy, once solidified, will exist in two phases, epsilon and delta. The alloy also passes through two, two-phase regions, liquid plus epsilon and epsilon plus delta.

Microsegregation (coring) of gallium occurs as Pu-Ga alloys cool through the epsilon plus delta phase region[3-5]. A theoretical gallium profile for two as-cast grains in a Pu-1 wt% Ga alloy[5] is shown in Figure 3. As a result of coring, an as-cast grain consists of a stable delta phase center surrounded by metastable delta phase. The metastable delta phase will transform directly to alpha phase when thermally cycled or mechanically stressed (i.e., rolled, isostatically pressed, etc.).

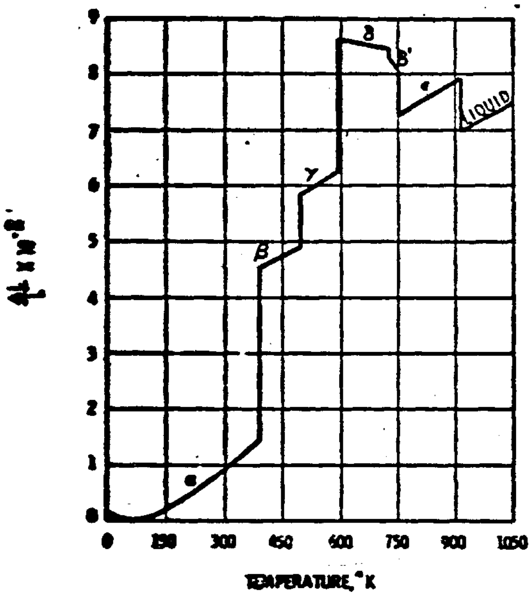


Figure 1

The idealized expansion behavior of plutonium.[1]

Phase	Stability Range, °C	Space Lattice and Space Group	Unit Cell Dimensions, A	Atoms per Unit Cell	X-ray Density, g/cm^3
α	Below ~ 115	Simple monoclinic $P2_1/m$	@ 21°C: a = 6.183 ± 0.001 b = 4.822 ± 0.001 c = 10.963 ± 0.001 β = 101.79° ± 0.01°	16	19.86
β	~115 - ~200	Body-centered monoclinic $I2/m$†	@190°C: a = 9.284 ± 0.003 b = 10.463 ± 0.004 c = 7.859 ± 0.003 β = 92.13° ± 0.03°	34	17.70
γ	~200 - 310	Face-centered orthohombic $Fddd$	@235°C: a = 3.159 ± 0.001 b = 5.768 ± 0.001 c = 10.162 ± 0.002	8	17.14
δ	310 - 452	Face-centered cubic $Fm3m$	@320°C: a = 4.6371 ± 0.0004	4	15.92
δ'	452 - 480	Body-centered tetragonal $I4/mmm$	@465°C: a = 3.34 ± 0.01 c = 4.44 ± 0.04	2	16.00
ε	480 - 640	Body-centered cubic $Im3m$	@490°C: a = 3.6361 ± 0.0004	2	16.51

Table 1

Crystal structure data for plutonium.[1]

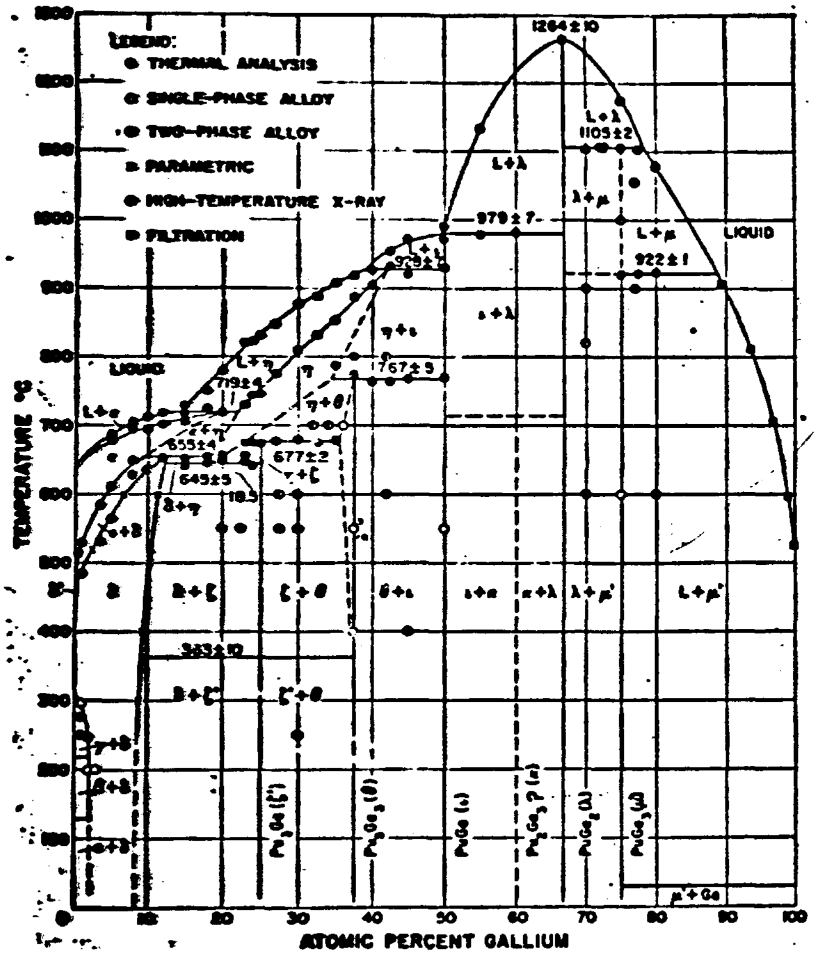


Figure 2

The plutonium-gallium equilibrium diagram.[2]

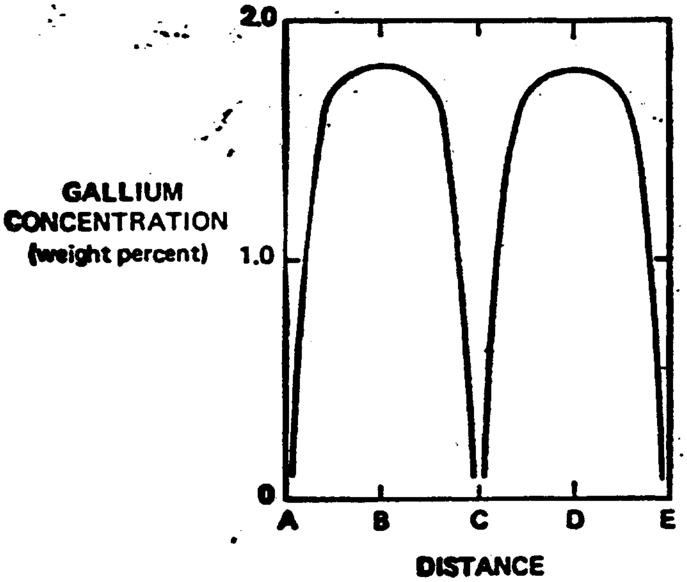


Figure 3

Theoretical gallium concentration profile of two delta phase grains. (Grain boundaries at points A, C, and E, and grain centers at points B and D.)[5]

Coring may be eliminated in as-cast plutonium gallium alloys by a high temperature delta-phase anneal (homogenization). Pu-1 wt% Ga alloy is commonly homogenized at 450°C. During homogenization, gallium diffuses toward an equilibrium concentration of 1 wt%. That is, gallium diffuses from the grain centers to the grain boundaries. The diffusion rate, or homogenization rate, is a function of the diffusion distance (as-cast grain size), and the homogenization temperature used.

Homogenization rates have been determined for as-cast Pu-1 wt% Ga alloy as a function of grain size. The process of rolling distorts the grain structure of metals such that the diffusion distance for homogenization should be a function of percent reduction. This project was initiated with the objective of determining the effect of percent reduction by rolling on the rate of homogenization of a cored Pu-1 wt% Ga alloy.

LITERATURE SURVEY

Gallium coring occurs during the cooling of Pu-Ga alloys from the liquidus to room temperature. Coring is described as a variation in gallium concentration within each grain, the central portion having a much higher gallium concentration than the grain boundary. For Pu-1 wt% Ga alloy the as-cast delta phase grains have gallium concentrations as high as 1.8 wt% at their centers and nearly depleted in gallium at their grain boundaries. It has been determined that coring observed across the individual delta phase grains results from the epsilon to delta phase transformation[3,4]. Coring from the transformation results from the diffusivity of Pu and Ga in the epsilon phase relative to the delta phase. The chemical diffusivity of Pu and Ga in the epsilon is $\sim 10^{-7}$ cm^2/sec[6]; whereas, the diffusivity of Pu and Ga in delta phase is only $\sim 5 \times 10^{-10}$ cm^2/sec[7].

By using the lever rule (for the epsilon plus delta phase region) and the partial equilibrium diagram shown in Figure 4, the theoretical gallium profile for two adjacent delta grains has been determined.[5] Gallium concentration profiles were determined with an electron microprobe. A comparison of theoretical and measured gallium concentration profiles is shown in Figure 5.

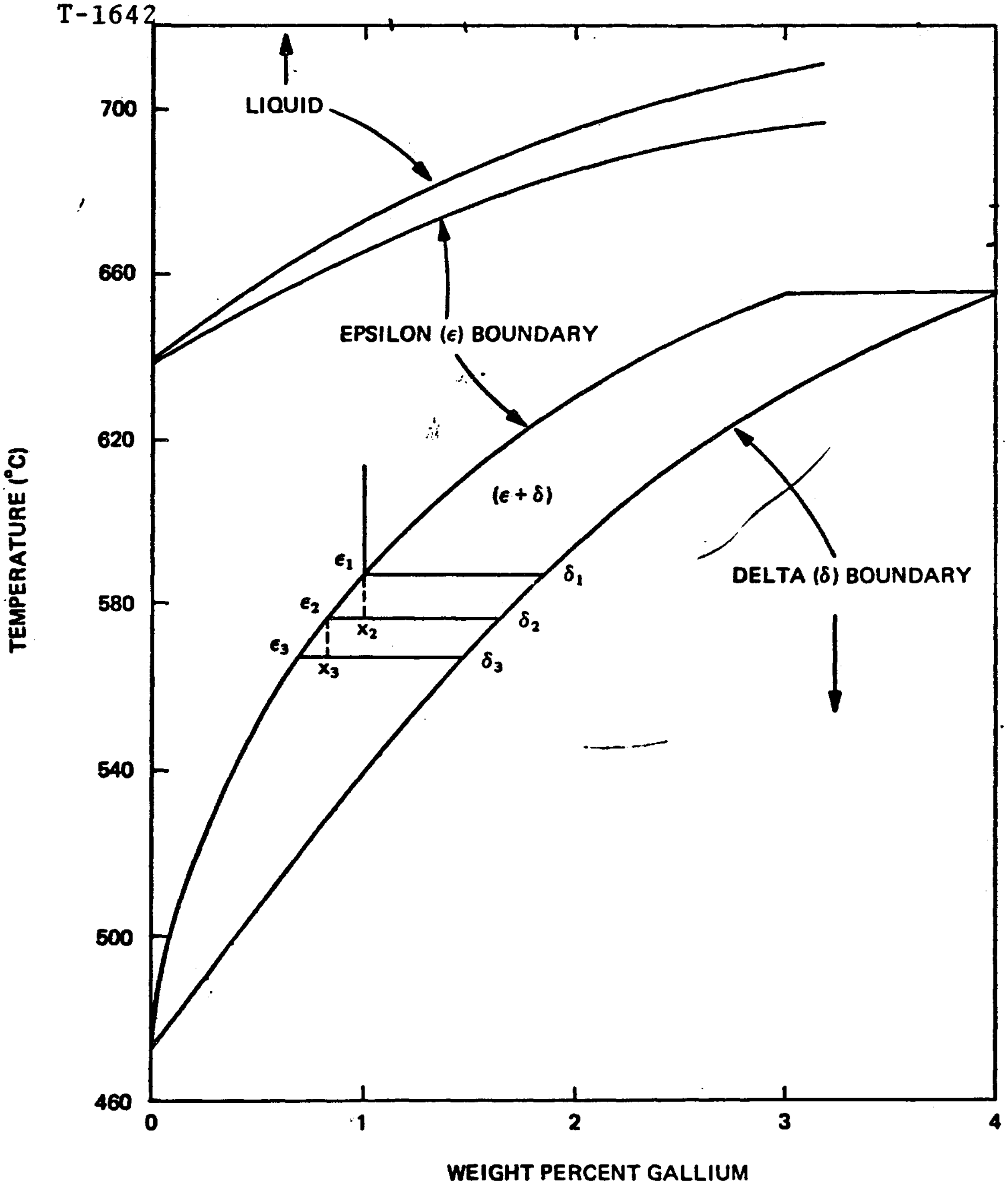
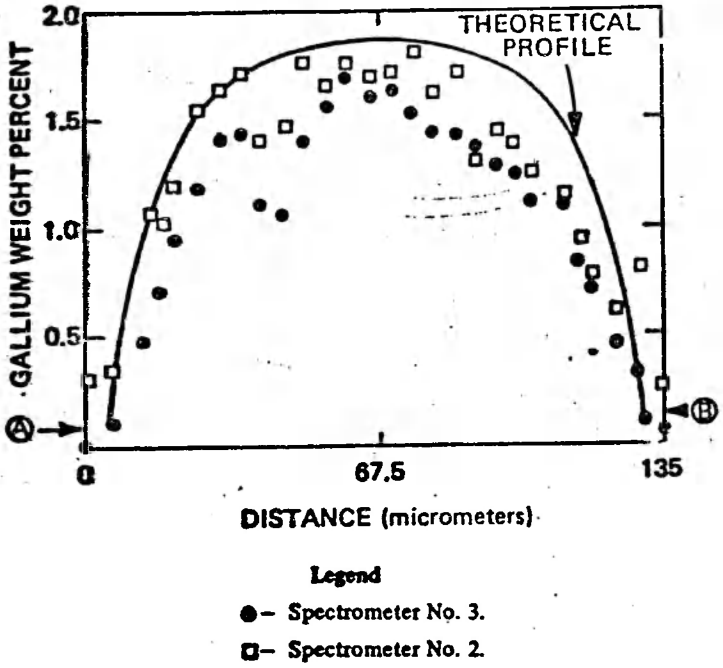


Figure 4

Partial plutonium-gallium phase diagram showing procedure for determining the gallium profile.

