205
5-19 c

2141

RFP-1800

May 11, 1972

GALLIUM CORING PROFILES FOR
PLUTONIUM-1 WEIGHT PERCENT GALLIUM ALLOYS

Dennis W. Ferrera

Joe H. Doyle

Malcolm R. Harvey

MASTER

DOW CHEMICAL U.S.A.
ROCKY FLATS DIVISION
P. O. BOX 888
GOLDEN, COLORADO 80401

U. S. ATOMIC ENERGY COMMISSION
CONTRACT AT(29-1)-1106

THIS DOCUMENT CONFIRMED AS
UNCLASSIFIED
DIVISION OF CLASSIFICATION
BY gH Kahn/and
DATE 5/25/72

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

R4617

DISCLAIMER

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

DISCLAIMER

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

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Printed in the United States of America
Available from the
National Technical Information Service
U. S. Department of Commerce
Springfield, Virginia 22151
Price: Printed Copy \$3.00; Microfiche \$0.65

Printed
May 11, 1972

RFP-1800
UC-25 METALS, CERAMICS,
AND MATERIALS
TID-4500 - 56th Ed.

**GALLIUM CORING PROFILES FOR
PLUTONIUM-1 WEIGHT PERCENT GALLIUM ALLOYS**

Dennis W. Ferrera

Joe H. Doyle

Malcolm R. Harvey

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

DOW CHEMICAL U.S.A.
ROCKY FLATS DIVISION
P. O. BOX 888
GOLDEN, COLORADO 80401

Prepared under Contract AT(29-1)-1106
for the
Albuquerque Operations Office
U. S. Atomic Energy Commission

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

fly

CONTENTS

Abstract	1
Introduction	1
Experimental Procedure	1
Theoretical Coring Model	2
Results	4
Samples Cooled at 1 °C per Minute	4
Samples Cooled at 10 °C per Minute	4
Samples Cooled at 100 °C per Minute	8
Discussion	8
References	9

ACKNOWLEDGMENTS

The authors gratefully acknowledge the efforts of D. H. Riefenberg on the microprobe and Dominick V. Ferrera for the casting and metallography of the samples. Editorial assistance from S. Beitscher was also greatly appreciated.

GALLIUM CORING PROFILES FOR PLUTONIUM-1 WEIGHT PERCENT GALLIUM ALLOYS

Dennis W. Ferrera, Joe H. Doyle, and Malcolm R. Harvey

Abstract. Cored plutonium-1 weight percent gallium alloys cooled at different rates through the two-phase delta plus epsilon field were examined with the aid of an electron microanalyzer. Gallium concentration profiles were determined across the cored grains and correlated well with predicted profiles, using a new theoretical coring model. Small differences between predicted and measured gallium concentrations at the grain centers were accounted for by a supercooling effect.

INTRODUCTION

A considerable amount of gallium (Ga) coring occurs during casting of delta stabilized plutonium-1 weight percent gallium (Pu-1 wt % Ga) alloy. The delta-phase grains have Ga concentrations as high as 1.7 wt % at their centers (for a nominal Pu-1 wt % Ga alloy), and are nearly depleted in Ga at their grain boundaries (1).¹ Findings show that the coring observed across the individual delta-phase grains results from the epsilon-to-delta phase transformation (1,2). Coring during the transformation results from the anomalously high diffusivity of Pu and Ga in the epsilon phase (3).

The low Ga delta-phase areas, noted previously; near the grain boundaries are metastable and can transform to alpha phase during cold working (2), metallographic mechanical polishing (4), or cold storage (5). Delta-phase homogenization treatments are required to eliminate these metastable areas. Usually, homogenization parameters of time and temperature are determined empirically. It is desirable however to be able to predict homogenization times based on a knowledge of the Ga concentration profile across individual grains, grain size, and the diffusivities of the elements present.

