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LOS ALAMOS SCIENTIFIC LABORATORY

OF THE UNIVERSITY OF CALIFORNIA ○ LOS ALAMOS NEW MEXICO

HOMOGENIZATION OF GALLIUM-STABILIZED DELTA-PHASE PLUTONIUM

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HOMOGENIZATION OF GALLIUM-STABILIZED DELTA-PHASE PLUTONIUM

by

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Abstract

The homogenization behavior of cast gallium-stabilized delta plutonium was investigated and characterized by metallographic and electron microprobe techniques. Approximate diffusion data for gallium in delta plutonium were calculated from parameters of the homogenization process. For comparison, the homogenization behavior of rolled, relatively impure gallium-stabilized delta plutonium was investigated. The effects of heat treatment in the epsilon temperature region and cooling through the delta-plus-epsilon field were also investigated.

Acknowledgment

I am especially indebted to J. W. Anderson and E. A. Hakkila for the alloy preparation and electron microprobe work, respectively.

Table of Contents

List of Figures

List of Figures

Introduction

This study was undertaken to determine the homogenization characteristics of cored delta plutonium. The coring or micro-inhomogeneities are caused by segregation of the gallium when the casting is cooled through the liquid-plus-epsilon and the delta-plus-epsilon regions. The areas that are lean in gallium can be plutonium allotropes other than delta, or delta that is unstable to mechanical or thermal treatment.

Experimental Procedures

The specimens used in the major part of this work were taken from a cylindrical casting that contained 1.00 w/o gallium and 1.05 w/o gallium by analysis in its top and bottom, respectively. A chemical analysis of the alloy is given in the Appendix.

The casting was sectioned into specimens weighing approximately 2 grams. The specimens were then individually sealed within vitreous silica capsules evacuated to 10^{-5} torr. Each specimen was annealed for a specific time at one or more of the following temperatures: 425, 500, 525, and 625 ± 2°C. All the specimens were quenched in water from the annealing temperature with the capsule <u>not</u> being broken except in several instances with the 625°C series.

After the heat treatment and quench, the specimens were mounted in polyester plastic, metallographically polished, electrochemically etched,* examined and photographed, and finally analyzed with an electron microprobe. The microprobe was able to provide a point-by-point quantitative analysis for gallium. The standard deviation of an individual analysis by the microprobe was 0.05 w/o gallium. The actual scatter in the microprobe data was larger due to a sampling problem. The operator could not always hit the highest or lowest gallium concentration points in the cores, nor did the section taken always intersect the highest or lowest concentration points.

Results

<u>Description of Starting Material.</u>

The typical cored microstructure in the cast specimens is illustrated in Figure 1. The islands are high and the valleys are lean in gallium. The results of the microprobe analysis indicate that the maximum gallium content in the cores is 1.50 w/o, while the gallium content in the lean regions ranges as low as 0.10 w/o.

<u>Homogenization and Diffusion of Relatively Pure Cast Alloy.</u>

<u>Annealed at 425°C.</u> Figures 2 through 7 are representative photomicrographs of the progressive homogenization of this alloy at 425°C. It is

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* The etching techniques are applicable to other delta alloys and will be reported later.

clear from the figures that the degree of coring decreased as the gallium diffused from the high to low concentration areas with increase in annealing time.

The microprobe results from the same series of specimens are plotted in Figure 8. These results also illustrate the progress of homogenization of this alloy at 425°C.

Annealed at 500°C. The next nine photomicrographs (Figures 9 through 17) and the microprobe results plotted in Figure 18 illustrate the faster progress of homogenization at 500°C than at 425°C.

Annealed at 525°C. The next set of photomicrographs (Figures 19 through 26) plus the microprobe results plotted in Figure 27 illustrate the even faster homogenization of delta plutonium at 525°C than at 500°C. In addition considerable grain growth occurred at 525°C but was not observed at 425 or 500°C.

Approximate Diffusion Data. From the photomicrographs and microprobe data the times for homogenization at the different annealing temperatures were estimated and plotted as log vs 1/T. The slope gave an activation energy of 38 kcal/g atom for the diffusion of gallium in delta plutonium.

Using the core size as measured on the photomicrographs, the starting high and low gallium concentrations, and the concentrations at some intermediate time, the following relationship for gallium diffusion in delta plutonium was found to fit the calculated D values:

$$D = \left(65 \pm 5\right) \exp \left(\frac{40,100}{RT}\right)$$

It should be emphasized that, although these values are reasonable, they are only approximate because of the number of assumptions involved.

Homogenization of Relatively Impure Rolled Alloy.

Annealed at 500°C. Some 1 w/o gallium-stabilized delta-plutonium sheet, as rolled to 37.5 per cent reduction, was obtained for comparison with the purer material. A chemical analysis of the rolled material is tabulated in the Appendix. The experimental procedures were identical with those used on the purer alloy. However, this series was annealed at only 500°C.

A set of photomicrographs (Figures 28 through 33) illustrates the microstructure of the starting material and the apparent effect of the annealing. After the first hour little change was observed. This may have been due to disruption, by the impurity phase or phases, of the etchant's normal sensitivity to gallium concentration.

The microprobe results plotted in Figure 34, if we ignore the low concentration level, show that this alloy homogenizes in 14 hours in contrast with a value of 60 hours for the purer material.

The relative stability of the low-level concentrations may result from the presence, at the annealing temperature, of a liquid impurity phase that has a low solubility for gallium. However, the large amount of impurity in these areas may cause absorption and fluorescence effects which would influence the accuracy of the microprobe results.

Effects of High Temperature Annealing of Relatively Pure Cast Alloy.

Annealed at 625°C. A series of the relatively pure alloy specimens was annealed at 625°C in the epsilon phase region. The next set of photomicrographs illustrates the resultant microstructures (Figures 35 through 42). There was little or no change with time. The microprobe results plotted in Figure 43 indicate essentially the same behavior.

Another specimen was annealed at 525°C for 89 hours to homogenize it and then was further annealed at 625°C for 25 hours. The resulting microstructure is shown in Figures 44 and 45 and the microprobe results are similar to those plotted in Figure 43. The results are the same as were obtained for those specimens which were annealed only at 625°C. This indicates that the epsilon-to-delta transformation is responsible for the microsegregation found in the 625°C annealing series.

Effect of Cooling Rate on Core Size.

Several specimens were cooled from 625°C at the following estimated rates:*

Furnace cool	2.5°/min
Air cool	32°/min
Intact capsule quench	> 100°/min
Broken " "	>> 100°/min

The next four photomicrographs (Figures 46 through 49) illustrate the

* For comparison, the cooling rate of the cast alloy was 9.5°C/min (see Figure 1).

resulting core size. The microprobe results are similar to those in Figure 43. It is apparent that the faster the cooling rate the smaller the core size, though the degree of coring with respect to composition remains approximately the same. However, if, during quenching, the capsules were broken under water the specimens were cooled fast enough to partially suppress the coring.

Summary

1. Cored delta plutonium in the relatively pure alloy was homogenized in the following minimum times:

   500 hours at 425°C

   60 hours at 500°C

   16 hours at 525°C

2. The following approximate diffusion equation was calculated:

$$D = \left(65 \pm 5\right) \exp \left(\frac{40{,}100}{RT}\right)$$

3. A relatively impure alloy, rolled to 37.5 per cent reduction took 14 hours to become homogenized at 500°C, if the impurity areas are ignored.

4. Cooling of 1 w/o gallium alloy through the epsilon-plus-delta field produces a substantial amount of microsegregation.

Figure 1. Microstructure of cast 1 w/o gallium-stabilized delta plutonium. 500 X

Figure 2. Microstructure of cast 1 w/o gallium-stabilized delta plutonium annealed for 1 hour at 425°C. 500 X

Figure 3. Microstructure of cast 1 w/o gallium-stabilized delta plutonium annealed for 8 hours at 425°C. 500 X

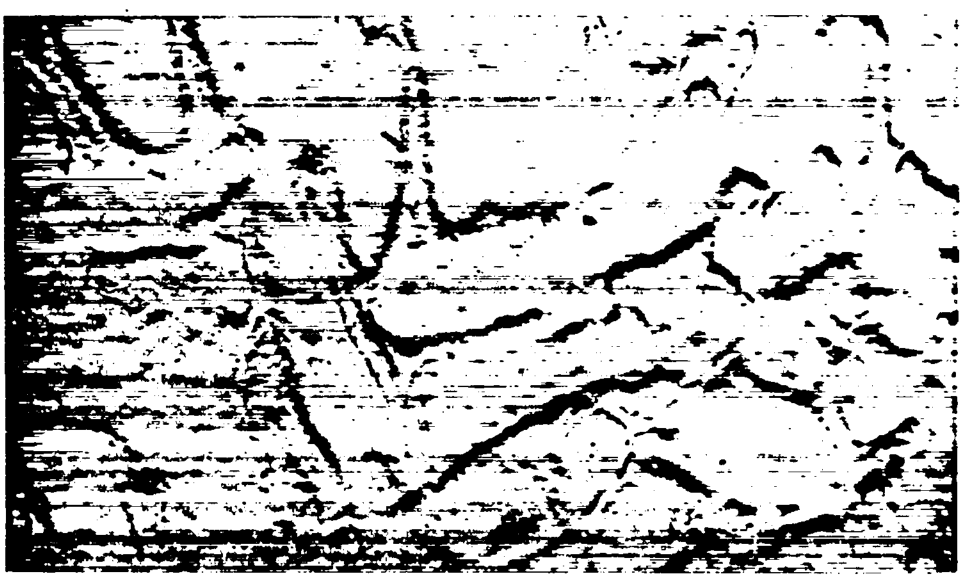

Figure 4. Microstructure of cast 1 w/o gallium-stabilized delta plutonium annealed for 24 hours at 425°C. 500 X