(a) Backscattered Electron Image of Sample Cooled 1 °C per Minute, Showing the Area of Analysis. Magnification 500X.



(b) Gallium Concentration Profiles Superimposed over Theoretical Curve.

Figure 5

Electron image of sample and corresponding gallium profile.[5]

The low gallium delta phase area, near the grain boundaries, is metastable and can transform to alpha phase during cold rolling[4], metallographic polishing[8], uniaxial compression[9], isostatic pressing[4], cold storage[10], and thermal cycling[11]. Delta phase homogenization treatments are required to eliminate the metastable areas. Homogenization occurs by diffusion of gallium to the mean concentration.

The electron microprobe was used to study the homogenization behavior of cast Pu-1 wt% Ga alloy[3]. The technique used was to determine the high and low gallium concentrations within a sample after various amounts of homogenization at a given temperature. A plot of high and low gallium concentration versus homogenization time at 500°C for a "relatively pure" Pu-1 wt% Ga alloy sample is shown in Figure 6. The cored grain size of the alloy was approximately 0.010 mm. The homogenization time for the sample was estimated to be 60 hours.

For comparison, the electron microprobe was used to study the homogenization behavior of a relatively impure sample of Pu-1 wt% Ga alloy rolled to 37.5% reduction[3]. A plot of high and low gallium concentration versus homogenization time at 500°C for that sample is shown in Figure 7. The as-cast grain size of the sample was not given. It is assumed that both the pure and impure samples

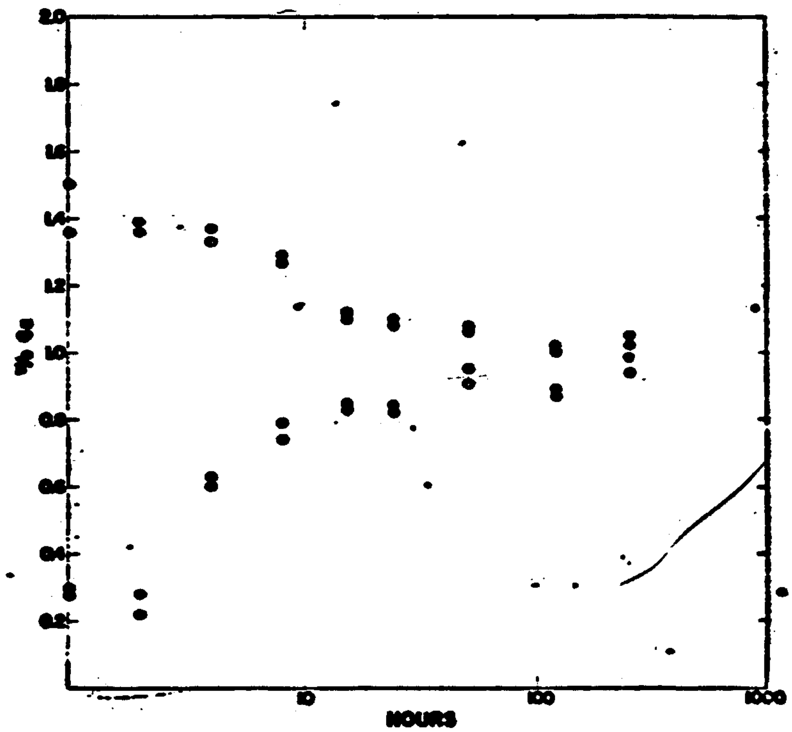


Figure 6

High and low gallium concentration levels found in the relatively pure cast alloy that had been annealed at 500°C.[3]

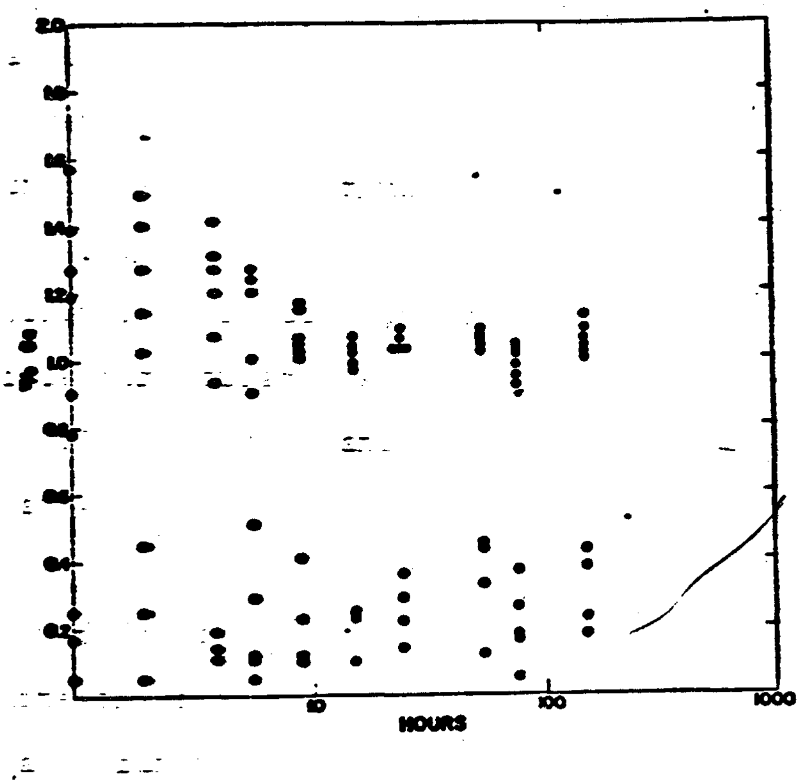


Figure 7

High and low gallium concentration levels found in specimens of the relatively impure rolled alloy that had been annealed at 500°C.[3]

were of the same as-cast grain size. The rolled alloy was estimated to be homogenized in 14 hours. However, some areas of low gallium concentration remained throughout homogenization. The areas of low gallium were attributed to a low solubility of gallium in a liquid eutectic phase. This would seem plausible particularly since the rolled sheet was relatively impure (270 ppm iron) and it is known that the Pu_6Fe eutectic melts at 410°C.

A X-ray diffraction, line broadening technique was used to determine the rate of homogenization at 450°C of Pu-1 wt% Ga alloy as a function of grain size.[4] A plot of as-cast grain size versus anneal time at 450°C required for homogenization is shown in Figure 8. In addition, the effect of annealing time for the same alloy at 450°C on the rate of homogenization as indicated by X-ray line broadening and density after a 150,000 psi compression is shown in Figure 9[4]. Even though the two methods compare fairly well, it is apparent that the compression technique gives a larger estimate of the homogenization time than does the X-ray technique. That is, extrapolation of the compression data indicates that approximately 53 hours would be required for homogenization; whereas, the X-ray data indicate 40 hours. However, the effect of gallium composition and 150,000 psi uniaxial compression on the density of fully homogenized Pu-Ga alloys is shown in Figure 10. It may be noted from

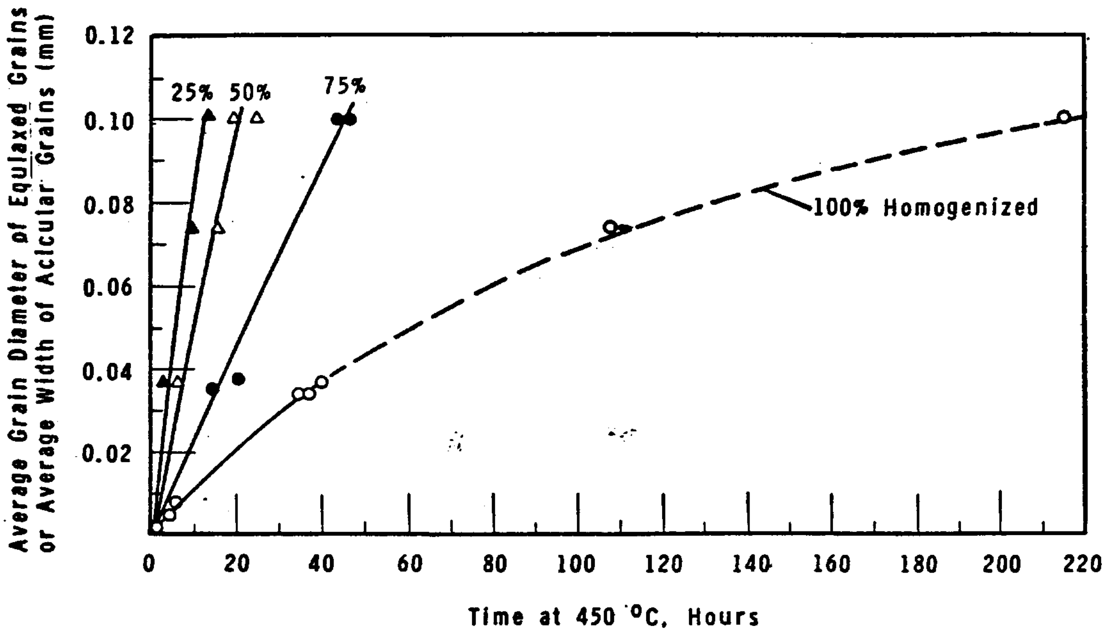


Figure 8

Relation between grain size and anneal time required for homogenization in a cored Pu-1 wt% Ga delta stabilized alloy.

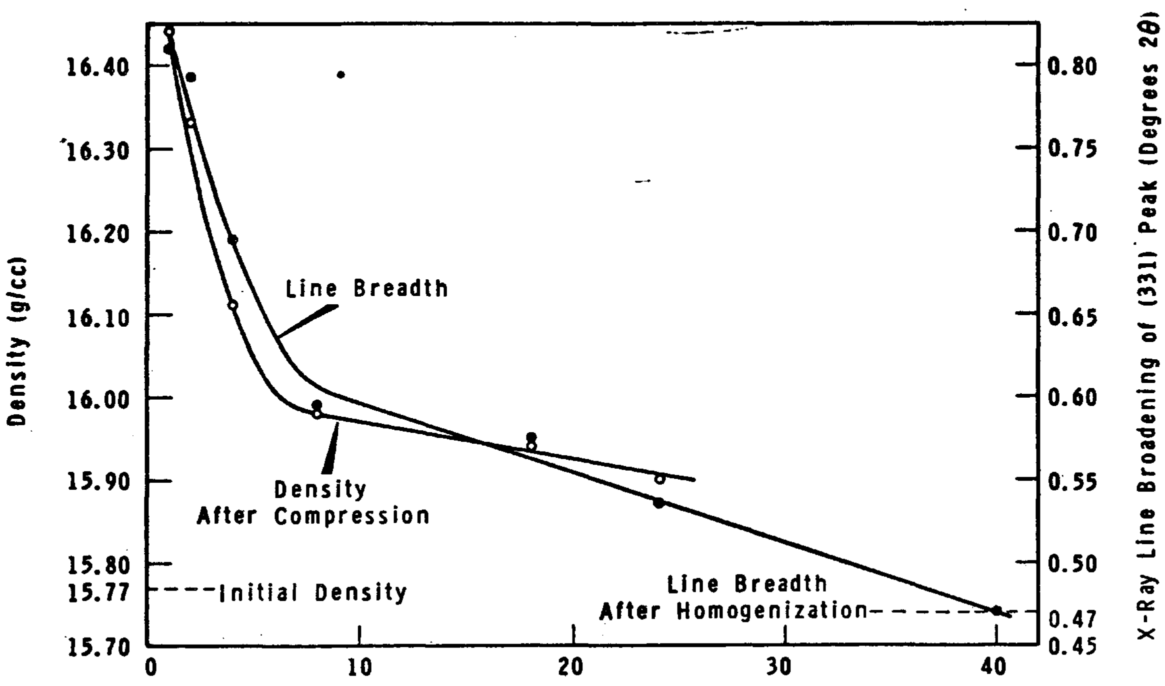


Figure 9

The effect of anneal time at 450°C on rate of homogenization as indicated by X-ray line broadening and density after a 150,000 psi compression in Pu-1 wt% Ga alloy.