A standard homogenization model used heretofore (6) assumes a sinusoidal composition gradient which gives a poor approximation of the actual Ga distribution. The coring profile across individual grains can be predicted using the partition function (7). However, the method is tedious and limited. A new theoretical model has been developed (8) to better predict the Ga concentration profile. The objective of the project described was to compare the actual profile with the one predicted by the theoretical

coring model. An electron microanalyzer was used to determine Ga concentrations for Pu-1 wt % Ga alloys in the as-cast condition and for several different cooling rates through the delta-plus-epsilon phase field.

EXPERIMENTAL PROCEDURE

Electrorefined Pu and 99.99-percent Ga were vacuum-induction melted at 980 °C for 20 minutes in an oxidized tantalum (Ta) crucible. The melt was poured into a calcium fluoride (CaF₂) coated graphite mold which was heated to 680 °C. The metal was then allowed to furnace-cool (~10 °C per minute at 550 °C) to ambient. Various other cooling rates were obtained by equilibrating the samples in the epsilon phase at 630 °C for two hours and then cooling at a controlled linear rate through the two-phase field. The samples were water-quenched when they reached 490 °C to prevent delta-phase homogenization.

Samples were prepared for the microprobe by metallographically polishing and etching. The etchant consisted of 8 parts phosphoric acid, 4 parts ethylene glycol, and 4 parts ethoxyethanol. A MAC-400S microanalyzer with scanning capability was used to examine the samples. Gallium-K_α radiation was excited by 19 kiloelectron-volt electrons and diffracted by a lithium fluoride (LiF) crystal. The X-ray intensities were converted to Ga concentrations by comparing the count with that obtained from a well homogenized Pu-1 wt % Ga standard. Individual thirty-second point counts across the cored grains could not be subjected to a statistical analysis. However, comparisons of the expected and observed standard deviations for the homogenized Pu-1 wt % Ga alloy were nearly identical.

A calibration was made with the standard to determine if moving the beam across a 100-millimeter (mm) distance (equivalent to the distance from the center of the cathode-ray tube to the edge at 500X) would effect the point count. As noted from Figure 1, the variation from the value of the standard (1.0 wt % Ga) is less than 0.06 wt % Ga, thereby establishing the experimental method.

The procedure for determining the Ga profile consisted of locating and centering a typical grain using a backscattered image at magnification of 500X. A line was drawn on the oscilloscope face through the centroid of the grain and a short distance into the adjacent grains (Figure 2) to insure

¹ Numerals in parentheses relate to references at end of text.

FIGURE 1. Results of Calibration Run on a Homogenized Plutonium-1.00 Weight Percent Gallium Standard. (Scatter is representative of expected standard deviation.)

analyzing the minimum Ga areas. The electron beam was placed in the DISABLE mode and thirty-second point counts taken along the line at two- or five-micrometer increments.

THEORETICAL CORING MODEL

Three assumptions were made in the development of the coring model:

1. The chemical diffusivities of Pu and Ga in the epsilon phase are high enough [$\sim 10^{-7}$ square centimeters per second (cm^2/sec)] (3) to permit that phase to remain homogeneous during the epsilon-to-delta transformation (if this condition does not exist, then new delta-phase grains would nucleate producing a duplex structure).
2. The chemical diffusivities in delta phase are low enough ($\sim 5 \times 10^{-10} \text{ cm}^2/\text{sec}$) (9) to prevent that phase from homogenizing appreciably during the transformation.
3. During continuous cooling of the alloy, the interface of the growing delta grain and the remaining epsilon phase are at equilibrium concentrations as predicted by the equilibrium phase diagram (10).

By using the lever rule and the equilibrium phase diagram, the theoretical coring profile may be determined. Illustrative calculations, based on 100 grams of Pu-1 wt % Ga alloy, are given below for 10°C temperature steps, rather than for continuous cooling. Assuming the epsilon phase to be homogeneous, a vertical line was drawn at 1 wt % Ga in the epsilon phase down to the epsilon-phase boundary (see ϵ_1 in Figure 3) (11). From this point, a tie line was drawn

FIGURE 2. Line A-B Represents Typical Line for Analyzing a Cored Grain, Using a Backscattered Image at Magnification 500X.