Figure 5. Microstructure of cast 1 w/o gallium-stabilized delta plutonium annealed for 50 hours at 425°C. 500 X

Figure 6. Microstructure of cast 1 w/o gallium-stabilized delta plutonium annealed for 120 hours at 425°C. 500 X

Figure 7. Microstructure of cast 1 w/o gallium-stabilized delta plutonium annealed for 504 hours at 425°C. 500 X

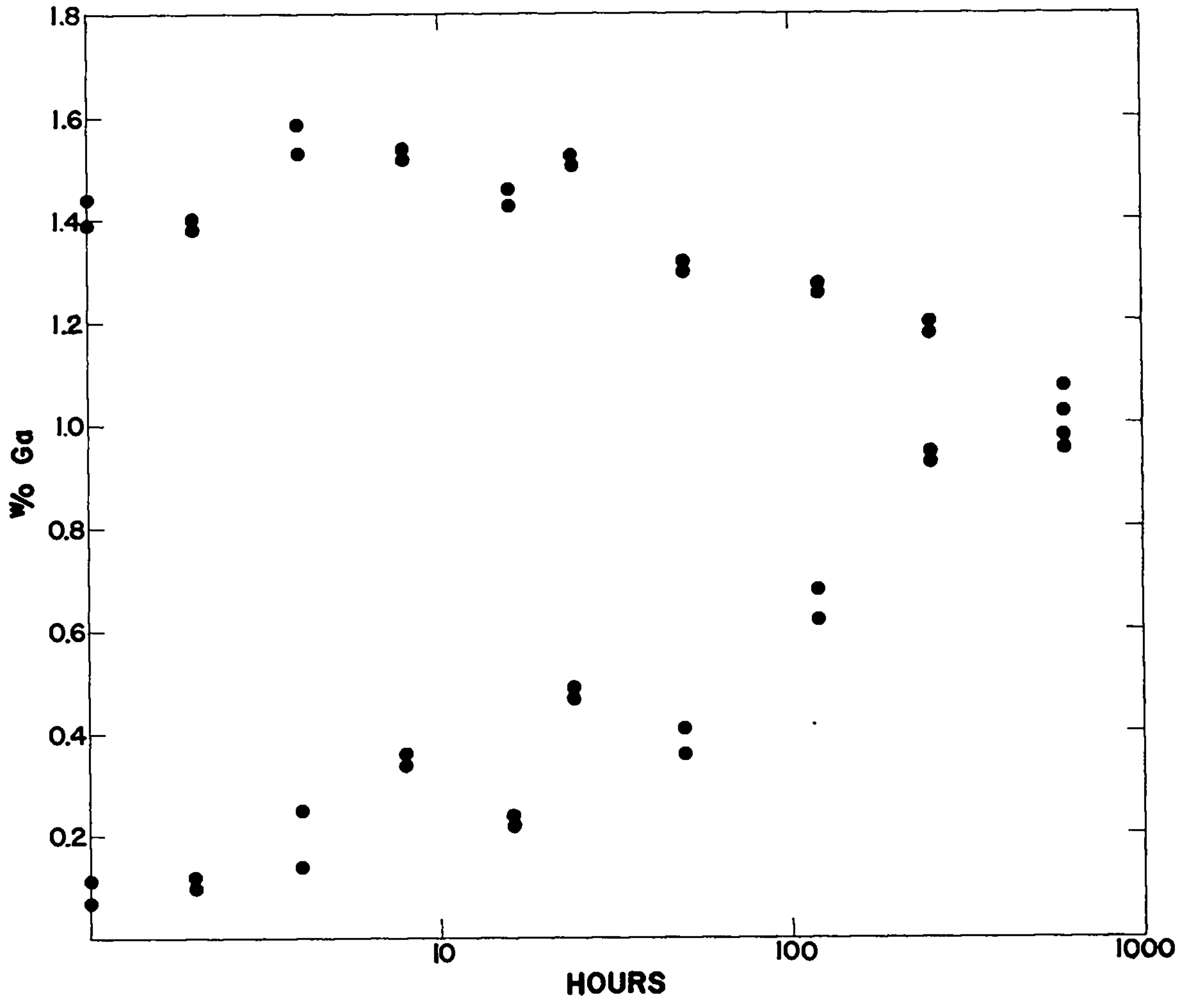

Figure 8. High and low gallium concentration levels found in specimens of the relatively pure cast alloy that had been annealed at 425°C.

Figure 9. Microstructure of cast 1 w/o gallium-stabilized delta plutonium annealed for 1 hour at 500°C. 500 X

Figure 10. Microstructure of cast 1 w/o gallium-stabilized delta plutonium annealed for 2 hours at 500°C. 500 X

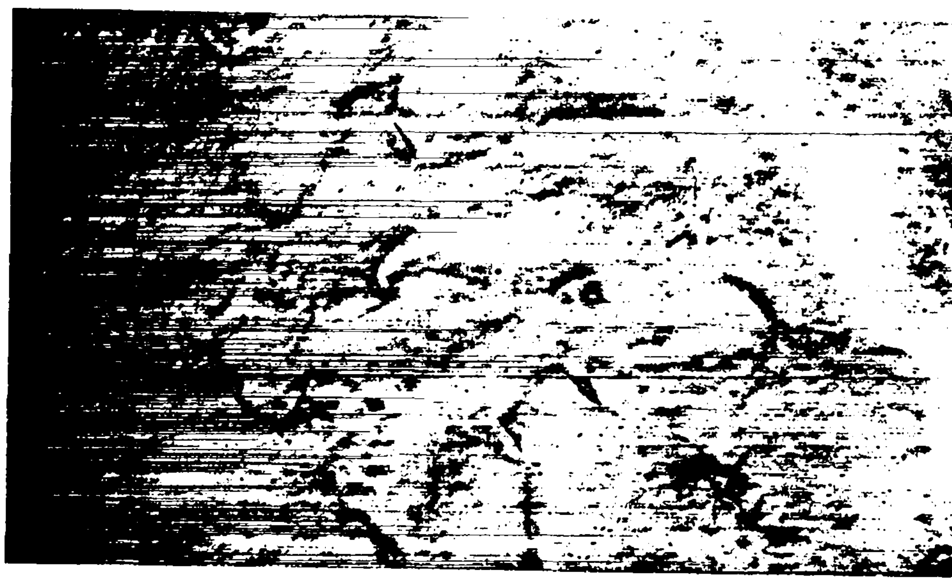

Figure 11. Microstructure of cast 1 w/o gallium-stabilized delta plutonium annealed for 8 hours at 500°C. 500 X

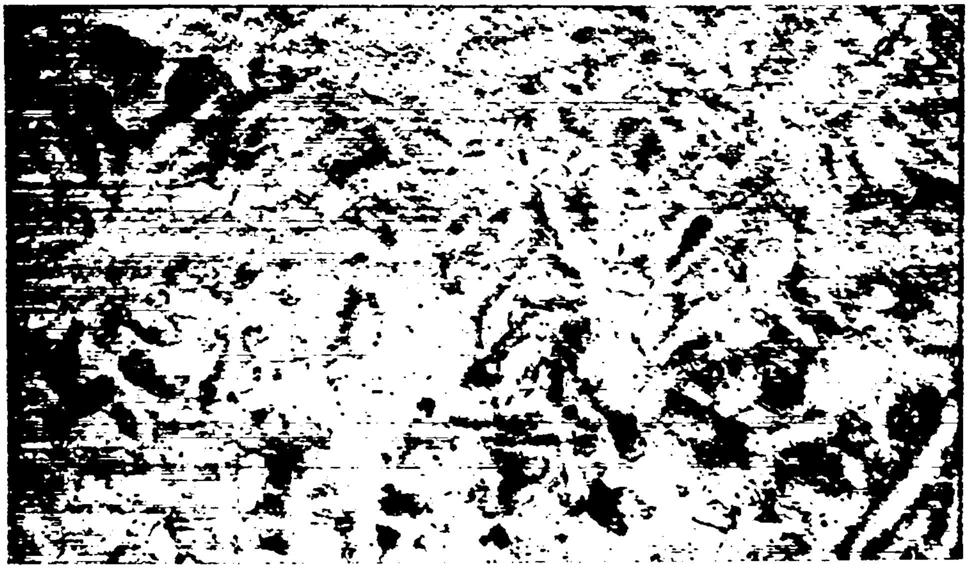

Figure 12. Microstructure of cast 1 w/o gallium-stabilized delta plutonium annealed for 16 hours at 500°C. 100 X

Figure 13. Same as Figure 12. 500 X

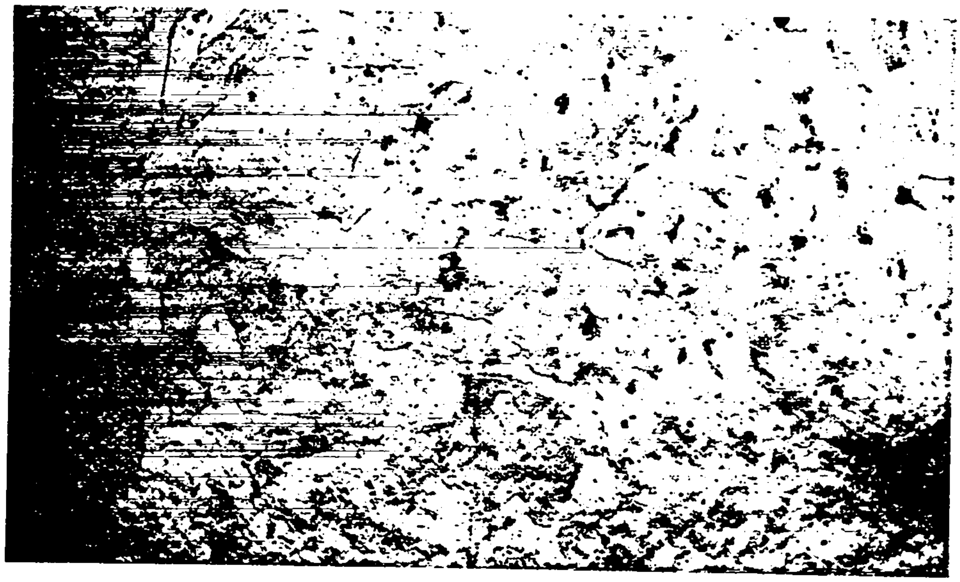

Figure 14. Microstructure of cast 1 w/o gallium-stabilized delta plutonium annealed for 50 hours at 500°C. 100 X