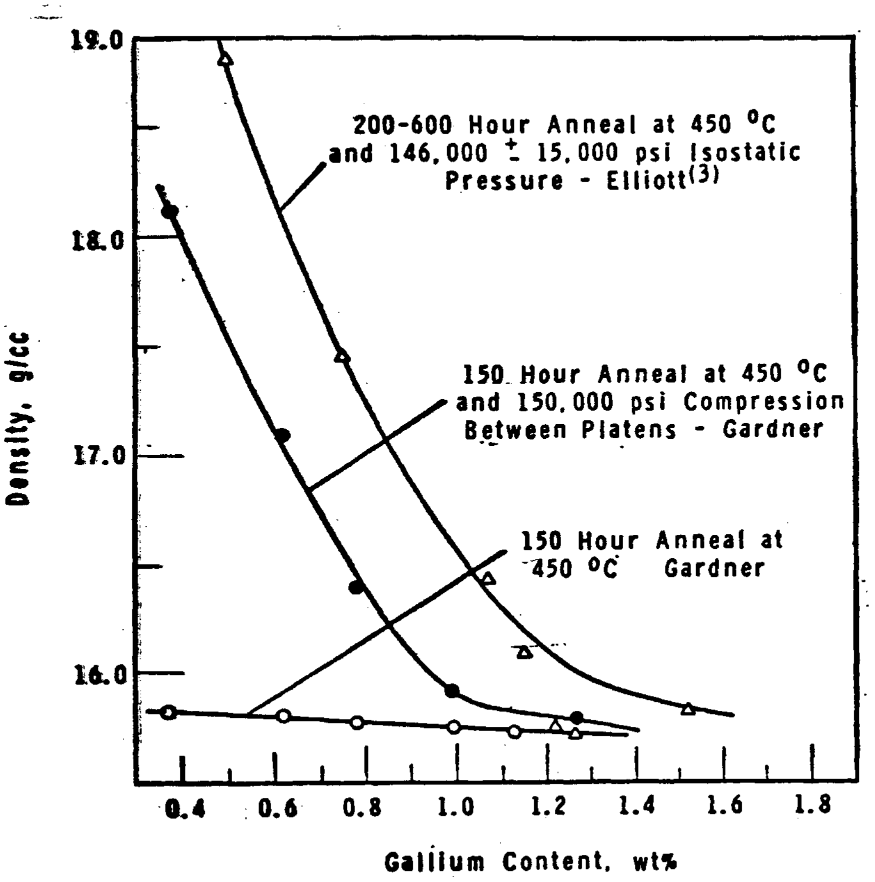


Figure 10

Effect of composition and 150,000 psi pressure on density in Pu-Ga alloys.[4]

the data that 150,000 psi will cause some density change in fully homogenized Pu-1 wt% Ga alloy. The effect of isostatic pressure and uniaxial compression on the density of a Pu-1 wt% Ga alloy that had been annealed for one hour at 425°C is shown in Figure 11. From the data it is evident that the isostatic pressure-density curve extrapolates well to 150,000 psi uniaxial compression.

Based on the data presented, it may be seen that a plot showing the rate of homogenization of a sample is somewhat dependent on the criteria used to define homogeneity. The relationship between grain size and anneal time required for various degrees of homogenization, as determined by X-ray line broadening is shown in Figure 8. If 150,000 psi had been used as the criteria for determining homogeneity, it is expected that the curves would have been shifted to the right because it would have taken longer to homogenize a sample adequately so that no alpha phase would form during compression.

It is known[12,14] that the distance over which diffusion occurs is described by the following equation: $X = K\sqrt{Dt}$

X - is distance over which significant transport by diffusion has occurred

K - is a constant, dependent on the initial concentration distribution geometry

D - is diffusivity which is a function of temperature. Diffusivity may be assumed constant at a given temperature.

t - is elapsed time during which diffusion occurred.

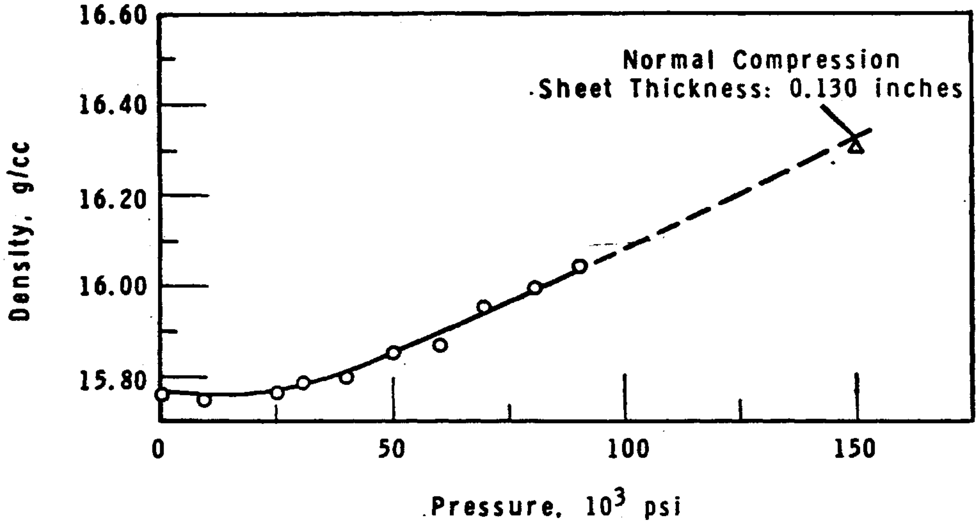


Figure 11

Effect of isostatic pressure and compression on density of a cored Pu-1 wt% Ga alloy heat treated for 1 hour at 425 °C. Original cored grain diameter: 0.037 mm.

It may be noted that the time necessary for homogenization will vary directly with the square of the diffusion distance, i.e., grain size. If rolling produces uniform deformation, then a reduction in thickness of the cored grain should occur, and the homogenization time should be decreased accordingly. This thesis project was initiated with the intent of better defining the relationship between percent reduction by rolling and the homogenization rate of Pu-1 wt% Ga alloy.

EXPERIMENTAL PROGRAM AND PROCEDURES

This chapter is divided into two categories: the Experimental Program which is devoted to describing the overall plan of collecting experimental data; and the Experimental Procedures which is devoted to describing the experimental equipment and procedures that were used in expediting the Experimental Program.

I. Experimental Program

Isostatic pressing at 85,000 psi was used as the means of determining the phase stability, and hence, the degree of homogenization possessed by Pu-1 wt% Ga alloy. It was noted earlier that coring produces relatively large gallium variations across as-cast grains of Pu-Ga alloys. As a result, it was of interest to determine a calibration curve that describes the relationship of density after 85,000 psi isostatic pressure, as a function of percent gallium. In order to determine whether the delta to alpha phase transformation by isostatic pressure was significantly affected by hold time at pressure, the samples were isostatically pressed a second time at the same parameters with a subsequent density determination.

It was intended that all homogenization rate data be generated at 450°C. First, it was planned to determine the isostatically pressed density of cast Pu-1 wt% Ga alloy as a function of homogenization time. Then for comparison, it was intended that similar data be generated for the alloy after it had been rolled to several percent reductions. A flow diagram depicting the overall experimental program is shown in Figure 12.

The unalloyed plutonium to be used for this project was vacuum induction melted and cast into an unheated CaF_2 coated graphite mold. The resultant ingot was sampled for chemical analysis. The master ingot was used as feed for 10 castings. The 10 castings were alloyed to 0.1-, 0.2-, 0.3-, 0.4-, 0.5-, 0.6-, 0.7-, 0.8-, 0.9-, and 1.0 wt% gallium. The melt for each casting was poured into an unheated CaF_2 coated graphite mold. Each ingot was sampled for chemical analysis. It is estimated that the cooling rate of the alloys through the epsilon-plus-delta phase region exceeded 100°C/minute, and therefore produced a cored grain diameter of less than 0.020 mm. As noted in Figure 8, 20 hours at 450°C should fully homogenize 0.020 mm diameter cored grains. However, in order to assure complete homogenization, the samples from the 10 alloys were homogenized for 135 hours at 450°C. The metallographic structure of the 0.4-, 0.7-, and 1.0 wt% gallium samples was determined.

A 4- by 4- by 1.125 in. ingot of Pu-1 wt% Ga alloy was cast from the remnants of the 10 ingots. The melt was cast into a CaF_2 coated mold that had been preheated for

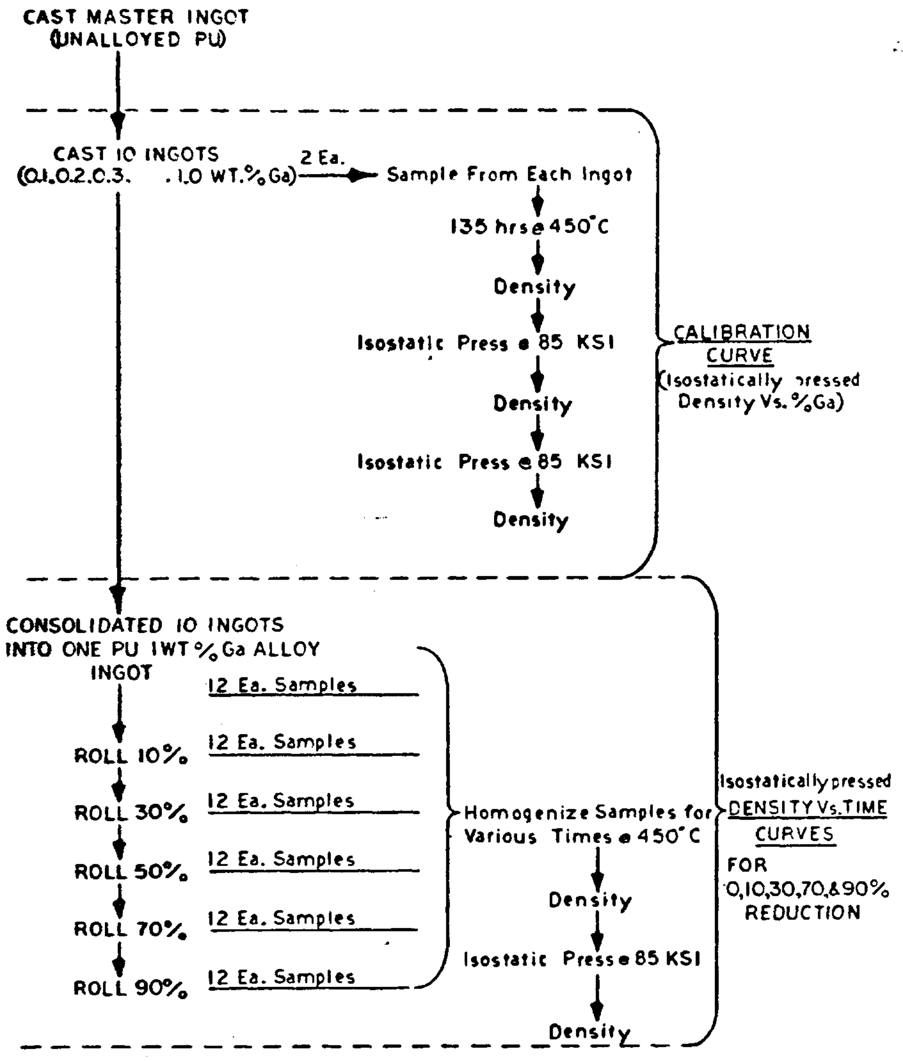


Figure 12

A flow diagram depicting the overall experimental program used for this project.

20 minutes at 680°C. The ingot and mold were cooled to through the epsilon-plus-delta phase region at approximately 6°C/min. The metallographic structure of the as-cast ingot was determined from three perpendicular directions. This was an attempt to determine whether the structure was randomly oriented and to characterize the size and shape of the cored grains. The ingot was sampled for chemical analysis. In addition, the 12 density samples were sawed from the ingot.

The remainder of the 4 by 4 by 1.125-in. ingot was rolled at 0.025-in. per pass to 5% reduction, rotated 90°, and cross rolled another 5% for a total of 10% reduction. A second set of 12 samples was cut from the ingot. The ingot was rolled, cross rolled, and sampled at 30-, 50-, 70-, and 90% reduction.

The metallographic structure of six samples was determined for comparison. The structure of a sample as-rolled 10% was compared to one rolled 10% and homogenized 10 hours at 450°C. A sample rolled 50% was compared to one rolled 50% and homogenized for three hours at 450°C. A 90% as-rolled sample was compared to one rolled 90% and homogenized 48 minutes at 450°C.

II. Experimental Procedures

This section describes the methods used for casting, homogenization, metallography, density, rolling and isostatic pressing.

Casting

Castings were made by vacuum induction melting in an oxidized tantalum crucible and bottom pouring into a CaF_2 coated graphite mold. During casting the furnace chamber was evacuated below 0.050 mm Hg. Generally, the charge was heated to 980°C and held at that temperature for 20 minutes prior to casting. After casting, the furnace was backfilled to 500 mm Hg with argon.

Homogenization

Homogenization was performed in a vacuum resistance heated furnace. The furnace was evacuated below 0.010 mm Hg prior to heat treating. Samples were heated at approximately 15°C/min. to 450°C and held for a specified length of time. At the end of the homogenization the furnace power was shut off and the furnace was backfilled to a pressure of 250 mm Hg with argon. The samples were cooled from 450°C to 300°C at approximately 12°C/min.

Metallography

The following metallography procedures were used:

1. The metal specimen was mounted in a 1-in. diameter by 1-in. high cylinder of room-temperature-setting epoxy.

2. Mounted samples were ground on 240- to 600-grit silicon carbide paper using carbon tetrachloride as a lubricant.
3. The samples were hand polished with 5- and 6-micron diamond paste on nylon cloth using lapping oil as a lubricant.
4. The samples were hand polished with 1-micron diamond paste on a medium nap cloth using lapping oil as a lubricant.
5. The samples were polished for 3 hours on an automatic vibratory polisher with 1/4-micron diamond paste and a lubricant of mineral spirits.
6. The samples were electropolished for 2 minutes at 12 volts (D.C.) in a solution which consists of 8 parts orthophosphoric acid, 5 parts ethyl alcohol, and 5 parts ethylene glycol.
7. The samples were etched for 1 minute at 12 volts (D.C.) in a solution that consisted of 116-grams citric acid, 400-ml ethyl alcohol, and 20-ml KNO_3 and 100-ml H_2O.
8. The mounted samples were viewed in a variable power optical metallograph.

Elongated grains were produced when the alloy was cooled down through the delta-plus-epsilon phase region. The cored structure was best observed when the metallographic sample was etched. The coring was depicted as light-grain-center regions of high gallium concentration surrounded by dark-grain-boundary regions of low gallium.

Density

Densities were obtained by the hydrostatic weighing method. Coupons were suspended in a wire holder in a bath of monobromobenzene. Weights were determined using a Mettler Gram-Atic balance with densities estimated reproducible to within ±0.002 g/cm^3 (one standard deviation).

Rolling

Rolling was accomplished on a two-high mill with 5-in. diameter work rolls. The ingot was rolled at 0.025-in. per pass.

Isostatic Pressing

The isostatic press used for this study has an 8-in. diameter by 6-in. long chamber. Herculube-C oil was used as the pressure transmitting medium. An isolation chamber minimizes possible leaking of radioactive contamination. Pressure is transmitted to the interior via a rubber diaphragm.