to the delta boundary (δ_1), giving 1.84 wt % Ga in the first delta phase to precipitate. Next the temperature was reduced 10° to 577°C which is in the two-phase field (x_2). The lever rule was applied using 1.0 wt % Ga as the alloy concentration which partially transforms to delta at 1.62 wt % Ga (δ_2) while the remaining epsilon decreases in Ga to 0.83 wt % (ϵ_2). Thus, the following calculation gives the weight percent of the delta phase that is formed during the first 10° decrease in temperature:

$$\frac{1 - 0.83}{1.62 - 0.83} \times 100 = 21.5 \text{ weight percent delta } (\delta)$$

Now the alloy consists of a two-phase mixture of 21.5 grams of delta with a composition of 1.62 wt % Ga and 78.5 grams of epsilon at 0.83 wt % Ga. (The diffusivity of Ga in delta is assumed to be so small that the 21.5 grams of delta will remain at 1.62 wt % Ga.)

The procedure is repeated and the temperature reduced 10° to 567°C . The amount and composition of alloy now available for transforming are 78.5 grams of epsilon at 0.83 wt % Ga (x_3). The temperature drop causes 19.2 wt % of the remaining epsilon to transform, giving 15.1 grams of additional delta phase with a composition of 1.46 wt % Ga (δ_3). This material precipitates on the original delta grains. At the start of the next 10°C drop in temperature, 63.4 grams of epsilon at 0.70 wt % Ga will be available. These temperature drops are continued until all of the epsilon transforms to delta which occurs near zero-Ga concentration.

FIGURE 3. Partial Plutonium-Gallium Phase Diagram Showing Procedure for Determining the Gallium Profile.

These sample calculations used 10-degree steps to indicate how the calculations are made. The theoretical profile was determined by computer techniques (8) using 0.05 °C temperature steps which nearly simulates continuous cooling. The program also converted wt % delta phase into volume percent (vol %) and then to an effective spherical radius of growing grain. A computer plot routine was used to illustrate wt % Ga in the delta grain as a function of its

radius. Thus, a theoretical concentration profile was available for the cored grains.

The theoretical gallium profile for two adjacent delta grains is shown in Figure 4. The centers of the grains have nearly a zero-concentration gradient while the concentration changes rapidly near the grain boundaries. This profile comes about because the first, or center, 10 vol % of a growing

FIGURE 4. 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.)

sphere accounts for 45 percent of its final radius while the last 10 vol % is concentrated in the outer 4 percent of the radius. The concentration profiles do not change with grain size, thus by properly scaling the abscissa all grains can be compared with the model.

The predicted profile assumes spherical grain growth which is reasonable until the grains impinge and form boundaries. Also since nucleation is random, some grains may nucleate closely together resulting in much higher Ga concentrations near their grain boundaries than predicted. The last material to transform and which is easy to locate on a sample occurs where three grains grow together to form a triple point. Obviously during microanalysis, care must be taken in order that analyses are taken in minimum Ga areas such as triple points.

RESULTS

Four differently heat-treated samples with three cooling rates through the epsilon-plus-delta phase field were examined. Photomicrographs of the samples, shown in Figures 5(a), (b), (c), and (d), indicate the delta-grain size is primarily controlled by the cooling rate through the two-phase field. The dark areas at the grain boundaries are where the low Ga, metastable delta, has transformed to alpha.

Samples Cooled at 1 °C per Minute:

The sample cooled at 1 °C per minute had an average grain size of 120 micrometers and was therefore relatively easy to examine. A backscattered electron image and the corresponding Ga profile are shown in Figures 6 (a) and (b). The grain boundary at Point B and the triple point at A had the same low (essentially zero) concentration. The measured profiles appear to follow the predicted profile well, except for the sharp drop at about 35 micrometers into the grain. The fact that both spectrometers monitored the drop indicates the possibility of an inclusion hidden under the surface.

