LIPT-RG 69-0259

HIGH PRESSURE CRYSTAL GROWTH OF ALPHA PLUTONIUM*

R. G. LIPTAI and R. J. FRIDDLE

Metallurgy Division, Argonne National Laboratory, Argonne, Illinois, U.S.A.

Reprint from: **JOURNAL OF CRYSTAL GROWTH**

NORTH-HOLLAND PUBLISHING COMPANY – AMSTERDAM

Reprinted from:
Journal of Crystal Growth **5** (1969) 216–218 © *North-Holland Publishing Co., Amsterdam*
Printed in the Netherlands

HIGH PRESSURE CRYSTAL GROWTH OF ALPHA PLUTONIUM*

R. G. LIPTAI and R. J. FRIDDLE

Metallurgy Division, Argonne National Laboratory, Argonne, Illinois, U.S.A.

Received 12 August 1968

Large single crystals of alpha plutonium are grown from the solid-state phase transformation beta to alpha at pressures of 55 kbar. The sample is cooled through the phase transformation between 480 and 400 °C at a rate of 40 °C/hr, annealed at 400 °C for several days, cooled to room temperature and then depressurized.

1. Introduction

In studies of the mechanical and physical properties of metals, use of single crystals is desirable and often mandatory. All attempts to grow single crystals of alpha plutonium by established techniques have been unsuccessful. In part, the lack of success results from the unusual properties of plutonium at atmospheric pressure. For example, plutonium undergoes five solid-state transformations upon cooling from the liquid state (640 °C) to the temperature range of the alpha phase. The low-temperature transformation alpha ⇄ beta occurs at about 112 °C and is accompanied by a 9% volume change.

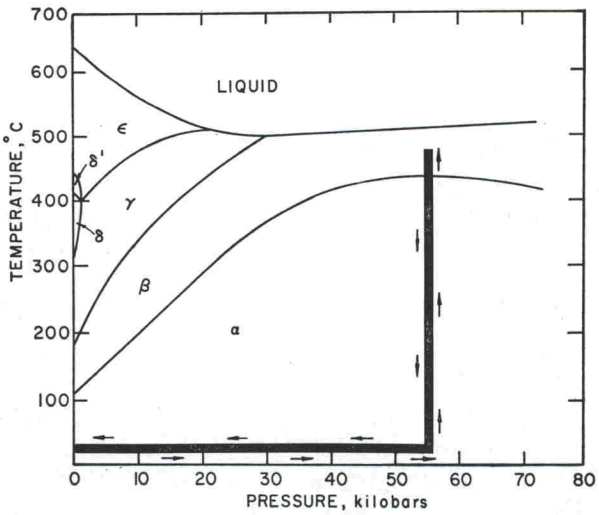


Fig. 1. The phase diagram of plutonium indicating the treatment followed for preparation of crystals of alpha plutonium.

* Work performed under the auspices of the U.S. Atomic Energy Commission.

The use of high-pressure and high-temperature has been suggested for the growth of alpha-plutonium crystals[1]). The pressure–temperature phase diagram of plutonium (fig. 1) shows that the temperature of the alpha ⇄ beta transformation is raised from 112 °C at atmospheric pressure to over 400 °C at 40 kbar. Also, pressures over 30 kbar reduce the number of solid-state phases to two, alpha and beta. In a previous report[2]), the volume change during the beta → alpha transformation was shown to vary linearly with pressure and the volume change that occurs during the beta → alpha transformation is zero at pressures of 55 kbar. From this, we conjectured that the phase-transformation technique could be used to grow crystals of alpha plutonium at pressures of this magnitude. The paper will describe high-pressure techniques that resulted in the successful preparation of single crystals of alpha plutonium.

