UC-25
Reporting Date: February 1976
Issued: April 1976

An Application of Transmission Electron Microscopy to Splat-Cooled Plutonium Alloys

by

Dana L. Rohr
R. O. Elliott

los alamos
scientific laboratory
of the University of California
LOS ALAMOS, NEW MEXICO 87545

UNITED STATES
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
CONTRACT W-7405-ENG. 36

Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22151
Price: Printed Copy $3.50 Microfiche $2.25

AN APPLICATION OF TRANSMISSION ELECTRON MICROSCOPY TO SPLAT-COOLED PLUTONIUM ALLOYS

by

Dana L. Rohr and R. O. Elliott

ABSTRACT

Plutonium alloy foils, thin enough for transmission electron microscopy (TEM), were made by rapidly quenching small specimens from the melt in a "gun"-type, splat-cooling device. Microstructures in selected regions of the nonequilibrium alloys thus produced are illustrated and discussed. To our knowledge, all previous attempts to do TEM on plutonium and its alloys have failed.

I. INTRODUCTION

The earliest attempt to make plutonium samples for transmission microscopy at the Los Alamos Scientific Laboratory (LASL) began in the fall of 1963, when rolled alpha (pure) and rolled delta (alloyed) sheets were thinned electrochemically. (See Ref. 1 for indirect reference.) The oxidation-sensitive nature of plutonium invariably caused the end product to be a sandwich of thin metal between relatively thick layers of oxide. Such samples were unsuitable and the work was discontinued. Other workers[2-4] also tried electrothinning with similar results. As far as we know no other attempts have been made since 1967. At that time elaborate inerting systems seemed necessary for both the dry box and thinning equipment; such a scheme was considered by Wadleigh[5] but was never implemented. Ion-thinning techniques were also considered,[6] but again experimental difficulties led to abandonment of the effort.

In 1962 Willens[7] had shown that rapid quenching from the melt (splat cooling) in a "gun"-type apparatus produced thin foils suitable for TEM. Since then it was known that this technique promised a way of obtaining TEM samples of plutonium alloys. However, it was more than a decade later before a splat-cooling apparatus of this type was built at LASL for work with plutonium and other alpha-radioactive materials.[8] Briefly, this splat-cooling apparatus quenches samples by means of a shock pulse which ejects a bead of molten metal through a hole ~1 mm in diameter in the bottom of a ceramic crucible and onto a relatively massive copper or silver target plate. The force of the shock wave ejects the molten material from the crucible at high velocity as a fine spray of micron-sized droplets that impinge on the target plate. Rapidly quenched samples thus produced are porous in nature; nevertheless they are suitable for analysis by standard x-ray diffraction methods and, in some cases, by TEM, as will be shown.

The porous, splatted deposit is made up of many thin foils of irregular size and shape that overlap in places and stick together. The thickness of individual foils varies from a few hundred angstroms near edges and around holes to many microns at the center. Small chips of the splatted deposit can be lifted from the target plate with tweezers or a needle. Such chips or flakes were mounted between two electron microscope grids and placed in the microscope for examination. In nearly every case, the edges of such chips were transparent to the electron beam and proved quite suitable for viewing. Using standard precautions for handling alpha-radioactive materials,[1] the sample was taken from the vacuum atmosphere of the splat-cooling apparatus and placed in the vacuum atmosphere of the microscope. Exposure to air was usually 10 min or less and no observable degradation of the sample surface occurred.

However, in regions thin enough for electron transparency the samples often showed a heavy oxide deposit which prevented observation of the microstructure of the metal or alloy. Table I lists the splat compositions examined by TEM. The plutonium-gallium alloys, pure plutonium deposits, and neptunium-cobalt alloys were particularly susceptible to oxidation based on electron diffraction evidence. The patterns of all alloys examined were made up of a mixture of alloy and oxide spots. These spots could be separated and indexed only with considerable difficulty under favorable circumstances. We also observed that when a sample was subjected to unusual electron beam heating it was converted to small grains of PuO_2, as illustrated in Fig. 1. The electron diffraction pattern of the sample is shown in the lower left-hand corner of the figure. In the plutonium-titanium and plutonium-cerium systems, however, a few regions were found where, under normal operating conditions, the splat deposits showed only a thin oxide layer that did not obscure the structures of interest.