Samples Cooled at 10 °C per Minute:

These samples had an average grain width of 55 micrometers. A typical grain on the as-cast sample was found using a backscattered image [Figure 7 (a)]. Three profiles were obtained, one on Line A [Figure 7 (b)] and two on Line B [Figure 7 (c)]. The profile from Line A shows that the Ga concentration at the triple point is lower than the opposite boundary. The higher indicated Ga concentration at the narrow grain boundary could be from errors in obtaining a point count directly from the boundary. Again an inclusion has reduced the X-ray count near the center of the grain. This time however, the inclusion is visible.

The two measured concentration profiles for Line B are nearly identical and are typical when care has been used in the selection of areas. The measured profile lies slightly below the theoretical value, but has nearly the same shape. An almost identical profile as shown in Figure 7 (c) was observed in eleven other traces run on this sample.

A simulated as-cast structure was produced by homogenizing a sample in the epsilon phase and then cooling 10 °C per minute through the two-phase field [compare in Figures 5(b) and 5(c)]. A semiquantitative method which indicates relative concentrations was used to determine the Ga profile across grains in the sample noted in Figure 8.

The indicated Ga profile has the same general shape as the predicted profile. Point counting at the maximum Ga concentration between A and B on Figure 8 yielded a value of 1.61 wt %. The Ga profiles for the grains in this sample appear to be identical to those measured on the as-cast sample giving further verification that the coring occurs during the epsilon-to-delta transformation.

(a) 1 °C per minute.

(b) 10 °C per minute (as-cast).

(c) 10 °C per minute.

(d) 100 °C per minute.

FIGURES 5(a), (b), (c), and (d). Photomicrographs of Plutonium-1 Weight Percent Gallium Samples after Being Cooled at Various Rates through the Two-Phase Delta-plus-Epsilon Field. Magnifications at 200X.

(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.

FIGURES 6(a) and (b). Electron Image of Sample and Corresponding Gallium Profile.

(a) Backscattered Electron Image of As-Cast Sample. Magnification 500X.

(b) Gallium Concentration Profile for Line A.

(c) Gallium Concentration Profile for Line B.

FIGURES 7(a), (b), and (c). Three Profiles were obtained of Samples Cooled at 10 °C per Minute: One on Line A (b) and Two on Line B (c).

FIGURE 8. Backscattered Electron Image of a Grain on Sample Cooled 10 °C per Minute with a Single Line Scan Taken on Line 1, Monitoring Gallium-K α Radiation (Line 2). Magnification 700X.

TABLE I. Average Grain Center and Grain-Boundary Gallium Concentration.

Cooling Rate through Epsilon-plus-Delta Phase Field (°C per minute)	Grain-Center Concentration (weight percent gallium)	Grain-Boundary Concentration (weight percent gallium)
1	1.62 $\pm$ 0.07	0.03 $\pm$ 0.02
10 (as-cast)	1.54 $\pm$ 0.10	0.12 $\pm$ 0.09
10	1.55 $\pm$ 0.08	Not measured
100	1.46 $\pm$ 0.11	Unable to measure

FIGURE 9. Effect of Cooling Rate on Gallium Concentration at Selected Grain Centers.

Sample Cooled at 100 °C per Minute:

The grain size of the sample cooled 100 °C per minute was only about 20 micrometers, which was too small to obtain meaningful concentration profiles. However, grain centers were analyzed giving 1.46 wt % Ga for 22 different grains. Minimum concentrations were not taken because of beam overlap. Some correlation appeared to occur between cooling rate and the maximum Ga concentrations in the grains (Table I). As noted, the maximum Ga concentration of the grain centers decreased with increased cooling rates (see Figure 9).

DISCUSSION

Considering all of the experimental difficulties in obtaining reliable data, the experimentally determined Ga concentration profiles correlate well with the predicted coring profile. The data from samples cooled 1 °C per minute show the best agreement with theory. The major discrepancies occurring were with respect to the Ga concentrations at the grain centers. The concentrations on other samples were consistently low and the differences increased with faster cooling rates. Two reasons for the differences are likely. The first is that the model was determined using

phase boundaries which have some uncertainty (probably $\pm 5^\circ\text{C}$) in their equilibrium location. The second is that supercooling would lower the starting temperature of the epsilon-to-delta transformation giving lower Ga concentrations at the grain centers. A total temperature change of 10°C from equilibrium conditions, from either supercooling or errors in the phase-boundary lines, will allow agreement between the predicted maximum and the measured maximum Ga concentrations.