Figure 15. Same as Figure 14. 500 X

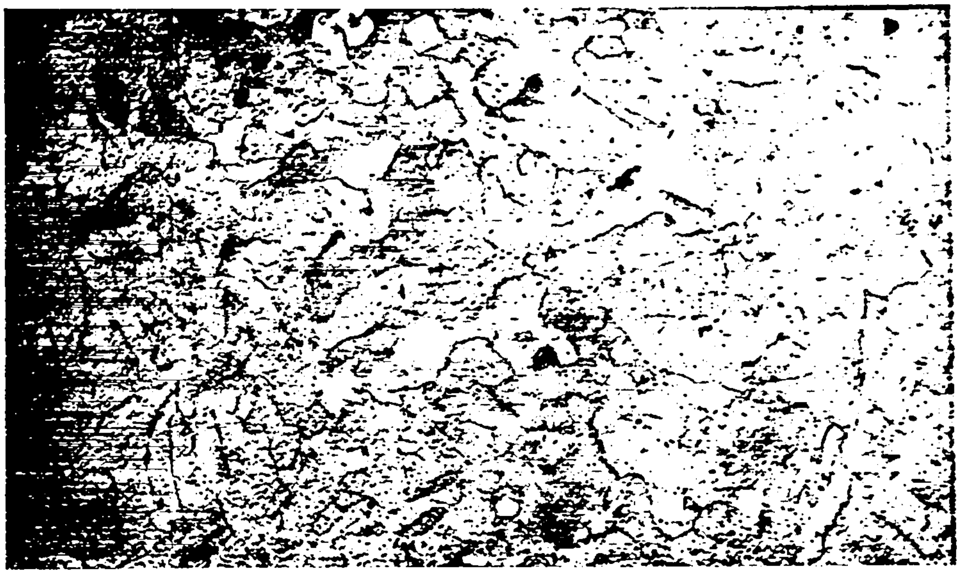

Figure 16. Microstructure of cast 1 w/o gallium-stabilized delta plutonium annealed for 248 hours at 500°C. 100 X

Figure 17. Same as Figure 16. 500 X

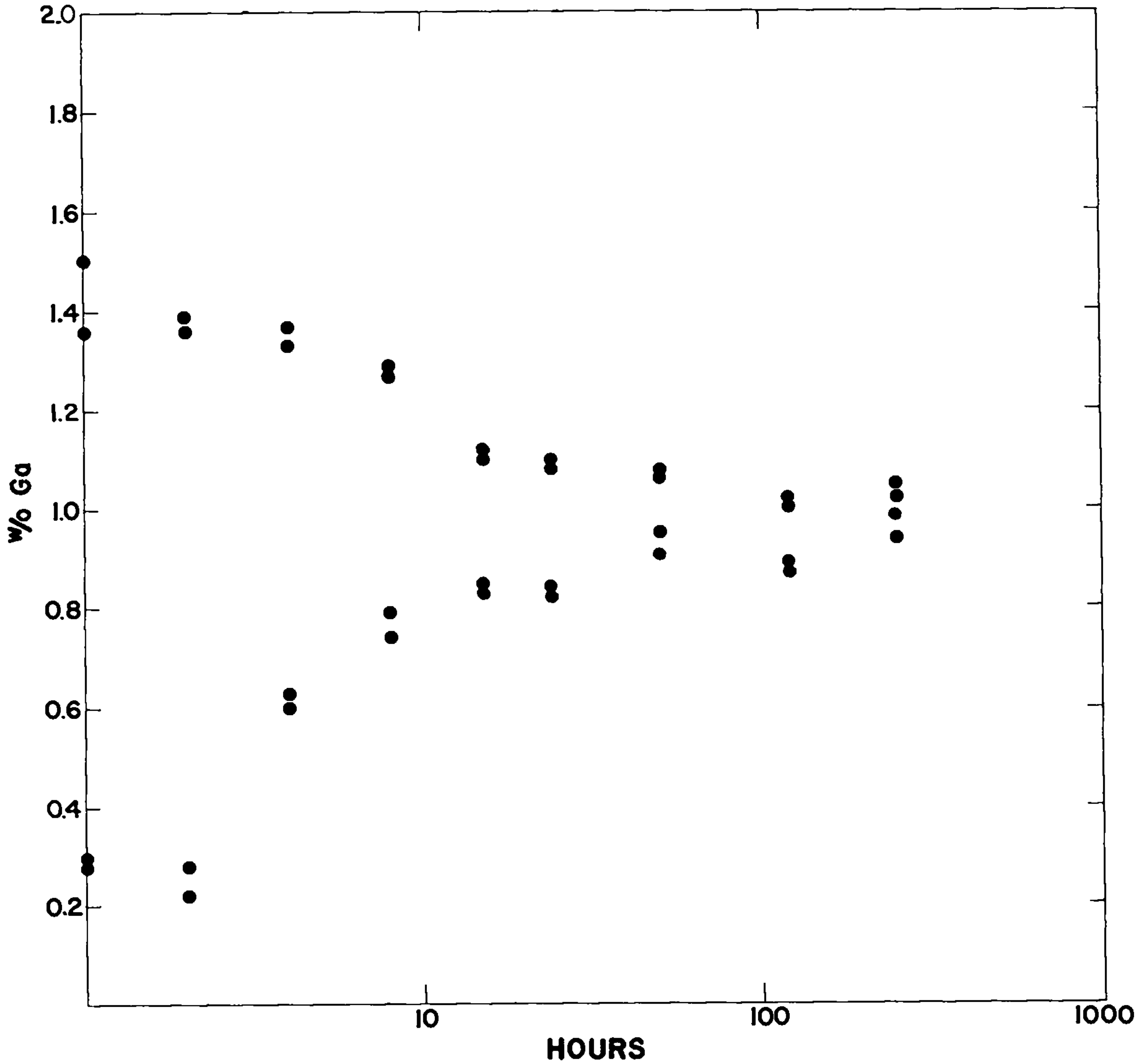

Figure 18. High and low gallium concentration levels found in the relatively pure cast alloy that had been annealed at 500°C.

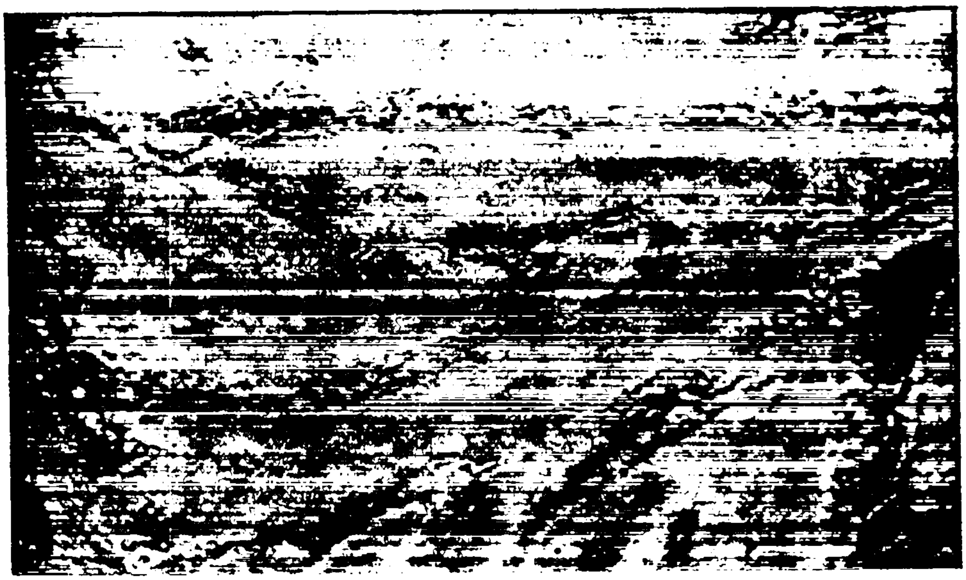

Figure 19. Microstructure of cast 1 w/o gallium-stabilized delta plutonium annealed for 1 hour at 525°C. 500 X