RESULTS AND ANALYSES

The nominal chemical impurities of the master ingot are shown in Table 2. Chemical analysis of each ingot verified that there were no significant impurities introduced during subsequent casting. The calibration curve of density after 85,000 psi isostatic pressure as a function of weight percent gallium is shown in Figure 13. It may be noted from the second isostatic pressing that hold time at pressure does not significantly effect the resultant density. The data indicate that plutonium with less than 0.7 wt% gallium undergoes some delta→alpha transformation when isostatically pressed at 85,000 psi. With the information presented in the calibration curve, the geometric shape of a cored grain, and the gallium profile across that grain, a theoretical density of the cored alloy may be calculated.

The metallographic structure of three Pu-Ga alloys after isostatic pressing was compared. The structure of a 0.4 wt% Ga alloy is shown in Figure 14. Note from the calibration curve that the sample density was approximately 18.3 g/cm^3 after the second isostatic pressing. Based on theoretical alpha and delta phase densities of 19.7- and 15.7 g/cm^3, respectively, a density of 18.3 g/cm^3 corresponds to approximately 70% alpha and 30% delta phase. For comparison, the structure of 0.7- and 1.0 wt% gallium

Element	
Pu Assay	99.92
Fe	76
U	23
Ga	73
C	12
Am	21
Ni	43

Spec Plate	
Al	26
B	<1
Ba	<1
Be	<.05
Bi	<3
Ca	<3
Cd	<3
Cr	12
Cu	2
Fe	76
In	<3
K	<15
Mg	<3
Mn	4
Mo	<3
Nb	<10
Ni	41
P	<100
Pb	<3
Pd	<3
Sb	<3
Si	20
Sn	10
Sr	<3
Ta	<20
W	<20
Zr	<15

Table 2

Listed above are the nominal impurities in the master ingot used for this study. Assay is determined by volumetric titration. Iron and nickel concentrations are determined by an atomic absorption technique. Carbon is determined by the combustion method. Uranium is obtained by the fluorometric method. Gallium is determined by a spectrophotometric method. Americium is determined by gamma counting. The spec plate results are determined by emission spectroscopy. All values are reported in ppm by weight except assay which is weight percent.

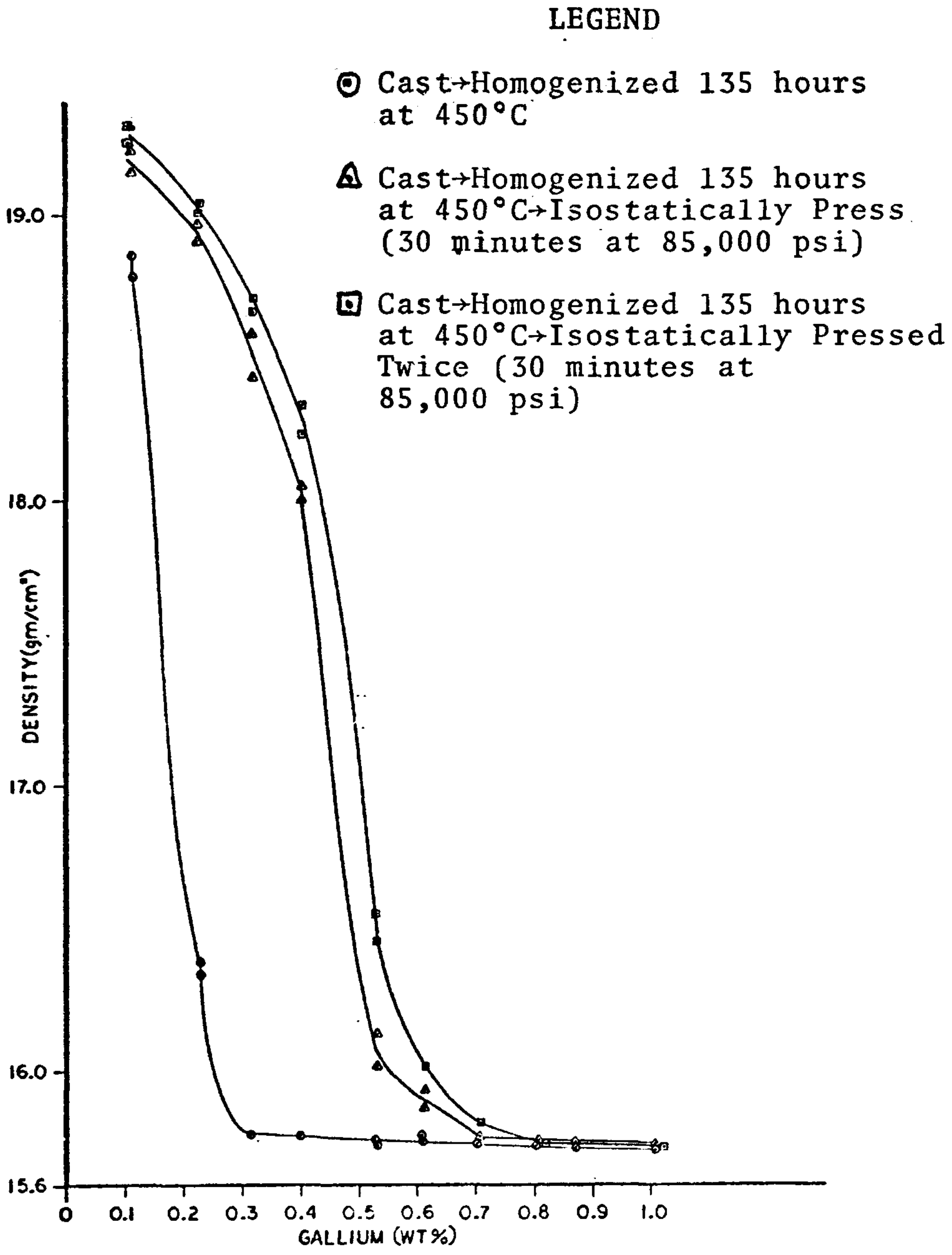


Figure 13

The relative stability of Pu-Ga alloys as a function of density. The samples were chill cast, homogenized for 135 hours at 450°C and isostatically pressed twice, both times at ambient temperature for 30 minutes

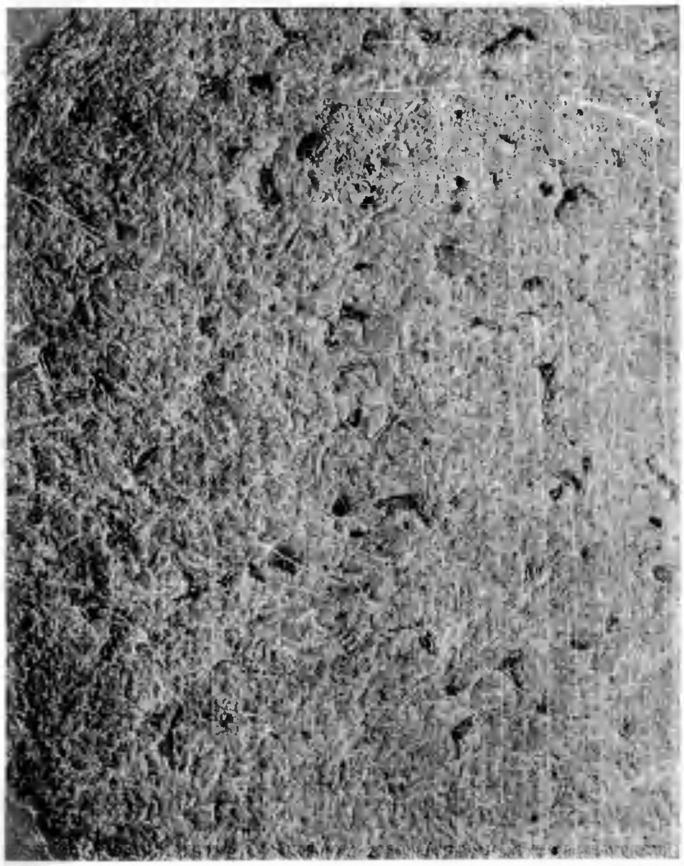


Figure 14

The metallographic structure of a 0.4 wt% Ga alloy sample that had been chill cast, homogenized for 135 hours at 450°C, and isostatically pressed twice at 85,000 psi, both times at ambient temperature for 30 minutes. The sample contains approximately 70% alpha phase and 30% delta phase as determined by density. Shown in the photomicrograph is a textured surface. The alpha and delta phases are not identifiable. The dark regions are etch pits. (Etched - 200X) are shown in Figures 15 and 16, respectively. Both alloys are nearly 100% delta phase.

The metallographic structure of the as-cast 4- by 4- by 1.125 in. ingot is shown in Figure 17. Metallographic structure determined from three perpendicular directions was identical. This verified that the grains were randomly oriented. In order to make any theoretical diffusion computations, a model of the cored grain must be used. Based on the metallographic results a right cylinder 0.050 mm diameter was assumed as the grain geometry.

The effects of rolling and subsequent isostatic pressing on the density of the as-cast, nonhomogenized, Pu-1 wt% Ga alloy ingot are shown in Table 3. Note that, except for the first 10% reduction, the sample densities varied directly with percent reduction. The results of density as a function of homogenization time for the ingot as-cast, and rolled to 10-, 30-, 50-, 70-, and 90% reductions are shown in Figure 18. It is obvious that the ingot homogenizes faster as the percent reduction increases. The isostatically pressed density of the cored, as-cast ingot was 16.23 g/cm^3. The homogenized density, corresponding to 100% delta phase, is 15.74 g/cm^3. Therefore, the total density change of the cored as-cast sample was 0.49 g/cm^3. Based on that density change, it was assumed that a sample density of [16.23-(0.49 x 0.25)] or 16.115 g/cm^3 corresponds to 25%

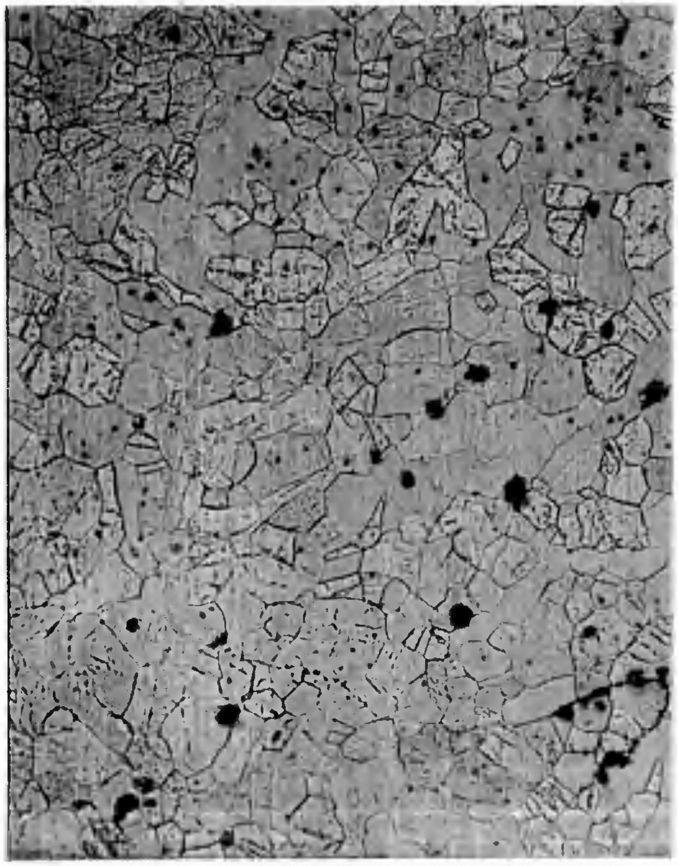


Figure 15

The metallographic structure of a 0.7 wt% Ga alloy sample that had been chill cast, homogenized for 135 hours at 450°C, and isostatically pressed twice at 85,00 psi, both times at ambient temperature for 30 minutes. The sample contains approximately 99% delta phase and 1% alpha phase, as determined by density. Note that the dark spots are etch pits. (Etched - 200X)

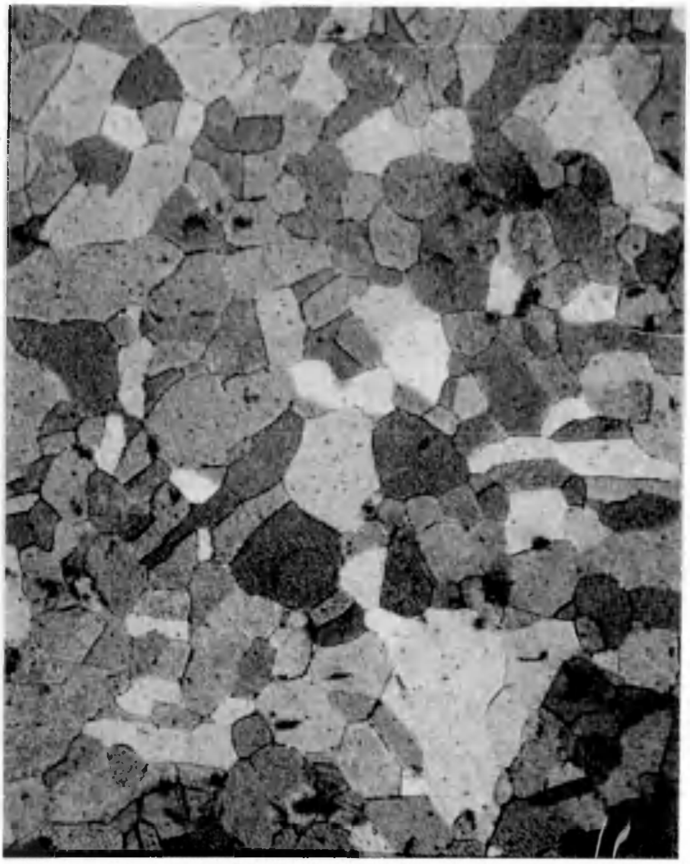


Figure 16

The metallographic structure of a 1 wt% Ga alloy that had been chill cast, homogenized for 135 hours at 450°C, and isostatically pressed twice at 85,000 psi, both times at ambient temperature for 30 minutes. The sample is 100% delta phase, as determined by density. (Etched - 200X)