DISCUSSION OF RESULTS

A transmission electron micrograph of an as-deposited fcc δ-plutonium solid solution containing 18 at.% titanium appears as Fig. 2. Bands of changing orientation, presumably twin bands or kink bands, are common; this might be expected in a material with a complex thermal and mechanical history such as occurs during splat cooling and non-equilibrium solidification. Appearance of twin bands in Fig. 2 is in agreement with a very large twinning fault probability in a nearly identical δ-plutonium alloy containing 15 at.% titanium, based on a line-broadening effect in the x-ray diffraction pattern.[9] Particles, presumably of the equilibrium α-titanium phase, that have precipitated can be seen in the matrix. The TEM evidence thus suggests that the δ-phase in this 18 at.% titanium alloy may not have formed directly from the melt during rapid quenching, but rather that it might have been the product of a solid-state martensitic transformation from the high-temperature bcc form of plutonium ($\mathcal{E}$-phase).

The microstructure of another as-deposited δ-plutonium solid solution containing 22.5 at.% cerium is shown in Fig. 3. Again, fine bands with a width of 50 to 80 Å can be seen in the figure, indicating that this alloy may also have been formed by transforming martensitically from an $\mathcal{E}$-plutonium solid solution during the quench. The streaked electron diffraction pattern in Fig. 3. indicates the existence of thin plates in the microstructure aligned parallel to the electron beam, in agreement with the appearance of the twinning seen in the micrograph.

Splat cooling of binary and multi-component alloys has produced many amorphous phases.[10] These are formed when molten alloys are quenched rapidly enough to suppress crystallization and may be considered to be undercooled liquids. The presence of such a phase may have been found in selected regions of splat-cooled plutonium-gallium alloys, where microstructures in the 25 to 50 at.% gallium range tended generally to appear free of structural details and where electron diffraction showed only very diffuse rings, as illustrated in Fig. 4. X-ray scattering patterns verified the non-crystallinity in 45-50 at.% gallium alloys.[11]

TABLE I

COMPOSITION OF SPLAT-COOLED SAMPLES EXAMINED BY TEM

plutonium 40 at.% titanium
plutonium 25 at.% titanium
plutonium 20 at.% titanium
plutonium 18 at.% titanium
plutonium 5 at.% titanium
plutonium 30 at.% cerium
plutonium 25 at.% cerium
plutonium 22-1/2 at.% cerium
plutonium 5 at.% cerium
plutonium 45 at.% gallium
plutonium 35 at.% gallium
plutonium 25 at.% gallium
plutonium 20 at.% gallium
plutonium 17-1/2 at.% gallium
plutonium 15 at.% gallium
plutonium 12-1/2 at.% gallium
plutonium 7-1/2 at.% gallium
plutonium 3-1/2 at.% gallium
plutonium 12 at.% nickel
neptunium 14 at.% cobalt
α-plutonium

SUMMARY

Our experience with splat cooling by the "gun" technique has demonstrated a limited usefulness of that method as a tool for producing thin foils of plutonium alloys for TEM. This has enabled us for the first time to look at and photograph the microstructures of plutonium alloys by TEM methods.