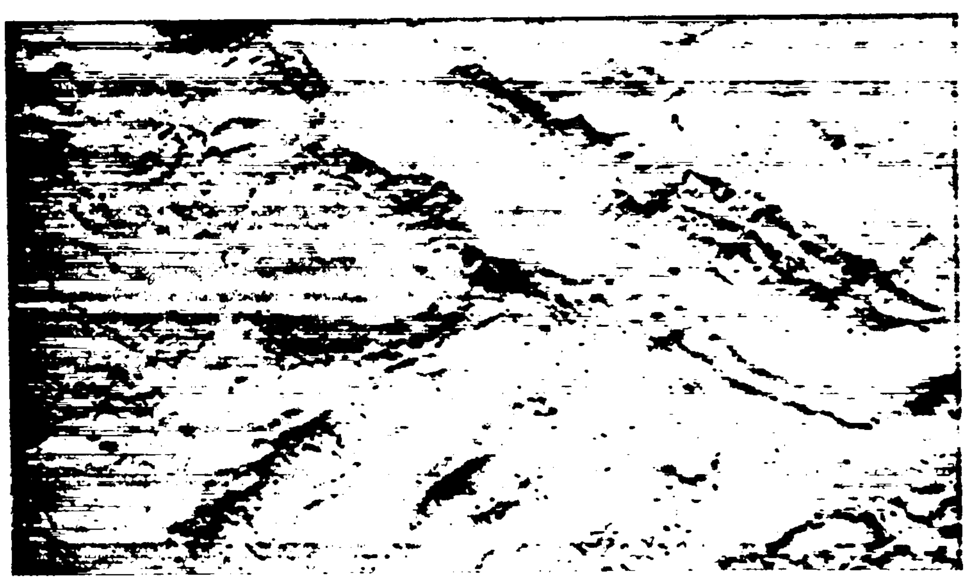

Figure 20. Microstructure of cast 1 w/o gallium-stabilized delta plutonium annealed for 2 hours at 525°C. 500 X

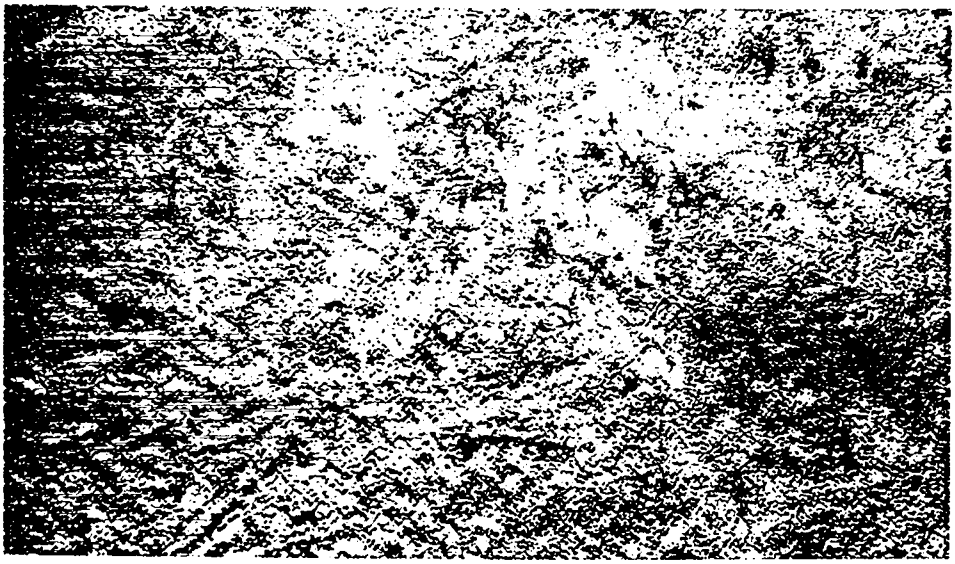

Figure 21. Microstructure of cast 1 w/o gallium-stabilized delta plutonium annealed for 4 hours at 525°C. 100 X

Figure 22. Same sample as Figure 21. 500 X

Figure 23. Microstructure of cast 1 w/o gallium-stabilized delta plutonium annealed for 8 hours at 525°C. 100 X

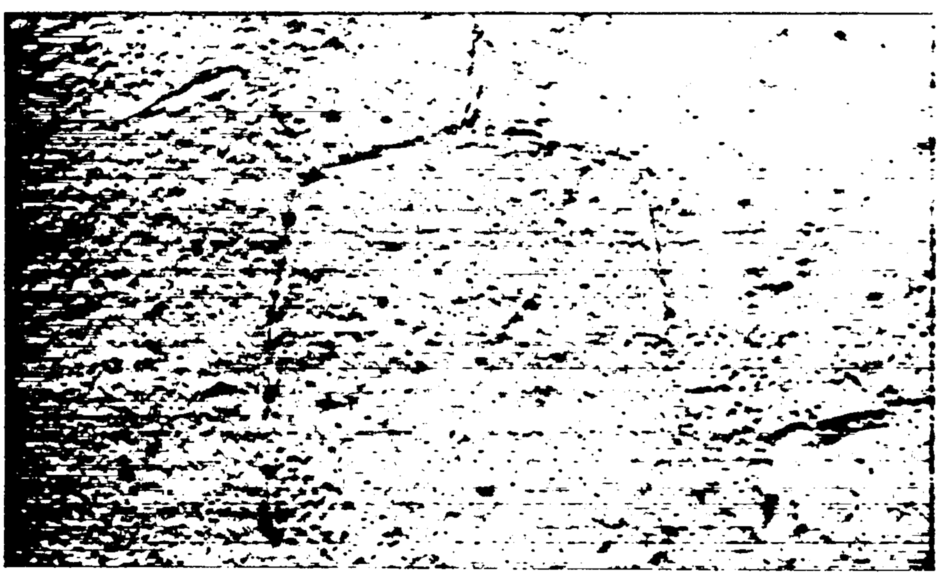

Figure 24. Same specimen as Figure 23. 500 X

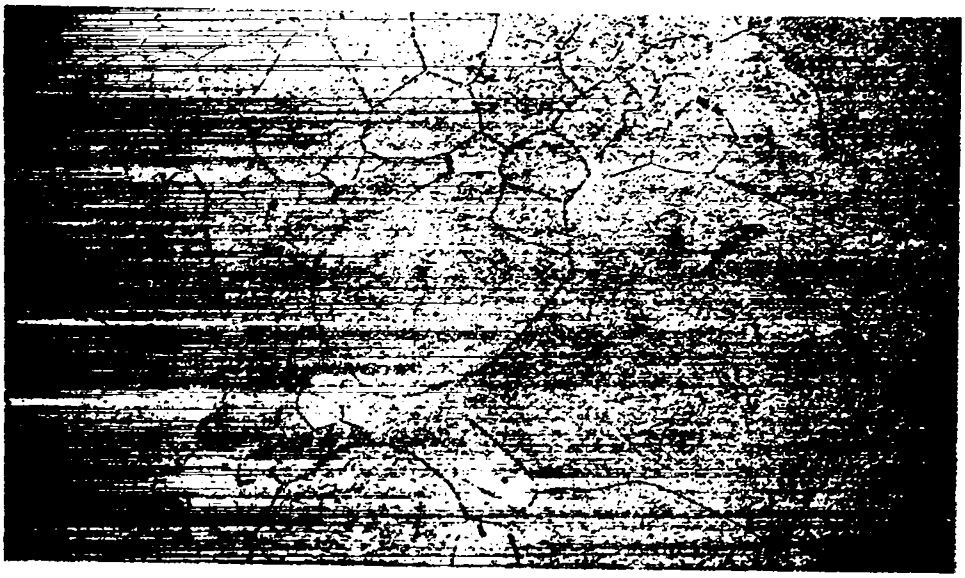

Figure 25. Microstructure of cast 1 w/o gallium-stabilized delta plutonium annealed for 24 hours at 525°C. 100 X