2. Experimental

Crystals of alpha plutonium were grown in a "belt-type" high-pressure apparatus (12.7 mm diameter "belt" cylinder). A specimen cell assembly is shown in fig. 2. Specimens were surrounded with an annulus of sodium and contained in a stainless steel capsule. Programmed heating and cooling were performed in a graphite-tube furnace. A chromel–alumel thermocouple (see fig. 2) was used to control and monitor temperature. Established experimental techniques and proce-

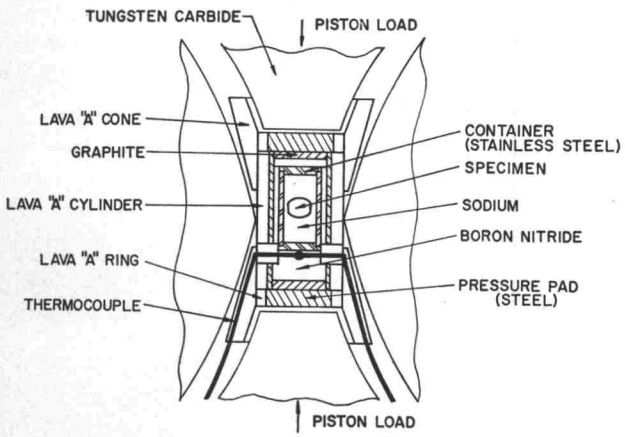


Fig. 2. High-pressure specimen cell assembly.

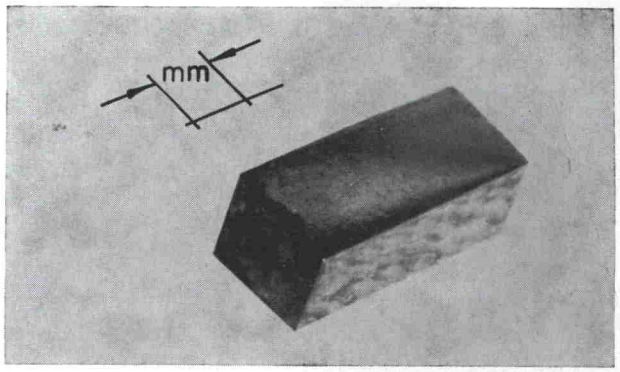
dures, which have been reported elsewhere[3]), were used.

The specimens were prepared by rolling at a temperature that corresponds to the beta phase, 150 °C, cooling in silicone oil to room temperature, and machining to size (5.0 mm diameter and 3.8 mm long with 1.5 mm radius corners). All of the plutonium used had been purified by fused-salt electrorefining[4]). Total impurity contents, exclusive of americium, were 300 ppm by weight. The americium content, which was due to decay of ^{241}Pu, was about 200 ppm at the time of the experiments. Metallographic and back-reflection Laue techniques were used to characterize the crystals.

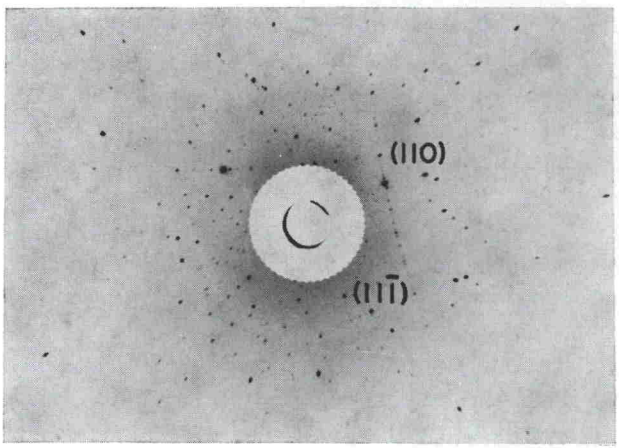
The chronology of a typical experiment for preparation of alpha-plutonium crystals follows. After insertion of the cell assembly into the pressure apparatus, the pressure was increased to 55 kbar (see fig. 1). The sample was quickly heated to 480 °C and maintained at 480 °C for 1 to 2 days. Then, the sample was cooled through the beta → alpha transformation at a rate of 40 °C/hr to 400 °C, held at this temperature for periods of 1 to 5 days, cooled to room temperature, and depressurized.

3. Results and discussion

A crystal prepared by solid state phase transformation technique at high pressures is shown in fig. 3a. The crystal was removed from a polycrystal matrix by mechanical grinding. The back-reflection Laue photogram of one of the surfaces (fig. 3b) shows individual spots free of asterism, which indicates a strain-free condition, as opposed to continuous and diffuse Debye rings observed on X-ray patterns of the rolled material.