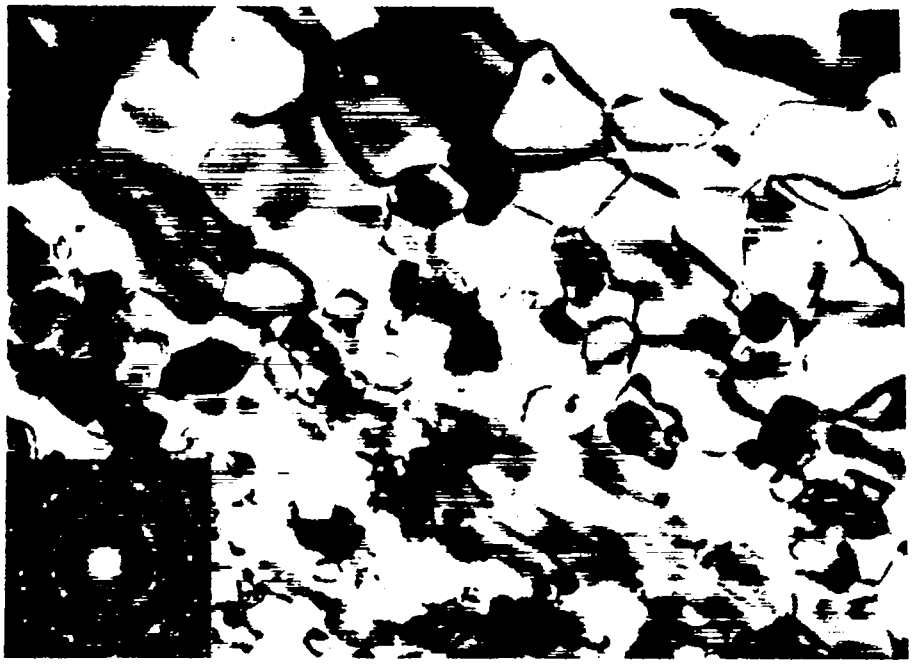

Fig. 1.
PuO_2 crystallites formed by electron beam heating in the electron microscope. Magnification = 70 000.

Fig. 2.
Fine twin bands in an 18 at.% titanium-plutonium alloy. Magnification = 70 000.

Fig. 3.
Microtwins in a 22-1/2 at.% cerium-plutonium alloy. Magnification = 125 000.

Fig. 4.
Amorphous phase in a 25 at.% gallium-plutonium alloy. Magnification = 80 000.

REFERENCES

1. D. L. Douglass, "Techniques for Handling Alpha-Active Specimens for Electron Microscopy," Los Alamos Scientific Laboratory report LA-3200 (March 1965).

2. A. W. Brewer and F. J. Fraikor, "Transmission Electron Microscopy of Pu - 1 wt% Ga," J. Nucl. Mater. **21**, 345-348 (1967).

3. D. L. Douglass and S. E. Bronisz, "Discussion of 'Transmission Electron Microscopy of Pu - 1 wt% Ga' by A. W. Brewer and F. J. Fraikor," J. Nucl. Mater. **23**, 107-108 (1967).

4. L. Ekbom, U. Johnaason, and M. Tornqvist, "An Electron Microscopic Study of Plutonium," J. Nucl. Mater. **24**, 230-231 (1967).

5. W. Wadleigh, Lawrence Livermore Laboratory, private communication, 1969.

6. J. W. Ward, "High-Vacuum Glow-Discharge Etcher and Ion-Thinner," Microstructures **2**, 11-18 (1971).

7. R. H. Willens, "A New Method for Preparing Samples for Transmission Electron Microscopy," Proc. 5th Int. Congr. Electron Microscopy, 5th, Philadelphia, 1962 (Academic Press, New York, 1962), Paper EE-6, Vol. I.

8. R. O. Elliott, A. M. Russell, and B. C. Giessen, "Retention of a Metastable bcc $\mathcal{E}$-Pu Solid Solution: $\mathcal{E}$-Pu(Ti)," J. Mater. Sci. **8**, 1325-1330 (1973).

9. R. B. Roof and R. O. Elliott, "Evidence for the Existence of Faulting in a Splat-Cooled δ-Pu (Ti) Alloy," J. Mater. Sci. **10**, 101-108 (1975).

10. J. J. Gilman, "Metallic Glasses," Phys. Today **28**, 46-53 (1975).

11. R. O. Elliott and B. C. Giessen, unpublished work (1973).