Figure 26. Same specimen as Figure 25. 500 X

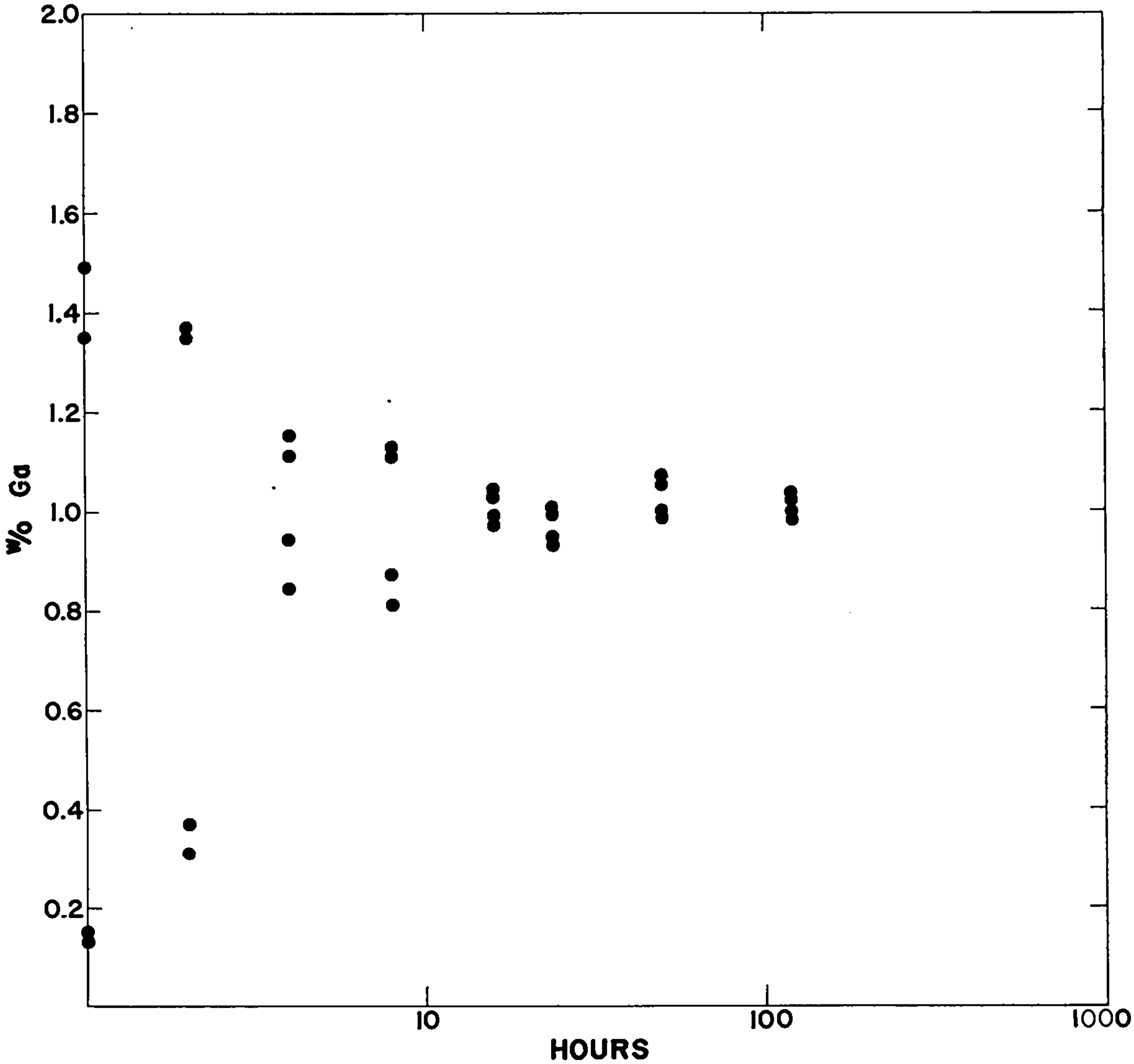

Figure 27. High and low gallium concentrations found in the relatively pure cast alloy that had been annealed at 525°C.

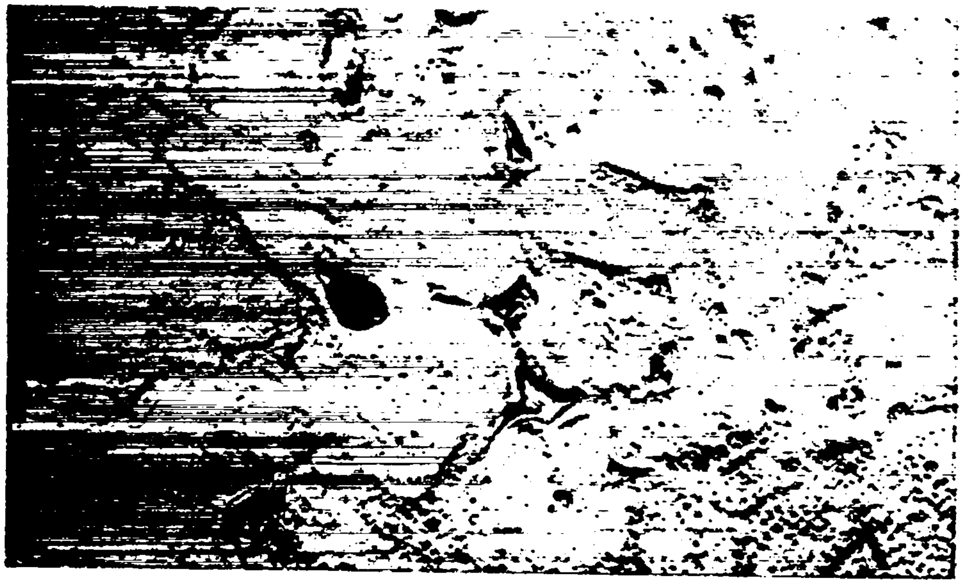

Figure 28. Microstructure of rolled relatively impure 1 w/o gallium-stabilized delta plutonium. 500 X

Figure 29. Microstructure of rolled relatively impure 1 w/o gallium-stabilized delta plutonium annealed for 1 hour at 500°C. 500 X

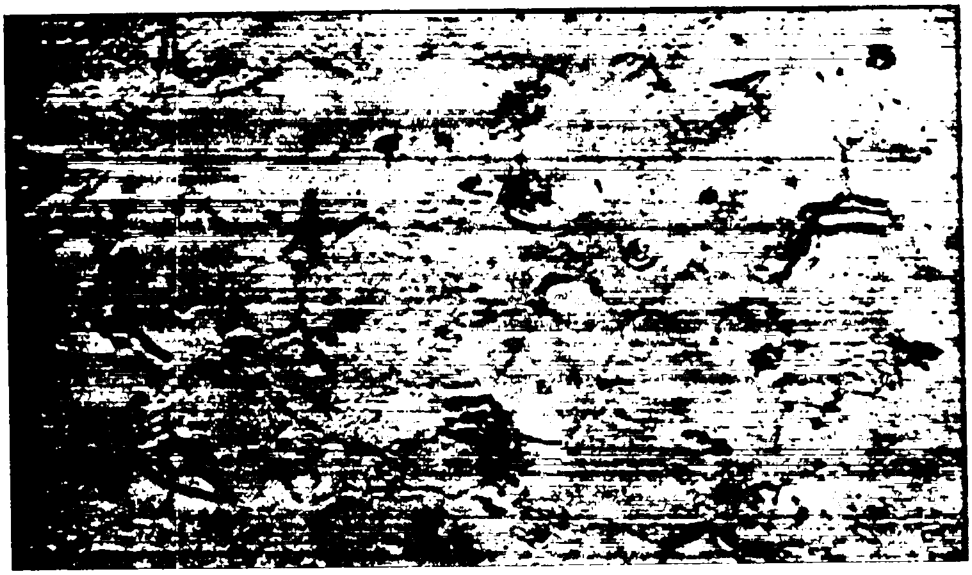

Figure 30. Microstructure of rolled relatively impure 1 w/o gallium-stabilized delta plutonium annealed for 6 hours at 500°C. 500 X

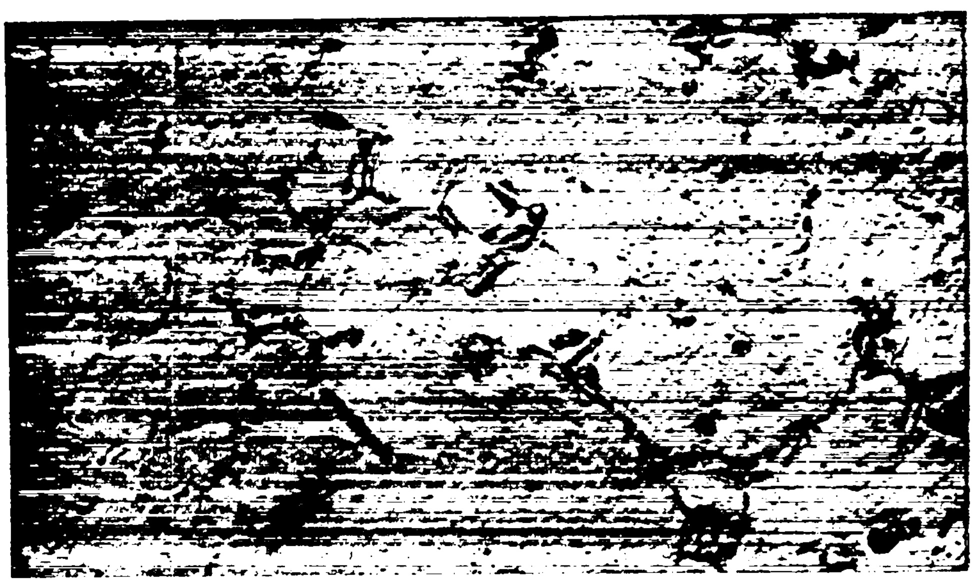

Figure 31. Microstructure of rolled relatively impure 1 w/o gallium-stabilized delta plutonium annealed for 15 hours at 500°C. 500 X

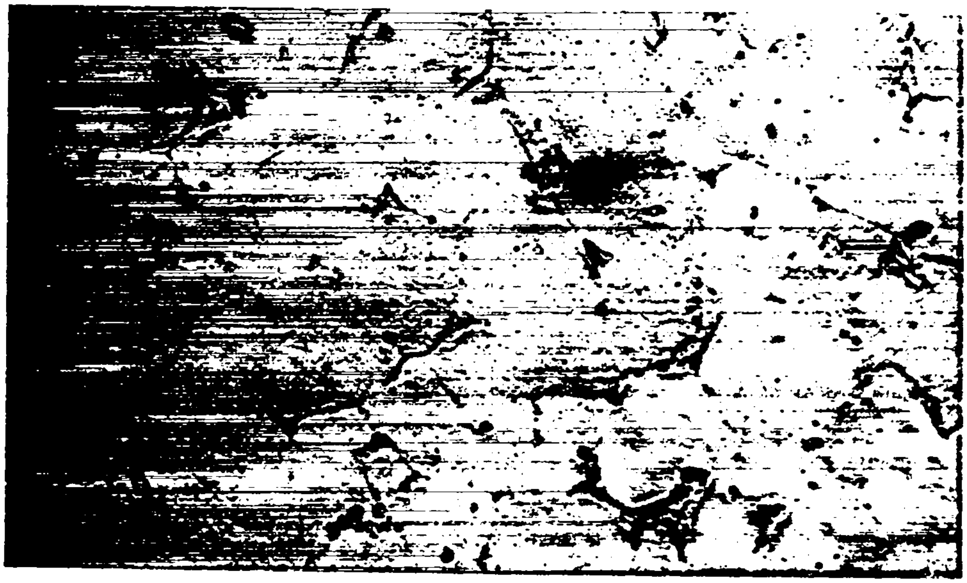

Figure 32. Microstructure of rolled relatively impure 1 w/o gallium-stabilized delta plutonium annealed for 53 hours at 500°C. 500 X