If one assumes that these alloys will supercool 10° for a 1°C per minute cooling rate, an additional 5° supercooling will account for the 1.54 wt % Ga concentration for the sample cooled at 10°C per minute. Another 5° , for a total of 20°C , will account for the 1.46 wt % Ga value obtained from the sample cooled at 100°C per minute. Thus by knowing the equilibrium phase diagram and the actual grain-center Ga concentrations, the degree of supercooling might be estimated.

Of interest is the steepness of the Ga profile near the grain boundaries and the narrowness of this region. Between two grains, the width of the region of phase instability (less than 0.25 wt % Ga) (12) is approximately 8 percent of the grain diameter (equivalent to 20 vol % of material). Using the conventional sinusoidal Ga concentration gradient (6), (which predicts wide low-Ga areas), 30 hours at 460°C should be required to raise the minimum Ga areas to 0.25 wt % for 50-micrometer grains. A modified thin-film solution (8) to Fick's diffusion equation predicts the homogenization parameters of 1.6 hours at 460°C for 50-micrometer grains. These latter parameters agree well with an experimentally observed stabilizing treatment of 2 hours at 460°C (13).

REFERENCES

1. K. A. Johnson. *Homogenization of Gallium-Stabilized Delta-Phase Plutonium*. LA-2989. Los Alamos Scientific Laboratory, University of California, Los Alamos, New Mexico. February 28, 1964.
2. H. R. Gardner. *Physical and Mechanical Metallurgy Studies on Delta-Stabilized Plutonium-Gallium Alloys*. BNWL-13. Battelle-Northwest Laboratory, Richland, Washington. April 1965.
3. M. R. Harvey *et al.* "Chemical Diffusivities of Plutonium-Gallium Alloys in the Epsilon (bcc) Phase." *Journal of Less Common Metals*, 23:446-50. 1971.
4. R. J. Jackson, R. J. Pinkney, and R. R. McDonald. "Measurement of Percent Alpha in Delta Stabilized Plutonium Alloys by X-Ray Techniques." *Proceedings of Twentieth Metallographic Conference*, Denver, Colorado. Page 168. June 1966.
5. B. R. Spicer and J. S. White. "The Effect of Thermal Cycling upon the Transformation Behavior of Metastable Delta-Phase Plutonium." *Journal of Nuclear Materials*, 22:269-75: 1967.
6. P. G. Shewmon. "Diffusion." *Physical Metallurgy*. Edited by R. W. Cahn. American Elsevier Publishing Company, Incorporated, New York. 1970. Page 388.
7. W. A. Tiller. "Solidification." *Physical Metallurgy*. Edited by R. W. Cahn. American Elsevier Publishing Company, Incorporated, New York. 1970. Page 412.
8. Joe H. Doyle. Report in Preparation.
9. A. L. Rafalski, M. R. Harvey, and D. H. Riefenberg. "Gallium Diffusion in Delta Stabilized Pu-Ga Alloys." *American Society for Metals Transactions Quarterly*, 60:721. 1967.
10. F. H. Ellinger, C. C. Land, and V. O. Struebing. "The Plutonium-Gallium System." *Journal of Nuclear Materials*, 12:226-36. 1964.
11. F. H. Ellinger of Los Alamos Scientific Laboratory, Los Alamos, New Mexico. Private Communication. 1969.
12. L. Ekbohm and S. Bogegard. "Phase Transformations in Metastable Plutonium-Gallium Alloys." *Plutonium 1970 and Other Actinides*. Edited by W. N. Miner. Nuclear Metallurgy, American Institute of Metallurgical Engineers, Volume 17. New York. 1970. Page 1027.
13. S. Beitscher. "The Tensile Behavior of Pu-1 wt % Ga at -60 , 30 , and 77°C ." *Journal of Nuclear Materials*, 24:113-17. 1967.