(a)



(b)

Fig. 3. (a) Single crystal of plutonium prepared by the high-pressure and temperature treatment indicated in fig. 1. (b) Back-reflection Laue pattern of one of the surfaces on the sample shown in (a). Tungsten radiation, 50 kV, 20 mA, 3 cm specimen-to-film distance, 1 mm collimator, 4 h exposure.

When samples were surrounded by a solid, pressure-transmitting medium such as boron nitride, severe subgraining occurred at all pressures. This condition suggested that during the high-pressure, high-temperature treatments the samples were subjected to nonhydrostatic components of pressure (shear stresses) that plastically deformed the samples and led to the formation of subgrains. Therefore, samples were surrounded by an annulus of sodium to achieve *truly* hydrostatic conditions.

Experiments conducted at 55 kbar were most successful since the zero volume change minimizes the transformation strains generated during the beta → alpha transition. Of course, the transformation strains due to the crystallographic relationships between the alpha and beta phases are still present. Since most evidence suggests that the beta → alpha transformation is mar-

tensitic, the crystallographic aspects are believed to play a significant role in the growth of large crystals from the beta phase[5,6]). Experiments at one atmosphere showed that the original grain size is retained after one cycle of heating and cooling (alpha → beta → alpha), but a considerable amount of substructure develops[6]). It is considered that a large beta grain size is desired during high-pressure, high-temperature experiments. Heat treating at 480 °C (beta phase) allowed sufficient grain growth, thus, reducing the anisotropic effects of thermal expansion and/or linear compressibility, and apparently minimizing the number of potential nucleation sites. Cooling through the beta → alpha transformation at rates substantially different than 40 °C/hr appeared to be detrimental to the growth of large grains of alpha plutonium. Holding at 400 °C and 55 kbar (alpha phase) allowed some grain boundary migration to a more equiaxed microstructure with regular grain boundaries. The rates of cooling, from 400 °C to room temperature, and depressurization had no observable effect on the final microstructure of alpha plutonium.

Large crystals of alpha plutonium were not obtained when samples were heated into the liquid phase prior to the beta and alpha phase treatments at a pressure of 55 kbar. Even though it was possible to contain liquid plutonium in liquid sodium (the oxide that covered the sample served as a container), results were not encouraging. The resulting microstructures consisted of small, strain-free grains (0.05 mm) that are slightly misoriented (0.2°) with respect to each other.

The size of the crystals produced is limited to the maximum specimen size that can be accommodated in the high-pressure "belt" apparatus. The maximum size obtained has corresponded to 75% of the specimen volume. Subgraining remains a problem, but the orientation difference is usually less than 0.5° and the subgrains are relatively large.

Acknowledgments

The authors wish to express their gratitude to Merwyn Brodsky for reviewing the manuscript. Thanks are extended to C. Barnes for editorial suggestions. Also, we wish to acknowledge Lowell Lloyd for his encouragement throughout this study.

References

1) R. G. Liptai, L. T. Lloyd and R. J. Friddle, in: *Crystal Growth*, Ed. H. S. Peiser (Pergamon, Oxford, 1967) p. 573.
2) R. G. Liptai and R. J. Friddle, J. Nucl. Mater. **20** (1966) 48.
3) H. T. Hall, in: *Metallurgy at High Pressures and High Temperatures*, Ed. K. A. Gschneidner, Jr. (Gordon and Breach, New York, 1964) p. 133.
4) B. Blumenthal and M. B. Brodsky, in: *Plutonium-1960*, Eds. E. Grison et al. (Cleaver-Hume, London, 1961) p. 171.
5) M. Rosen, L. T. Lloyd and R. G. Peterson, *Plutonium-1965*, Eds. A. E. Kay and M. B. Waldron (Chapman and Hall, London, 1967) p. 18.
6) R. J. Friddle and R. G. Liptai, unpublished work.

PRINTED IN THE NETHERLANDS