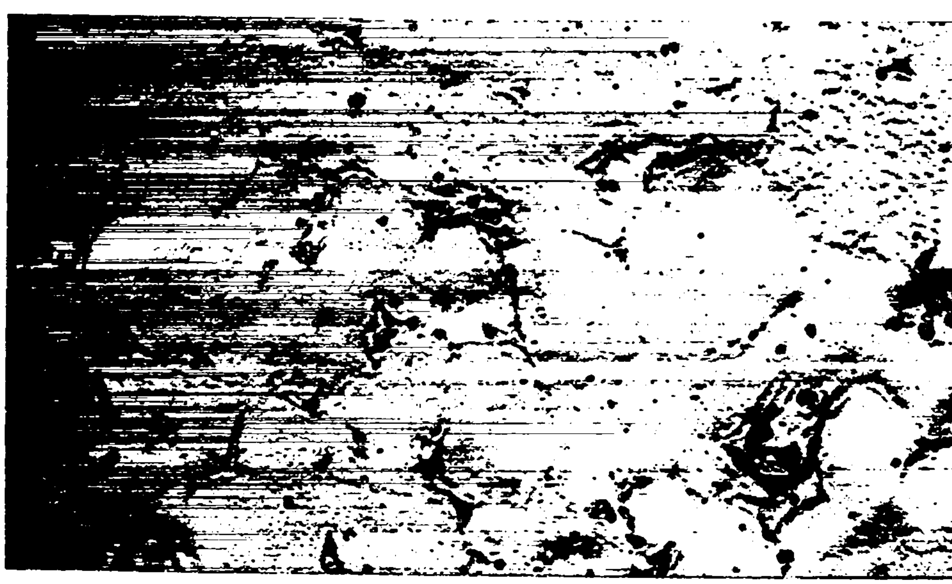

Figure 33. Microstructure of rolled relatively impure 1 w/o gallium-stabilized delta plutonium annealed for 150 hours at 500°C. 500 X

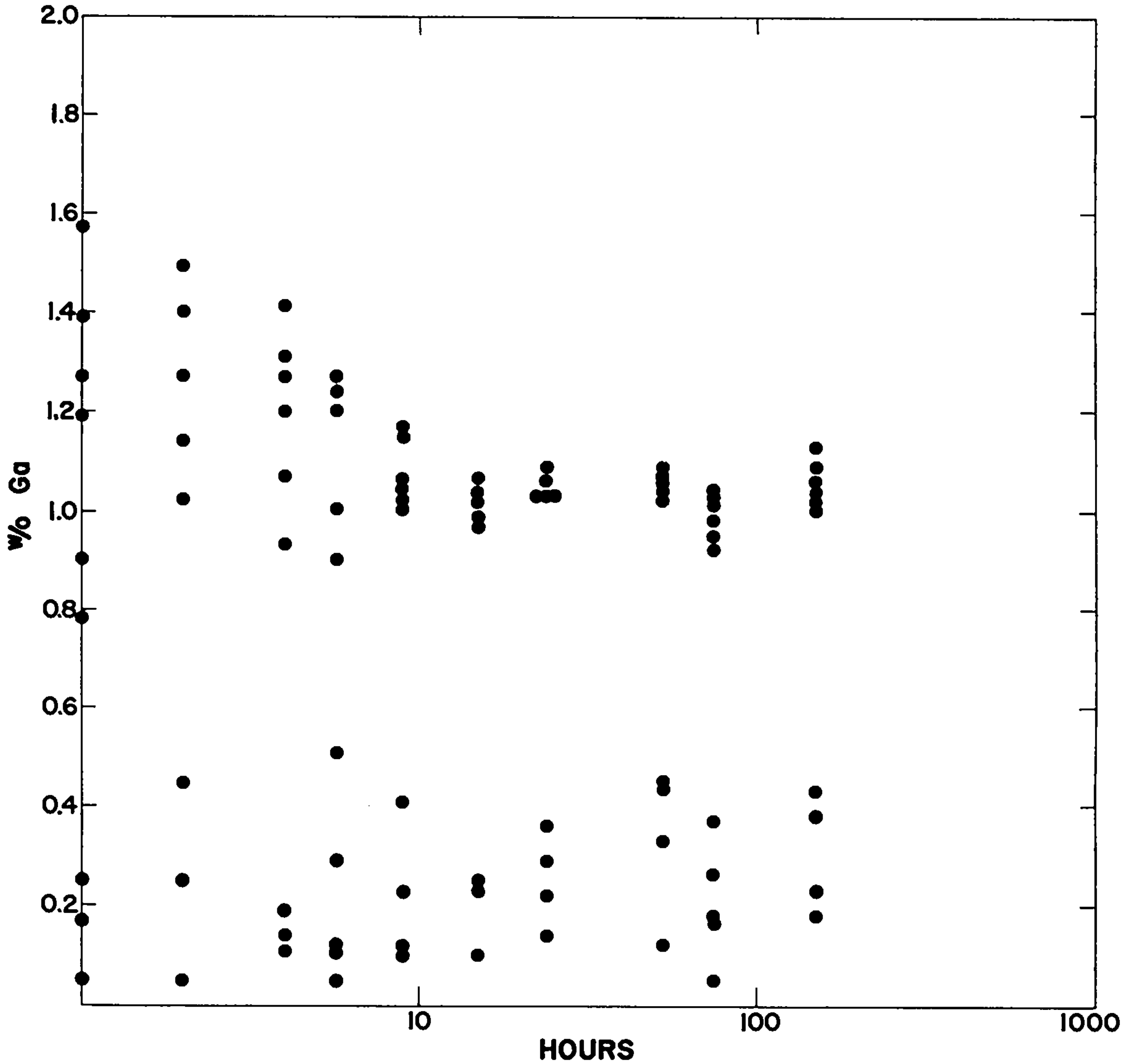

Figure 34. High and low gallium concentration levels found in specimens of the relatively impure rolled alloy that had been annealed.

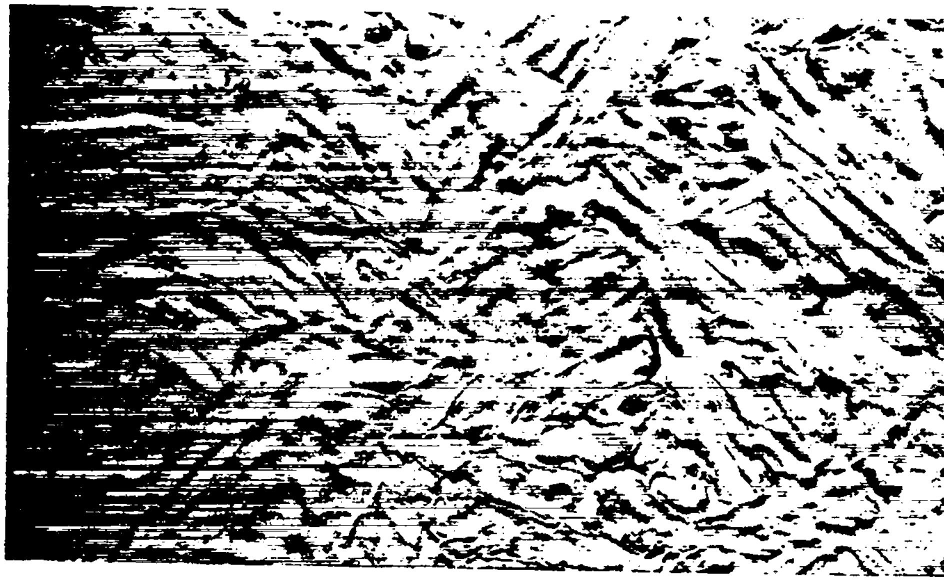

Figure 35. Microstructure of cast 1 w/o gallium-stabilized delta plutonium annealed for 1 hour at 625°C. 500 X

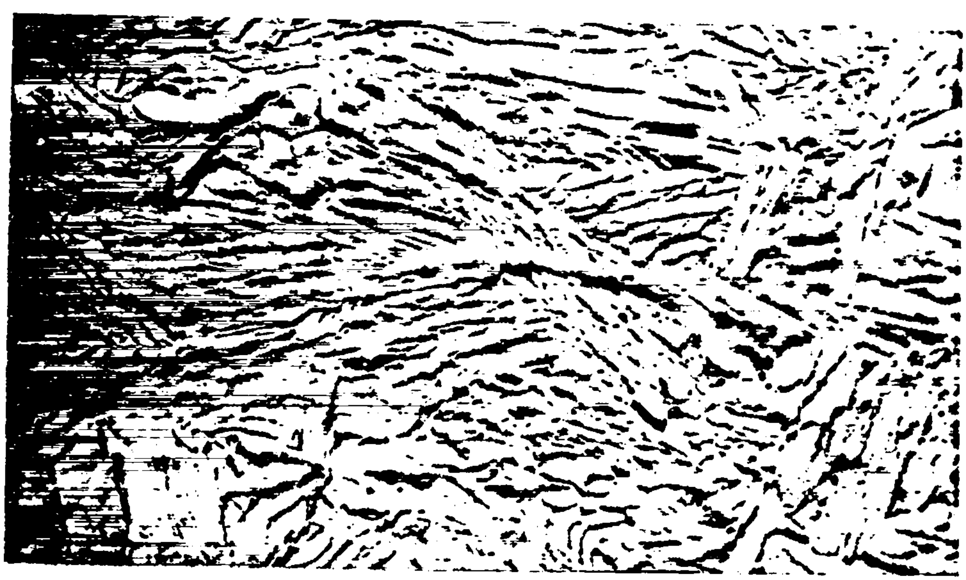

Figure 36. Microstructure of cast 1 w/o gallium-stabilized delta plutonium annealed for 4 hours at 625°C. 500 X