Figure 17

A photomicrograph showing the as-cast structure of a 4 x 4 x 1.125 in. ingot of Pu-1 wt% Ga alloy. Note that the structure contains randomly oriented elongated grains. The black spots are etch pits. The light colored elongated delta phase grains are surrounded by the darker alpha phase in the grain boundary and triple point regions. (Etched - 200X)

LEGEND

⊙	Cast				Homogenized→	Isos.	Pressed
x	Cast →	Rolled	10%	Reduction →	"	"	"
⊡	"	"	30%		"	"	"
△	"	"	50%		"	"	"
+	"	"	70%		"	"	"
●	"	"	90%		"	"	"

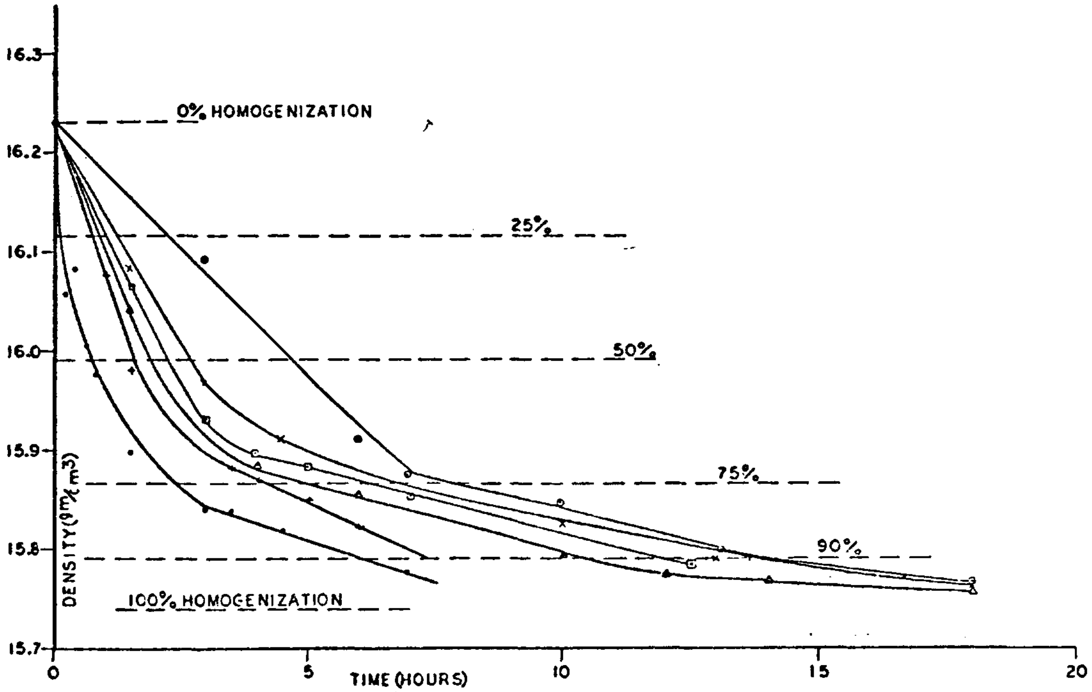


Figure 18

The effect of homogenization time at 450°C on the isostatically pressed (30 minutes at 85,000 psi) density of Pu-1 wt% Ga alloy. A comparison is made between the density response of as-cast samples and samples that were rolled to 10-, 30-, 50-, 70-, and 90% reduction, prior to homogenization.

Reduction %	As-Rolled Density (g/cm^3)	Isostatically Pressed Density (g/cm^3)
0	15.951	16.231
10	15.927	16.218
30	15.995	16.215
50	16.026	16.220
70	16.061	16.227
90	16.167	16.275

Table 3

The effect of rolling and subsequent isostatic pressing on the density of as-cast Pu-1 wt% Ga alloy.

homogenization. By the same technique, the densities of 15.990, 15.865, and 15.790 correspond to 50-, 75-, and 90% homogenization, respectively. Using those density values and the plot of density versus homogenization time shown in Figure 18, the curves of homogenization versus annealing time shown in Figure 19 were generated. An interpretation of the results presented in Figure 19 will be covered in the Discussion section.

The metallographic structure of an isostatically pressed sample that was rolled to 10% reduction and not homogenized is shown in Figure 20. For comparison, the structure of an isostatically pressed sample that was rolled to 10% reduction and homogenized for 10 hours at 450°C is shown in Figure 21. The homogenized sample has somewhat larger grains as may be expected due to grain growth. Other than that, there is very little difference noted between the two samples. A similar comparison was made for samples rolled at 50- and 90% reduction. The structure of a sample as-rolled to 50% reduction with no homogenization, Figure 22, may be compared to one rolled to 50% reduction and homogenized for 3 hours at 450°C, Figure 23. Note the presence of a cold worked structure with the lighter areas being delta phase surrounded by the darker alpha phase. The homogenized specimen has a recrystallized grain structure. The flowing color contrast

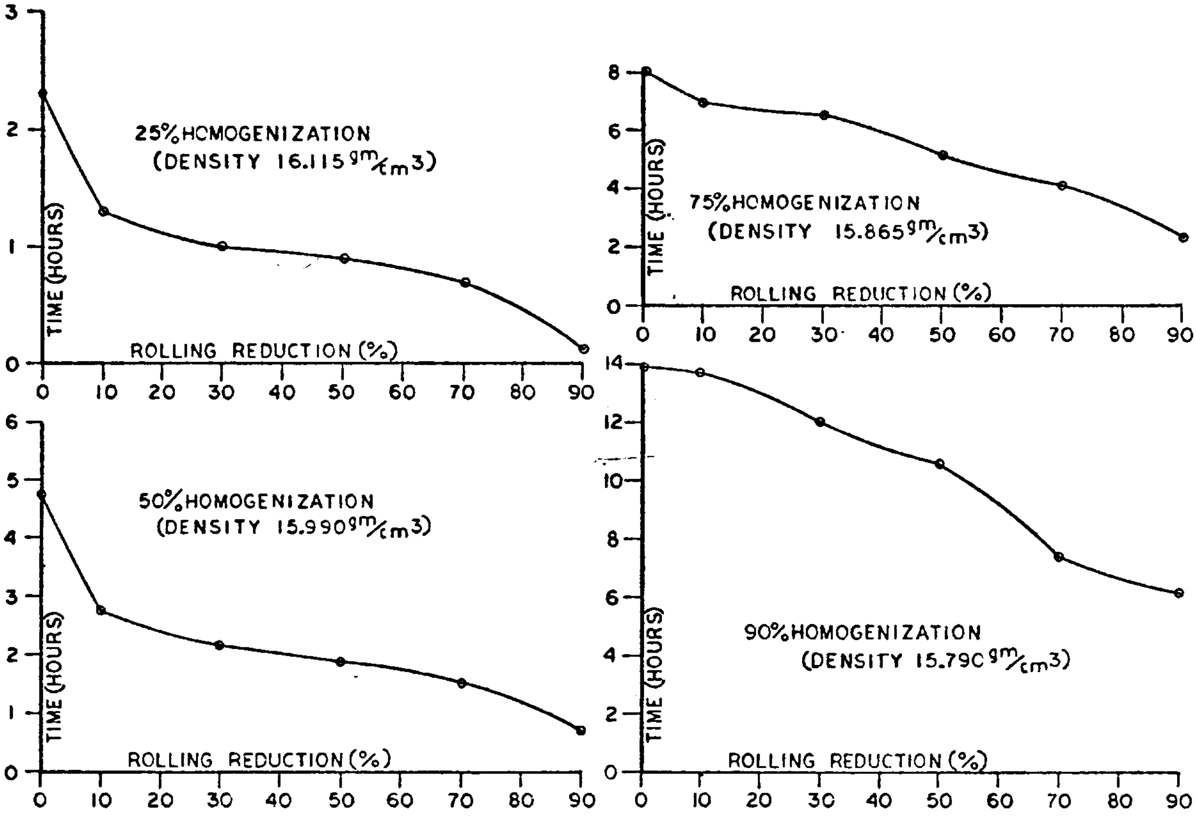


Figure 19

The time required for 25-, 50-, 75-, and 90% homogenization as a function of percent reduction by rolling.

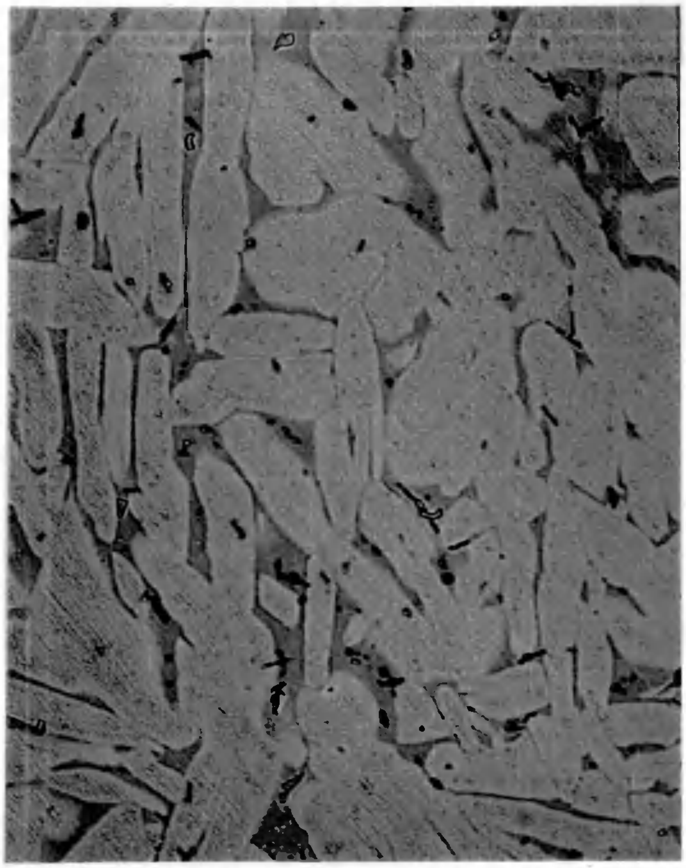


Figure 20

The metallographic structure of Pu-1 wt% Ga alloy after 10% rolling reduction and isostatic pressing (30 minutes at 85,000 psi). Note that the 10% deformation made no significant effect on the microstructure. The light colored delta phase grains are surrounded by the darker alpha phase. (Etched - 200X)

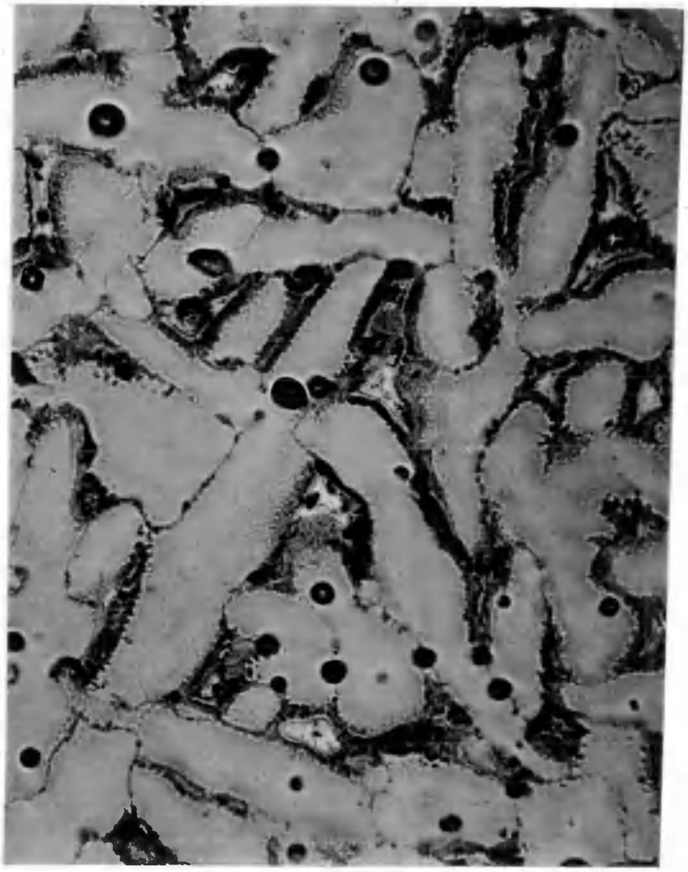


Figure 21

The metallographic structure of Pu-1 wt% Ga alloy after 10% rolling reduction, a 10-hour homogenization at 450°C, and isostatic pressing (30 minutes at 85,000 psi). Other than some evidence of grain growth, this structure appears to be near identical to the 10% as-rolled structure. The black spots are etch pits. (Etched - 200X)

Figure 22

The metallographic structure of Pu-1 wt% Ga alloy after 50% rolling reduction and isostatic pressing (30 minutes at 85,000 psi). Note the deformed structure with the light colored delta phase grain cores surrounded by the darker alpha phase in the grain boundaries. (Etched - 200X)

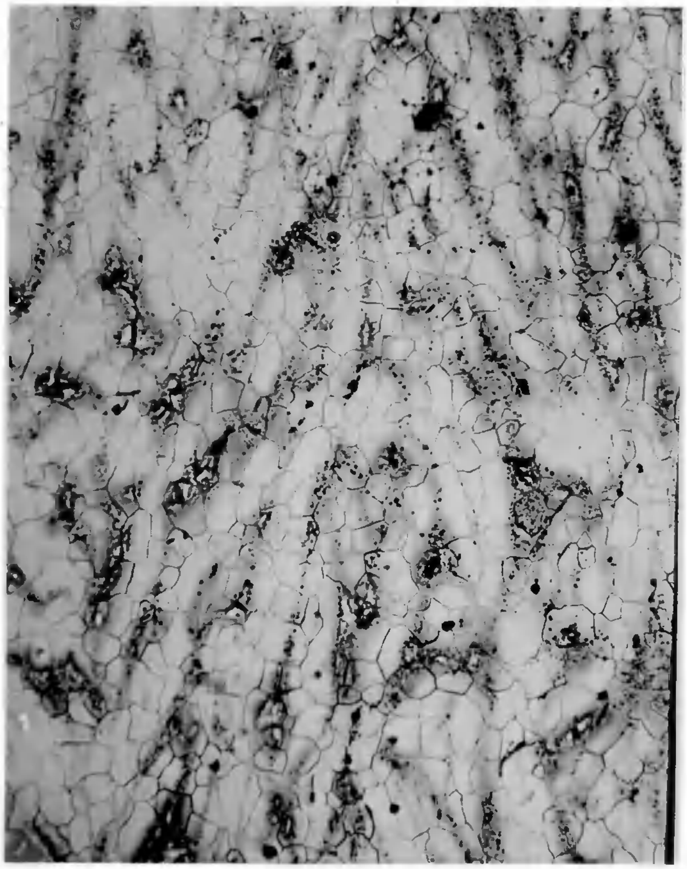


Figure 23

The metallographic structure of Pu-1 wt% Ga alloy after 50% rolling reduction, a 3-hour homogenization at 450°C, and isostatic pressing (30 minutes at 85,000 psi). Note the equiaxed recrystallized grain structure. Also note that the etch has stained the regions of low gallium, thereby depicting the remaining partially cored structure. (Etched - 200X) is an effect commonly caused by differences in etching characteristics of low versus high gallium composition. Figures 24 and 25 show, respectively, isostatically pressed samples that were: as-rolled to 90% reduction, and one rolled to 90% reduction and homogenized for 48 minutes at 450°C. It is theorized that the localized areas of alpha phase (darker in color) are triple points, the interstitual areas between the grains that were the last to solidify, thus containing the least amount of gallium.