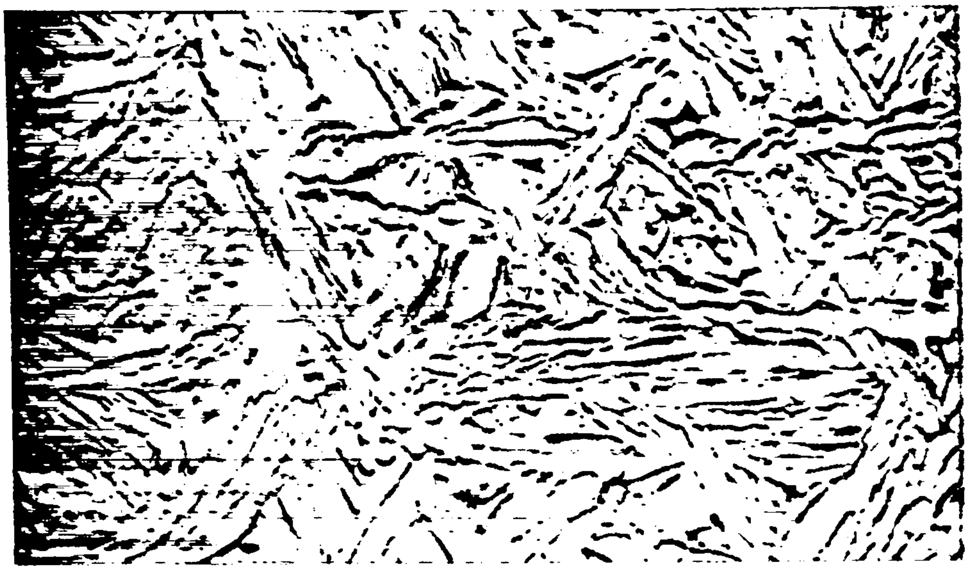

Figure 37. Microstructure of cast 1 w/o gallium-stabilized delta plutonium annealed for 16 hours at 625°C. 500 X

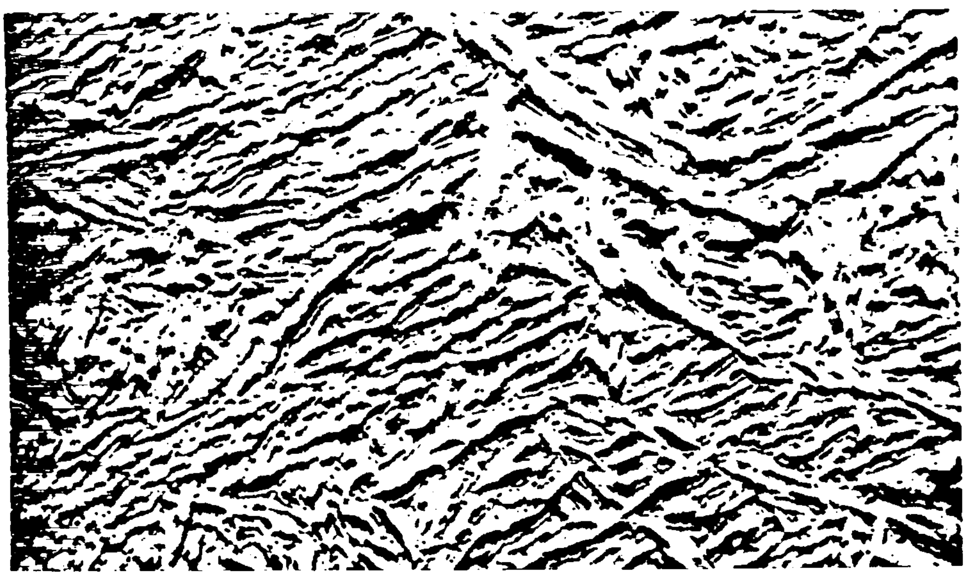

Figure 38. Microstructure of cast 1 w/o gallium-stabilized delta plutonium annealed for 24 hours at 625°C. 500 X

Figure 39. Microstructure of cast 1 w/o gallium-stabilized delta plutonium annealed for 50 hours at 625°C. 500 X

Figure 40. Microstructure of cast 1 w/o gallium-stabilized delta plutonium annealed for 120 hours at 625°C. 500 X

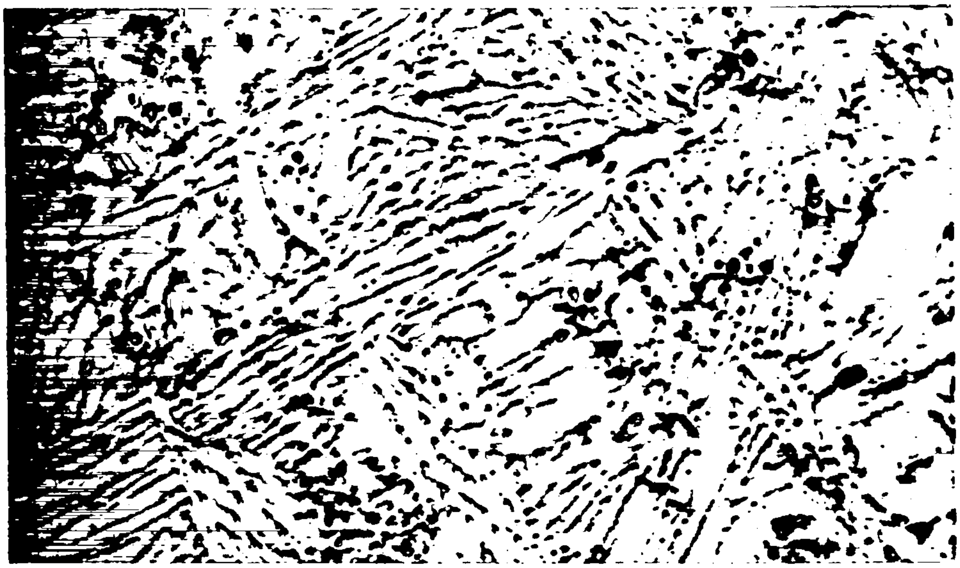

Figure 41. Microstructure of cast 1 w/o gallium-stabilized delta plutonium annealed for 250 hours at 625°C. 500 X

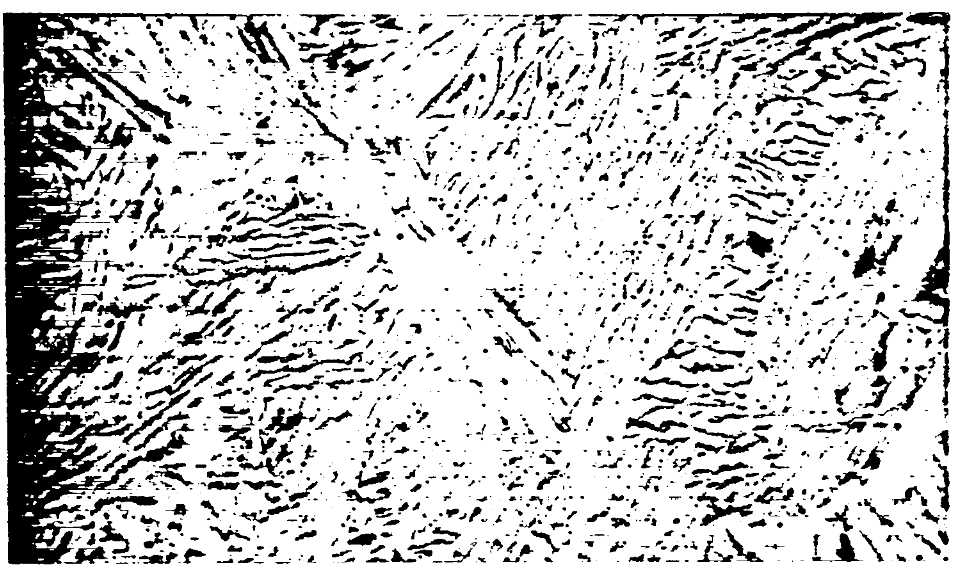

Figure 42. Microstructure of cast 1 w/o gallium-stabilized delta plutonium annealed for 400 hours at 625°C. 500 X