In summary, rolling has been found to reduce the time required to achieve homogenization of gallium in plutonium; the decrease in annealing time increasing with increasing reduction prior to homogenization. The next chapter will attempt to explain the mechanism by which the rolling reduces the annealing time.

Figure 24

The metallographic structure of Pu-1 wt% Ga alloy after 90% rolling reduction and isostatic pressing (30 minutes at 85,000 psi). Note the dark localized areas of alpha phase, assumed to be triple points and/or segments of grain boundary alpha phase surrounded by a matrix of light colored deformed delta phase. The small black spots are etch pits. (Etched - 200X)

Figure 25

The metallographic structure of Pu-1 wt% Ga alloy after 90% rolling reduction, 48 minutes homogenization at 450°C, and isostatic pressing (30 minutes at 85,000 psi). Note the equiaxed structure of recrystallized grains. The dark stained areas around the localized alpha phase indicate the areas of low gallium. (Etched - 200X)

DISCUSSION

This chapter is devoted to explaining the results obtained experimentally. Two subsections are used, one to discuss the homogenization of the as-cast samples and the other to predict the homogenization of the rolled samples.

I. Predictions of Homogenizing Times for As-Cast Samples

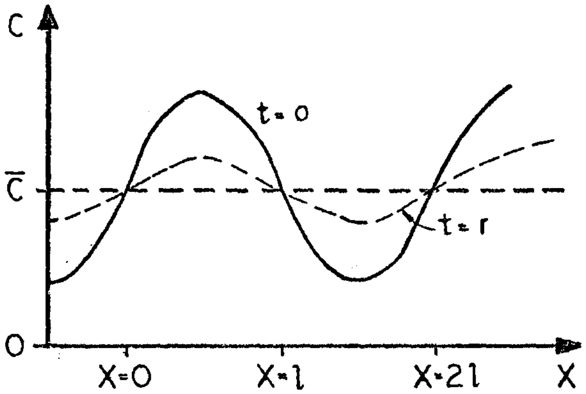
Predicting homogenizing times for the cast samples was accomplished in several steps. First, diffusion models were developed so theoretical gallium concentration profiles could be calculated. Next, assuming an as-cast cylindrical grain, 0.050 mm in diameter, theoretical concentration profiles calculated by the diffusion models were compared to an actual concentration profile determined by other investigators. Then, the diffusion models were used to further predict the concentration profiles after homogenization at 450°C for various periods of time. The predicted profiles were converted into theoretical densities. A comparison of theoretical and actual curves of density versus homogenization time was made.

Diffusion Models

Three diffusion models were evaluated as potential means of predicting the homogenization of as-cast Pu-1 wt% Ga alloy. The three models are introduced as:

A. Sinusoidal[12]

$$C(x,t) = C_1 + (C_1 - C_0)\cos[\pi x/\ell]\exp[-Dt\pi^2/\ell^2]$$



$C(x,t)$ Concentration (wt%) at distance x from the grain boundary (x=0) at time (t)

C_1 - Nominal Ga concentration of the alloy (wt%)

C_0 - Minimum Ga concentration in the grain (wt%)

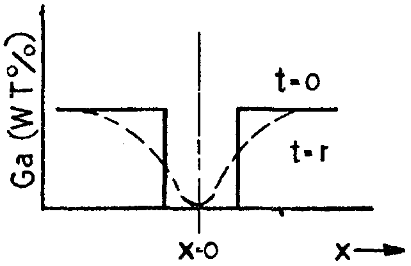
ℓ Radius of grain (cm)

D - Diffusivity (cm/sec)

Given a gallium concentration profile, as described by the equation above, the homogenization characteristics of the alloy may be calculated. This analysis only accounts for diffusion in one dimension.

B. Thin Film[13]

$$C = \frac{\alpha}{2\sqrt{\pi Dt}}\exp(-x^2/4Dt)$$



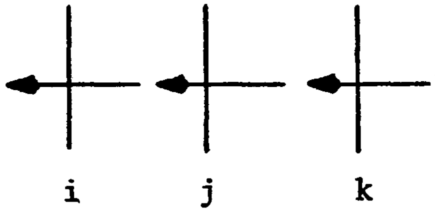
This solution assumes that a thin film (α cm thick) of unalloyed plutonium is instantaneously bonded between two infinite rods of Pu-Ga alloy of constant gallium composition. Gallium in the composite rod is then allowed to diffuse until the theoretical gallium profile in the rod simulates the known gallium profile in a cored grain. Using the elapsed time as a baseline, the homogenization response of as-cast grains may be calculated. This solution also assumes one dimensional diffusion.

C. Incremental

Using a cylindrical model and Fick's First Law of Diffusion, an incremental concentration change may be calculated

$$J = -D \, \Delta c/\Delta x$$

if three reference planes within the model are considered as shown in the following:



Starting at the grain boundary, the change of concentration at the j plane is given by the equation:

$$\Delta Cj = -D\,[Cj - Ci]\,\frac{\Delta t}{\Delta r^2}$$

It should be noted that the general relationship between diffusion time and distance, namely that $r^2 \sim t$, results from the fact that the concentration gradient and the volume of material into which diffusion is occurring have an r dependence.

In the grain interior the change of concentration is given by the equation:

$$\Delta Cj = -D[(Ci-Cj)\frac{rj}{rk} - (Cj-Ck)]\,\frac{\Delta t}{\Delta r^2}$$

At the grain center the change of concentration is given by the equation:

$$\Delta Cj = -D[Ck-Cj]\,\frac{\Delta t}{\Delta r^2}$$

This method incorporates the cylindrical geometry and therefore, takes into account two-dimensional diffusion (i.e., radially).

Fitting the Initial Gallium Concentration Profile

Attempts were made, using the three diffusion models described, to predict the density response of the as-cast samples, as shown in Figure 18. The sinusoidal and thin film methods were fitted to the gallium concentration profile determined by Ferrera, et al.[5], for an as-cast 0.050 mm diameter Pu-1 wt% Ga alloy grain. The results are shown in Figure 26. Note that the two theoretical curves are in reasonable agreement with the experimental data except that the sinusoidal solution predicts unrealistic gallium concentrations in the grain center.

Comparing Theoretical and Actual Homogenization

The thin film solution was used to calculate gallium concentration profiles for several homogenization times at 450°C. Using the calculated concentration profiles and the calibration curve shown in Figure 13, theoretical densities were calculated. The following equation was used to incrementally calculate the theoretical density of a grain:

$$\rho_T = \frac{\rho_0 \pi r_0{}^2 h + \rho_1 \pi (r_1{}^2 - r_0{}^2) h + \rho_2 \pi (r_2{}^2 - r_1{}^2) h \text{ ----}}{\pi r_T^2 h}$$

A comparison of the thin film solution and the experimental data collected on the cast Pu-1 wt% Ga alloy samples is shown in Figure 27. Note that the two curves are not in good agreement. The originally cored theoretical

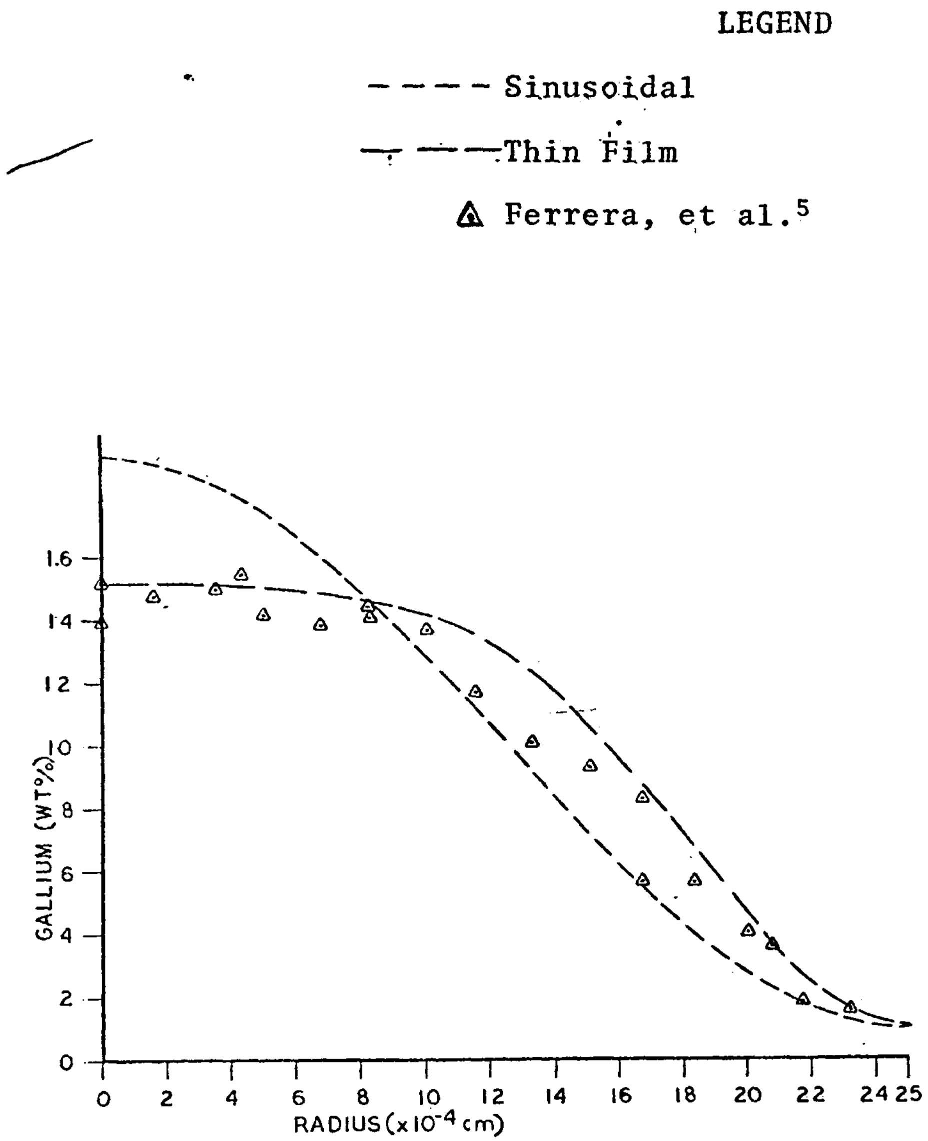


Figure 26

A comparison of the theoretical gallium concentration profiles, calculated by the sinusoidal and thin film solutions, and the gallium concentration profile determined experimentally by Ferrera, et al., on a cored 0.050 mm diameter grain by Pu-1 wt% Ga alloy.

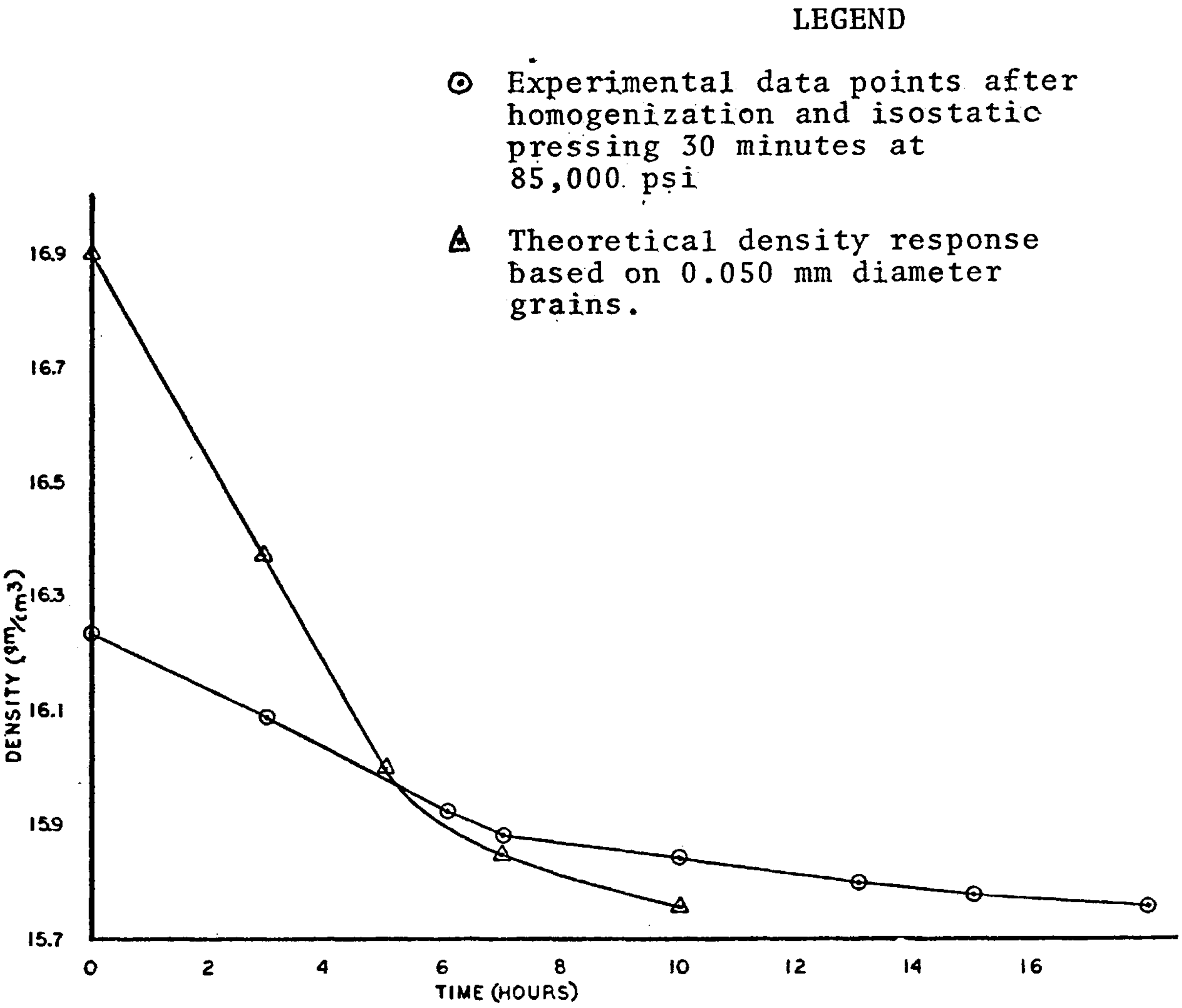


Figure 27

The theoretical "Thin Film" homogenization of a 0.050 mm diameter grain of Pu-1 wt% Ga alloy, compared to the actual homogenization of the alloy.

grain density was significantly higher than the experimental density. Based on this, it was assumed that actual gallium concentration profile in the cast structure is not represented by the profile determined by Ferrera, et al. It may also be that the cylindrical grain model does not adequately describe the system.

A similar set of calculations was completed for the sinusoidal solution. Again, the theoretical calculations did not agree with the experimentally determined results. Several sets of calculations were made using the incremental solution. However, it was determined that in order to minimize accumulative errors that are inherent in that type calculation, extremely small increments of distance and time would have to be used. Since the overall objective of this project was to determine the effect of percent reduction by rolling on homogenization rates, predicting the homogenization rate of the cast alloy was considered to be of secondary importance.

However, it was decided that a modified gallium concentration profile, one that would predict the as-cast density, would be useful. The data obtained by Ferrera, et al., indicated gallium concentrations of ~0.1 wt% in the grain boundaries. Using that value as the gallium concentration in the grain boundary, the slope of a linear concentration profile was adjusted until the theoretical density agreed with the actual isostatically pressed density (16.23 g/cm^3) of the as-cast alloy. The modified gallium concentration profile shown in Figure 28 is used later to help explain the effect of rolling on homogenization rates.

In summary, it should be noted that poorly defined initial conditions were probably responsible for the lack of agreement between predicted and measured values of homogenization times in the cast samples. The use of one-dimensional diffusion models, while incurring some error, are not altogether inaccurate because most of the diffusion occurred near the grain boundary of the cylindrical grains. When the diffusion distance is short relative to the cylinder radius, diffusion may be effectively described by a one-dimensional model.

II. Predictions of Homogenization Times for Rolled Samples

Two assumptions may be made in analyzing the effect of percent reduction on the time required for homogenization; namely, that the mechanical properties are uniform across the cored grain or that the mechanical properties are nonuniform. Deformation resulting from both cases are discussed. The mechanical properties of Pu-Ga alloys were used to predict the deformation of cored Pu-1 wt% Ga alloy grains. Finally, the theoretically predicted homogenization of rolled samples based on uniform and nonuniform deformation was compared to the actual homogenization as determined experimentally.

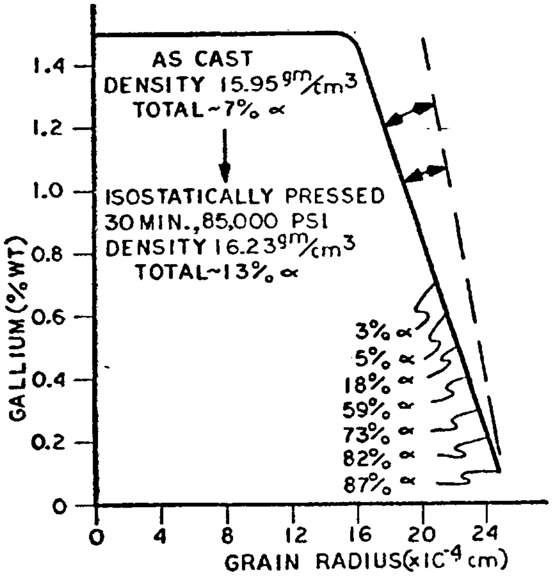
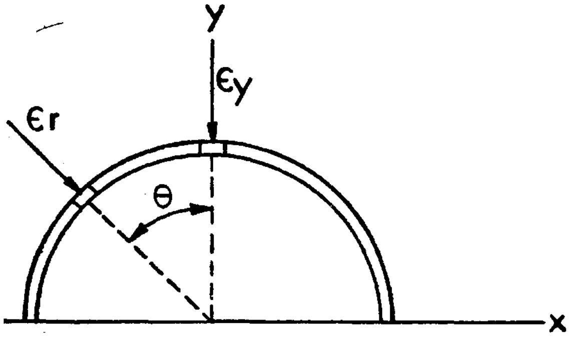


Figure 28

A theoretical gallium concentration profile for the as-cast grains of Pu-1 wt% Ga alloy.

Uniform Mechanical Properties

Rolling is known to produce plane strain in rolled sheet. That is, the sheet gets longer and thinner, but not wider. Assuming that, on the average, plan strain exists in rolled grains, then the following condition exists:



$\varepsilon_z = 0 \quad \varepsilon_x = \varepsilon_y$

$\varepsilon_r = \varepsilon_y \cos\theta$

As shown earlier, homogenization time varies with the square of the distance that gallium atoms must be transported, $(t \sim x^2)$. Based on the assumption of uniform mechanical properties, it may be assumed that diffusion distance in a grain varies with the amount that the ingot is rolled, percent reduction.

$$x = x_0 \ (1-R)$$

$$t = [x_0(1-R)]^2 \approx t_0 \ (1-R)^2$$

This relationship is simplified in that it does not correct for plain strain considerations. The equation below averages the effect of strain variation across a grain:

$$\bar{t} = \frac{\int_0^{\pi/2} X_0^2[1-R\cos\theta]^2 \, d\theta}{\int_0^{\pi/2} d\theta}$$

$$\bar{t} = X^2[1- \frac{4R}{\pi} + \frac{R^2}{2}]$$

Nonuniform Mechanical Properties

It is expected that the gallium variations across a cored grain will be accompanied by mechanical property variations. This should result in localized deformation across the grain and hence will effect the rate of homogenization. Localized deformation may effect the homogenization of the grain in several ways depending on what portion of the grain is deformed. Consider a grain of two separate regions. The overall deformation of the grain is based on the accumulative deformation of both regions ($XR = X_1R_1 + X_2R_2$). If one region, say Area 1, accommodates all deformation, then the deformation in that region may be expressed by the following relationship:

$$R_2 = 0; \quad R_1 = \frac{XR}{X_1} = KR \qquad K = \text{Constant of nonuniformity deformation}$$

For the purpose of homogenization, the critical diffusion zone is the region with gallium <0.7 wt%. That is, the regions below 0.7 wt% Ga are not stable to isostatic pressing and require gallium diffusion to become stable. If localized deformation occurs, it may be that the high gallium (>0.7 wt%) region accepts all the deformation or that the low gallium region (<0.7 wt%) accepts all the deformation. The effects of deformation in the two regions on the homogenization time are discussed.

The mechanical properties of Pu-Ga alloys are reviewed and used to predict the type deformation of an as-cast grain of Pu-1 wt% Ga alloy.

A. Deformation of the High Gallium Region

If the deformation within a grain occurs in the high gallium region, the concentration gradient outside the critical diffusion zone will be increased. The effect of a change of concentration gradient on the homogenization time may be expressed by: $t = [X_0(1-R)]$ With localized deformation the equation becomes: $t = [X_0(1-KR)]$ That relationship as corrected for plain strain considerations is shown below:

$$\bar{t} = \frac{\int_0^{\pi/2} X_0(1-KR\cos\theta)\,d\theta}{\int_0^{\pi/2} d\theta}$$

$$\bar{t} = X_0[1-KR\,\frac{2}{\pi}]$$

This indicates a linear dependence of homogenization time and percent reduction.

B. Deformation of the Low Gallium Region

If the deformation within a grain occurs in the low gallium region, the result would be an increase of concentration gradient and a decrease of diffusion zone thickness. The relationship between homogenization time and percent reduction is shown below:

$$t = [X_0(1-KR)]^2$$

That relationship corrected for plain strain considerations is shown below:

$$\bar{t} = \frac{\int_0^{\pi/2} X_0{}^2[1-KR\cos\theta]^2\,d\theta}{\int_0^{\pi/2} d\theta}$$

$$\bar{t} = X_0{}^2[1 - \frac{4}{\pi}KR + \frac{K^2R^2}{2}]$$

C. Deformation of the Cored Pu-1 wt% Ga Alloy Grains

It is known[15] that the mechanical properties of Pu-Ga alloys vary, as a result of solution hardening, with percent gallium. The tensile yield strength of plutonium as a function of weight percent gallium is shown in Figure 29. In addition, the mechanical properties of unalloyed plutonium and Pu-1 wt% Ga alloy are compared in Table 4. Based on the mechamical properties, it is expected that as-cast grains of Pu-1 wt% Ga alloy will deform nonuniformly when rolled.

The schematic diagram shown in Figure 30 depicts the predicted behavior of a cored grain when an ingot is rolled to 10% reduction. The diagram is developed from the theoretical gallium profile

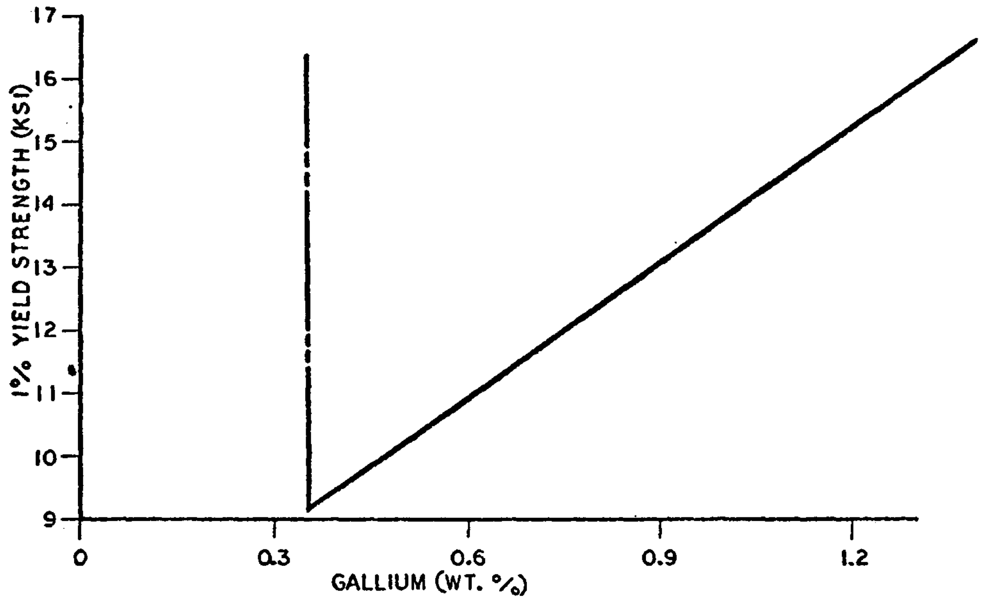


Figure 29

The 1% tensile yield strength of plutonium as a function of percent gallium[15].

Table 4

A summary of the compressive and tensile room temperature properties of unalloyed and gallium alloyed plutonium.