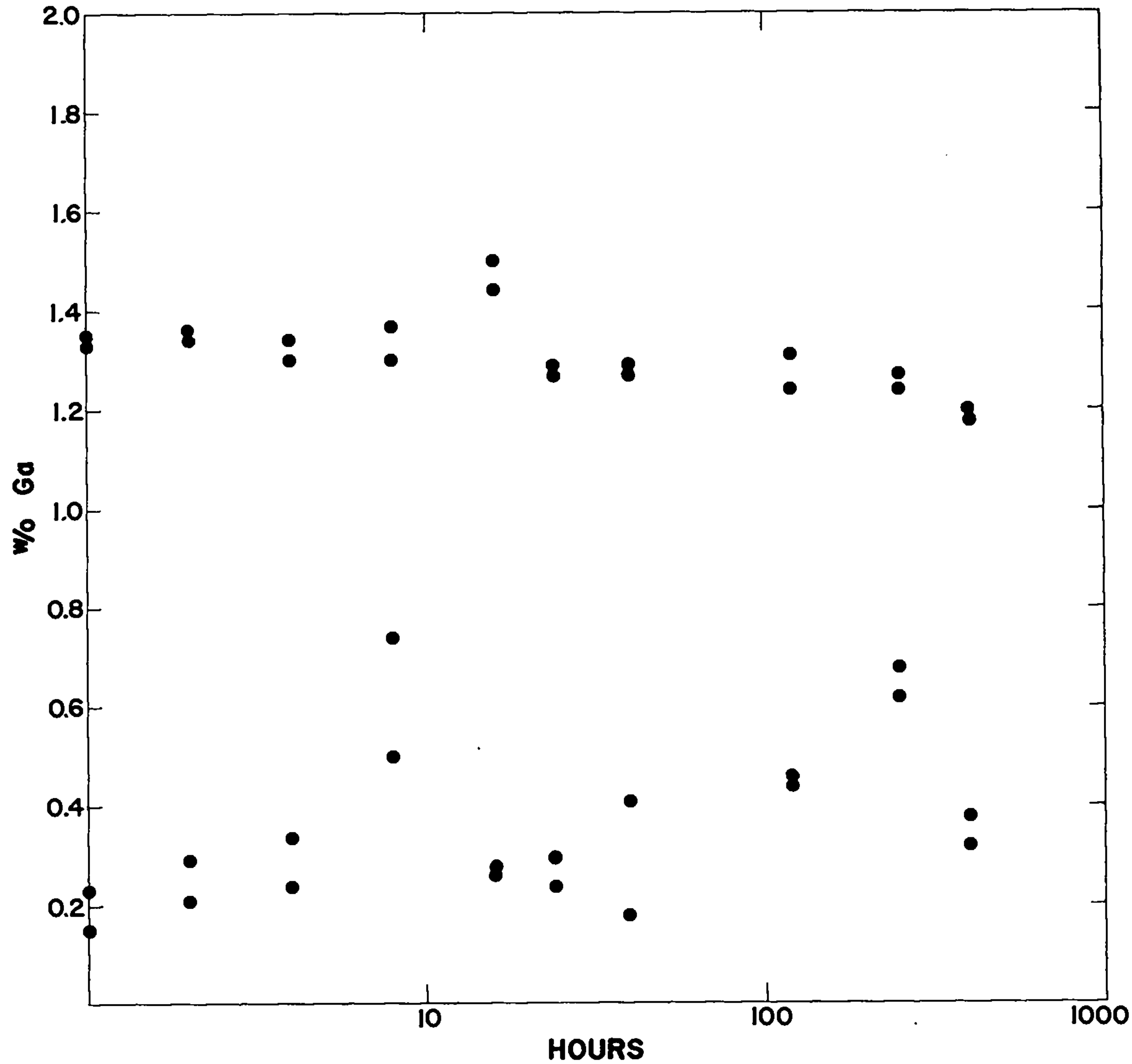

Figure 43. High and low gallium concentration levels found in the relatively pure cast alloy that had been annealed at 625°C.

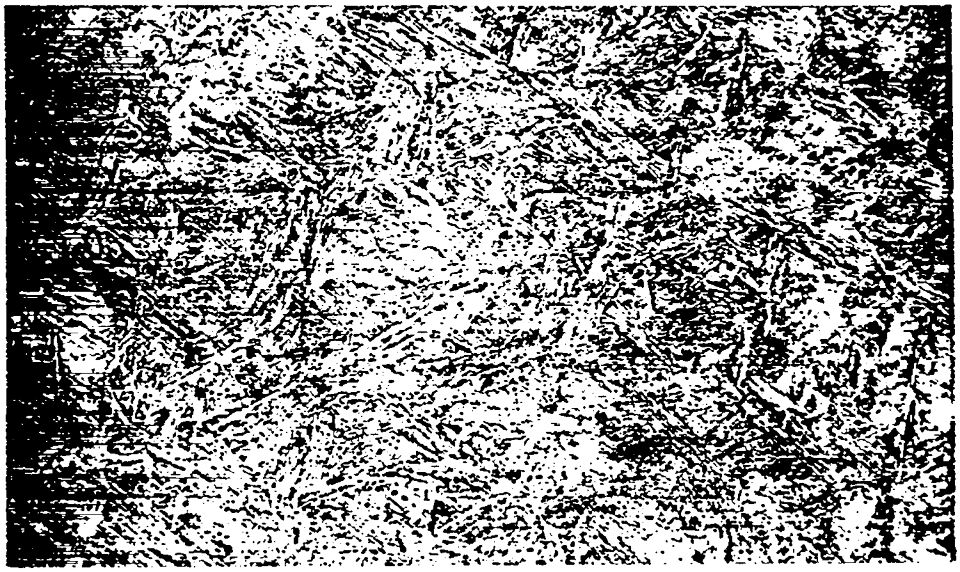

Figure 44. Microstructure of cast 1 w/o gallium-stabilized delta plutonium annealed for 89 hours at 525°C and an additional 25 hours at 625°C. 100 X

Figure 45. Same specimen as Figure 44. 500 X

Figure 46. Microstructure of cast 1 w/o gallium-stabilized delta plutonium annealed for 64 hours at 625°C and furnace cooled through the epsilon-to-delta transformation. 500 X

Figure 47. Microstructure of cast 1 w/o gallium-stabilized delta plutonium annealed for 64 hours at 625°C and air cooled through the epsilon-to-delta transformation. 500 X

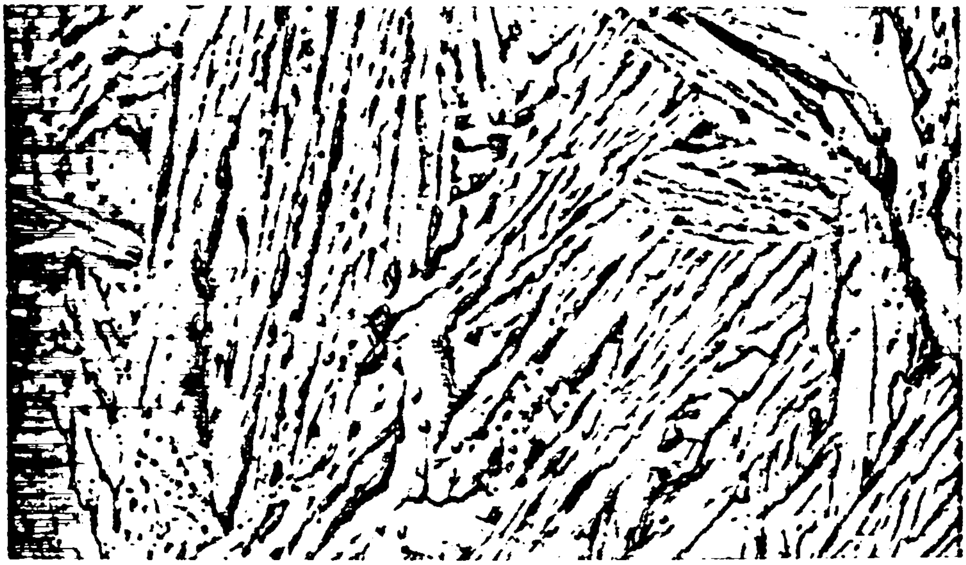

Figure 48. Microstructure of cast 1 w/o gallium-stabilized delta plutonium annealed at 625°C for 50 hours and quenched in water with the capsule unbroken. 500 X

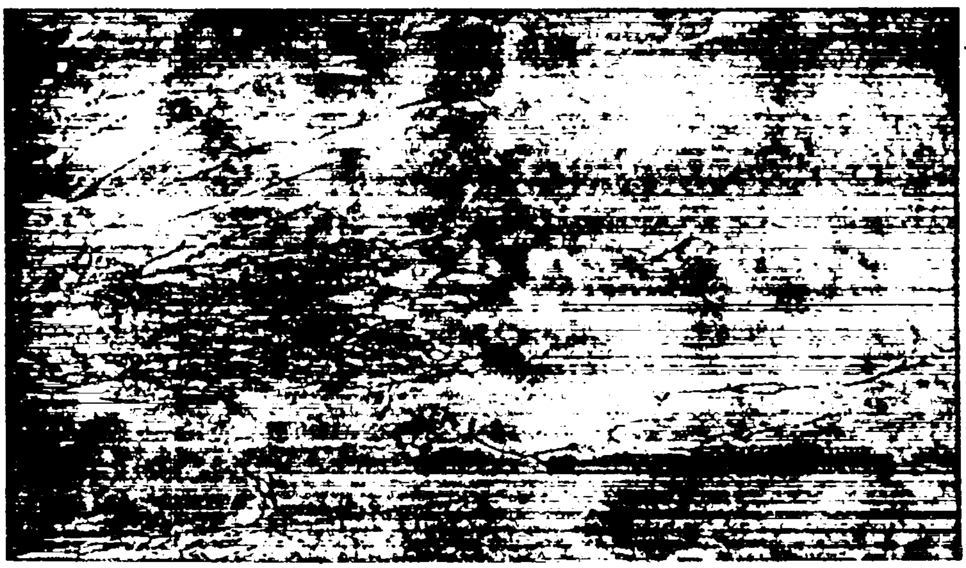

Figure 49. Microstructure of cast 1 w/o gallium-stabilized delta plutonium annealed at 625°C for 90 hours and quenched with the capsule broken under water. 500 X

APPENDIX

Chemical analysis results for the two types of alloy material used. The results are reported as ppm except as noted.

Element	Pure Alloy	Impure Alloy
Al	15	90
B	< 0.5	< 0.5
Be	< 0.1	< 0.1
Bi	< 1	< 1
C	30	130
Ca	10	< 10
Co	< 10	< 10
Cr	< 5	75
Cu	< 2	25
F	< 2	< 2
Fe	20	270
Ga	1.00 w/o	0.99 w/o
La	< 10	< 10
Li	< 0.2	< 0.2
Mg	< 10	10
Mn	< 2	10
Mo	< 1	4.5
Na	< 10	< 10
Ni	< 10	150
Pb	< 10	5
Si	< 10	45
Sn	< 1	2
Ta	< 35	< 35
Th	< 15	< 15
U	< 30	60
W	28	< 2.5
Zn	< 10	< 10