TENSILE PROPERTIES

Pu-1 wt% Ga (As-Rolled)[16]

Rolling Reduction (%)	0.2% Ys (10^3 psi)	% Elong. in 2 in
0 (full softened)	11.6	26
20	19.9	12
40	20.7	10
65	24.6	8
80	25.7	7

Unalloyed Plutonium[17]

0.1% Ys (10^3 psi)	% Elong. in 1 in
32.1	<0.1

COMPRESSIVE PROPERTIES

Pu-0.9 wt% Ga[4]

0.2% Ys (10^3 psi)	% Decrease in Length
14.0	82

Unalloyed Plutonium[17]

0.1% Ys (10^3psi)	% Plastic Dec. In Length Prior to Failure
38	22.8

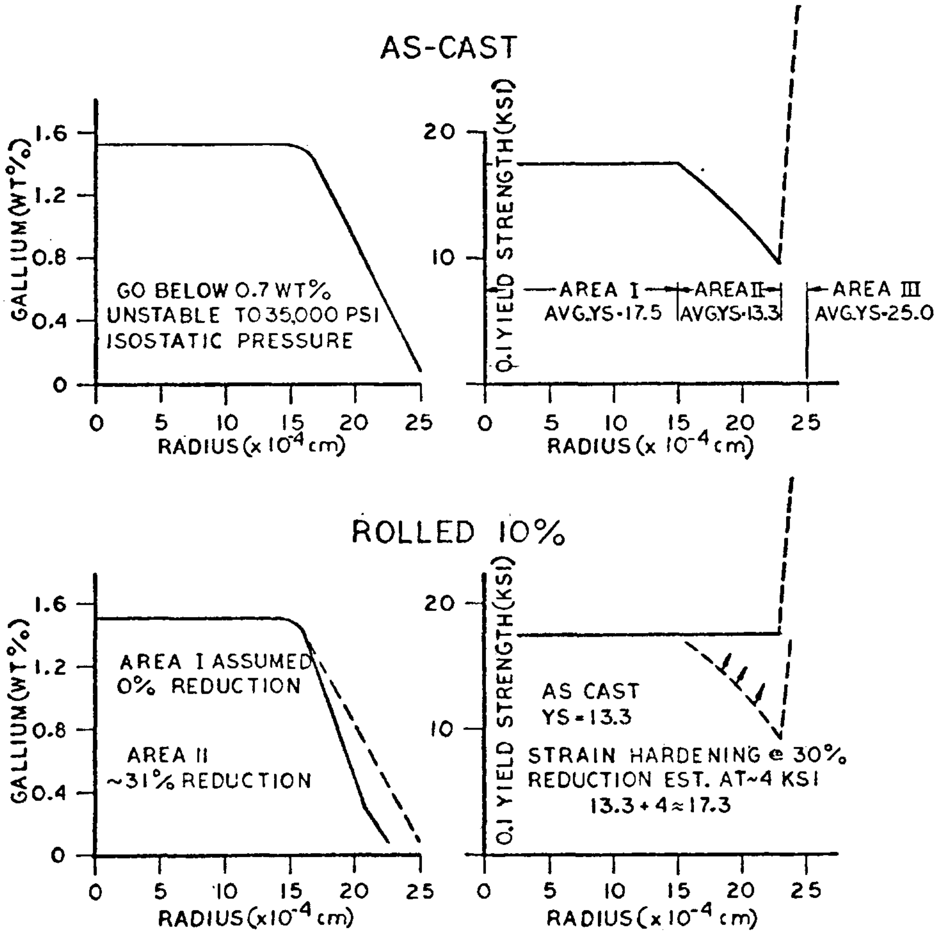


Figure 30

A schematic diagram that depicts the nonuniform mechanical properties within a grain, the predicted localized deformation, and the resultant localized strain hardening.

shown in Figure 28. In the diagram, three areas of different mechanical properties are categorized.

Area 1 is the core of the grain and is estimated to contain essentially all 1.5 wt% gallium. The average tensile yield strength of Area 1 is estimated as 17.5 ksi.

Area 2 has gallium ranging from 0.35- to 1.5 wt%. Keep in mind that the portions of the grain below 0.7 wt% gallium will have to be brought up to that concentration before the grain will be completely stable to 85,000 psi isostatic pressure. Area 2 has an estimated average yield strength of 13.3 ksi.

Area 3 contains gallium from 0.1 to 0.35 wt%, has the largest percent alpha phase, and thus, is the strongest with an estimated average yield strength of 24 ksi.

Based on the mechanical property differences between the three areas, it is assumed that, initially, Area 2 will accommodate essentially all deformation within the grain. The localized percent reduction in Area 2 (R_2) may be calculated as follows:

$$R_2 = \left(\frac{X}{X_2}\right)R = KR \quad \text{if } X = 0.025 \text{ mm} \quad K = 3.1$$

$$X_2 = 0.008 \text{ mm}$$

$R_2 = 3.1\ R$

If the grain is deformed 10%, R = 0.1, then the localized deformation in Area 2 is 31%. From Table IV it may be seen that Pu-1 wt% Ga alloy, when rolled to 30% reduction, strain hardens ~8 ksi. Therefore, it is expected that Area 2 will accommodate all deformation in the grain until such time that strain hardening equalizes the mechanical properties of Areas 1 and 2. At that time the grain deformation will be accommodated by both Areas 1 and 2. Based on the data presented in Table 4 , it may be expected that the mechanical properties of Areas 1 and 2 will equalize by the time the ingot is rolled to 10% reduction (31% in Area 2).

As shown in Table 4 , Pu-1 wt% Ga alloy strain hardens to ~26 ksi when rolled to 80% reduction. Therefore, it is expected that large percent reductions of the ingot will cause strain hardening in Areas 1 and 2 such that portions of Area 3 will deform.

Comparing Theoretical and Actual Homogenization

Three theoretical relationships of homogenization time as a function of percent reduction were developed by assuming either uniform or nonuniform mechanical properties in a rolled grain. A theoretical constant of nonuniform deformation K for Pu-1 wt% Ga alloy was calculated to be 3.1. The three theoretical relationships of homogenization time as a function of percent reduction, applied to Pu-1 wt% alloy, are superimposed on the experimental data obtained for 25-, 50-, 75-, and 90% homogenization. The results are shown in Figure 31. It appears that the grains are initially deformed nonuniformly, but as larger percent reductions (>10%) are attained, the strain hardening across the grain causes essentially uniform deformation. It also appears that the triple points and possibly other regions of low gallium resist deformation enough to be relatively insensitive to percent reduction. This is shown by the curve of 90% homogenization. This also verified metallographically in Figure 24 by the areas of localized alpha phase in the matrix of rolled delta phase.

LEGEND

- ⊙ Experimental Data
- ● Theoretical - Uniform Mechanical Properties
- ■ Theoretical - Nonuniform Mechanical Properties - Deformation of Low Gallium
- ▲ Theoretical - Nonuniform Mechanical Properties - Deformation of High Gallium

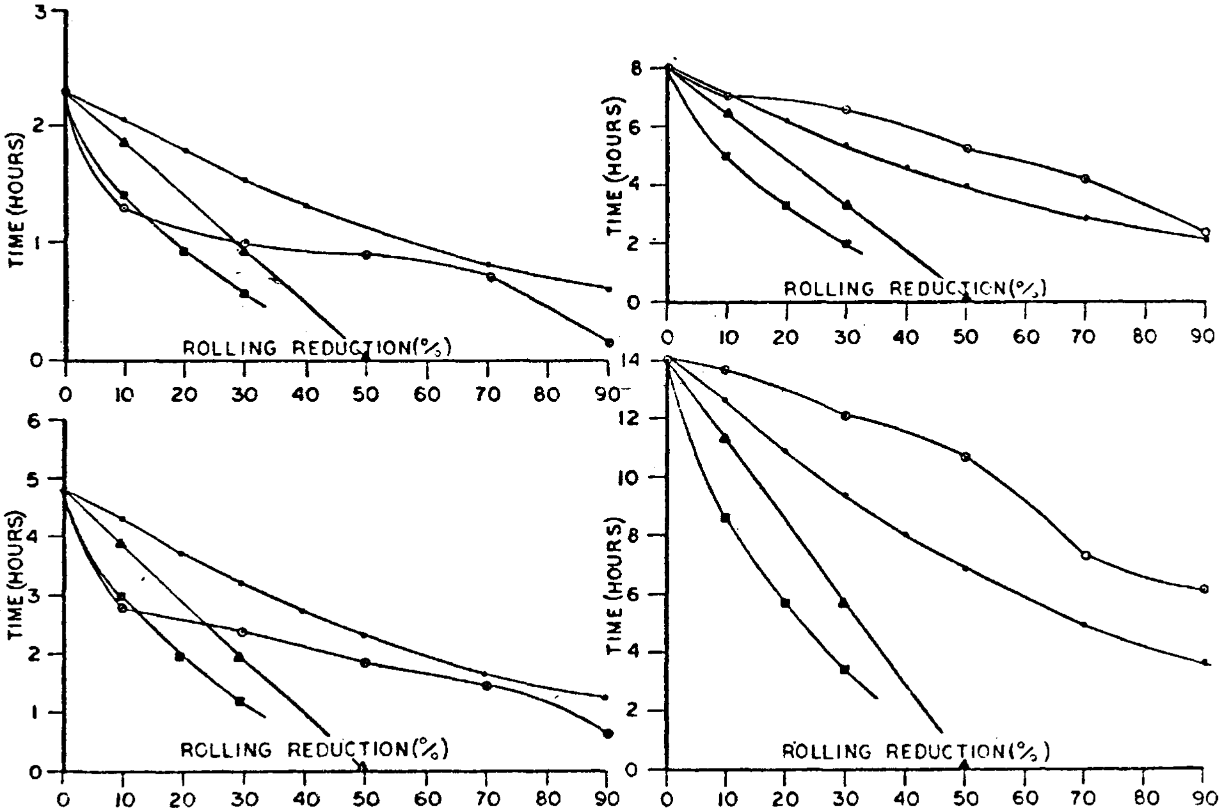


Figure 31

The time required for 25-, 50-, 75-, and 90% homogenization as a function of percent reduction by rolling. Also plotted are the theoretically predicted effects caused by both uniform and nonuniform mechanical properties across the grains of Pu-1 wt% Ga alloy.

CONCLUSIONS

The following conclusions were reached as a result of this project:

1. The minimum concentration of gallium necessary to stabilize the delta phase of plutonium to 85,000 psi isostatic pressure is 0.7 wt%.
2. The effect of rolling on the homogenization of Pu-1 wt% Ga alloy is dependent on the degree of homogenization desired. The following conclusions were obtained for partial, 25- to 50% homogenization:
    a. Small rolling reductions ($\leq$10%) cause relatively large increases in the rates of homogenization. This is caused by localized deformation in the as-cast grains. Essentially all deformation is accommodated by the low gallium region of the grain which is adjacent to the very low gallium, high strength, grain boundary region.
    b. Additional rolling reductions (>10% <70%) cause some additional increases in the homogenization rate, but much less increase per increment of strain compared to the initial 10% reduction. This is attributed to equalization of the mechanical properties

across the grains, as a result of strain hardening, and thus, more uniform deformation.

   c. Large rolling reductions (>70%) cause the rate of homogenization to increase. This is attributed to strain hardening across the delta phase region of the grain such that the higher strength grain boundary region accommodates some of the overall grain deformation.

3. The following conclusions were obtained for near complete (90%) homogenization:

   a. The rate of homogenization is relatively insensitive to rolling reductions, as compared to the effect of rolling on partial homogenization. This is attributed to the resistance of high strength, low gallium areas, such as triple points and grain boundary regions, to deformation during rolling.

SELECTED BIBLIOGRAPHY

1. Miner, W. N., and Schonfeld, F. W., "Physical Properties," Plutonium Handbook, Gordon and Breach, Science Publishers, New York, 1967, pp 31-59.
2. Ellinger, F. H., et al., "The Plutonium-Gallium System," Journal of Nuclear Materials, 12:226-36, 1964.
3. Johnson, K. A., Homogenization of Gallium-Stabilized Delta-Phase Plutonium, LA-2989, Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico, February 28, 1964.
4. Gardner, H. R., Physical and Mechanical Metallurgy Studies on Delta-Stabilized Plutonium-Gallium Alloys, BNWL-13, Battelle-Northwest Laboratory, Richland, Washington, April, 1965.
5. Ferrera, D. W., et al., "Gallium Coring Profiles for Plutonium-1 Weight Percent Gallium Alloys," USAEC RFP-1800, Rocky Flats Division, Dow Chemical U.S.A., May 11, 1972.
6. Harvey, M. R., et al., "Chemical Diffusivities of Plutonium-Gallium Alloys in the Epsilon (bcc) Phase," Journal of Less Common Metals, 23:446-50, 1971.
7. Rafalski, A. L., et al., "Gallium Diffusion in Delta Stabilized Pu-Ga Alloys," American Society for Metals Transactions Quarterly, 60:721, 1967.

8. Jackson, R. J., et al., "Measurement of Percent Alpha in Delta Stabilized Plutonium Alloys by X-Ray Techniques," Proceedings of Twentieth Metallographic Conference, Denver, Colorado, June, 1966, p 168.

9. Hambling, P. G., et al., "The Effect of Uniaxial Compression upon the Transformation of Metastable Delta-Phase Plutonium," Journal of Nuclear Materials, 17:172, 1965.

10. Knight, R. A., et al., "Alpha Precipitation in Delta Phase Plutonium," Journal of Nuclear Materials, 24:223, 1967.

11. Spicer, B. R., and White, J. S., "The Effect of Thermal Cycling upon the Transformation Behavior of Metastable Delta-Phase Plutonium," Journal of Nuclear Materials, 22:269-75, 1967.

12. Shewmon, P. G., "Diffusion," Physical Metallurgy, edited by R. W. Cahn, American Elsevier Publishing Company, Incorporated, N.Y., 1970, p 388.

13. Konobeevsky, S. T., "Equilibrium Diagrams of Certain Systems on Plutonium Bases," Session on the Peaceful Uses of Atomic Energy, Academy of Sciences, U.S.S.R., Proceedings of the Division of Chemical Sciences, III: 362-374, Academy of Sciences of the U.S.S.R., Moscow, 1955.

14. Shewman, P. G., "Diffusion in Solids," McGraw-Hill Series in Materials Science and Engineering, 1963, p 7.

15. Miller, D. C., and White, J. S., "The Tensile Properties of Plutonium-Gallium Alloys in the Temperature Range 20-100°C," Journal of Nuclear Materials, 17:54-59, 1965.

16. Beitscher, S., "Annealing of Cold Rolled Pu-1 wt% Ga Alloy,", Journal of Nuclear Materials, 45:1-9, 1972/73.

17. Gardner, H. R., and Mann, I. B., "Mechanical Property and Formability Studies on Unalloyed Plutonium," Plutonium 1960, Cleaver-Hume Press Ltd., London, 1961, pp 513-570.