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DEVELOPMENTS IN THE TEM EXAMINATION OF PU AND PU ALLOYS

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ABSTRACT

Microstructural characterization of plutonium utilizing Transmission Electron Microscopy (TEM), has previously been shown to be difficult because of the extreme toxicity and high oxidation rate of plutonium metal. Recent developments in plutonium sample preparation have shown that TEM foils of both alpha and delta phases may be prepared without the use of inert atmospheric systems or complex preparation devices. Using standard electropolishing techniques, samples may be produced which yield important microstructural data on plutonium and plutonium alloys.

INTRODUCTION

Characterization of plutonium microstructures by Transmission Electron Microscopy (TEM) has met with only limited success over the past several decades[1-7]. The limitation of these results may be attributed to several factors, including general inaccessability to plutonium metal as well as its high toxicity and radioactive nature.

Without the use of TEM many questions concerning the microstructure and phase transformation behavior of plutonium remain unknown[8-10]. Plutonium is a complex metal[11], having six allotropic transformations over a 600C temperature range as well as other unusual characteristics, making it a well suited material for study by TEM. Previous TEM studies of plutonium have discerned some details of the true microstructure of this metal in the annealed[2,3] and mechanically deformed condition[1], however, most of these studies have been hindered by difficult sample preparation. It is generally believed that the difficulty in producing TEM specimens of plutonium is directly related to the metal's high oxidation potential. Several studies have designed preparation facilities incorporating complex inert atmosphere apparatus to reduce the potential of surface oxidation of the plutonium foils[2,3]. While such a system helps preserve the metallic nature of the TEM foils it also reduces sample production and preparation flexibility. These systems have met

with some success, allowing observation of general microstructures in Pu and electron diffraction analysis.

The purpose of this investigation was to establish whether inert atmospheric or other complex TEM sample preparation systems are prerequisites to the examination plutonium metal and alloys.

EXPERIMENTAL PROCEDURE

Material for this study was obtained from the Plutonium Facility at Los Alamos National Laboratory (LANL). Both high purity plutonium and a plutonium-1.5w/o gallium alloy were used, for the primary purpose of observing microstructures from several phases of plutonium, specifically alpha and delta. Normally, the monoclinic alpha phase allotrope is stable at room temperature, however, additions of gallium can stablilze the delta phase to room temperature[12]. The 1.5w/o gallium alloy used was produced over 20 years ago and therefore also allowed observation of long term self-irradiation damage accumulated in the plutonium microstructure.

The experimental apparatus included a commercially available TEM electropolishing unit placed in an open-front ventilation hood as shown in Figure 1, and a specimen holder with a transfer device to safely transport and introduce specimens into the electron microscope.

Initial sample preparation required cutting bulk samples into thin slices which were subsequently thinned by mechanical grinding to a thickness of 75 to 125 microns. TEM discs were punched and cleaned of burrs and residual surface oxide. It was found important that all surface oxide be removed from the discs before beginning the electopolishing procedure, due to the strong adherence and rapid growth of any residual oxide after completing the electropolish. All grinding operations were done in a closed glove box system to ensure

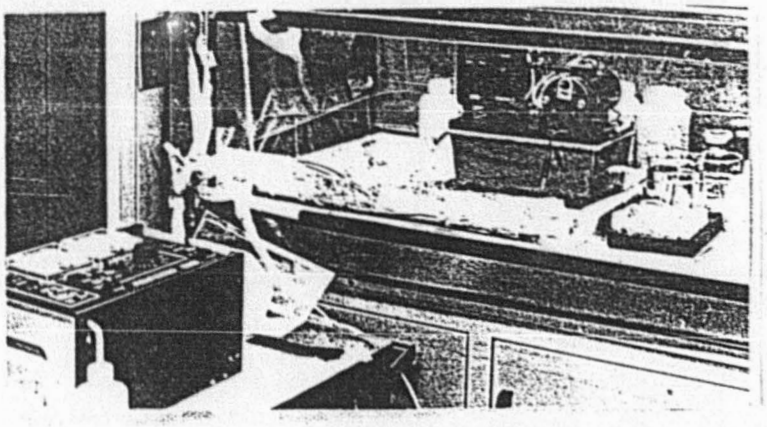

Figure 1. Electropolishing unit for TEM disc preparation.

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confinement of plutonium dust created. The discs were then transported in a sealed plastic container to the electropolishing apparatus and the twin-jet electropolishing procedure was begun.

A detailed discussion of standard jet polishing procedures will not be given here and is described elsewhere[13,14]. It should be pointed out that no modifications were made to the electropolishing apparatus used in this investigation. The electropolishing procedure was typically carried out by two individuals who worked as a team, with one person working the electopolisher inside the hood while the other person supplied consumables into the hood as was found necessary during the procedure. This helped to increase productivity as well as reduce the risk of spreading contamination to areas outside the hood. All materials physically introduced into the hood were assumed contaminated with plutonium and were disposed of as radioactive waste, including electrolytic and rinse solutions, absorbent paper materials, and all gloves. Due to the high degree of contact with contaminated solutions, a double set of gloves were worn at all times while working inside the hood. This ensured protection from leakage of the radioactive solutions to the hands. The greatest hazard of working inside the hood was from spillage of the contaminated solution to outside areas of the hood. Precautions were therefore taken to contain such a spill, including locating the electropolisher inside a plastic tray and construction of splash guards to contain the solution inside the hood in case of an accidental spill. The gaurds were fabricated from aluminum foil, allowing any shape to be formed, as well as offering good disposability once contaminated with electropolishing solution.

Both alpha and delta phases of plutonium were successfully thinned using two different electrolytic solutions. A solution found to work well on high purity alpha phase plutonium consisted of 25% nitric acid and 75% dimethylformamide. A solution using these components also works well for the preparation of polished metallographic specimens of Pu[15]. Electropolishing conditions were 20 volts at -10C, producing a current of approximately 80 mA. A medium jet speed was used. The photoelectric cell sensing the perforation of the foil during electropolishing was not set to maximum sensitivity as is usually done to produce the maximum thin region, but rather to a lower setting which gave a number of small perforations in the foil, and in most cases better thin area. The other solution used consisted of 530 ml glacial acetic acid, 100 grams chromium trioxide, and 100 ml distilled water. This solution was found to work better on the 20 year old delta phase Pu-1.5w/oGa alloy used in this study. Electropolishing conditions which produced the optimum thin area for this solution were 17-21 volts at 10-12C, producing a current of 150-200 mA. A very low jet speed was used to produce these conditions.

Immediately after a sample was electropolished, it was rinsed several times in methanol and then placed in a container filled with fresh ethanol. The ethanol reduced oxygen and water exposure to the foil surface and thereby temporarily preserved the foil until it could be loaded into the microscope for

examination. Ethanol was used as a preservative primarily because of its high purity, leaving no film or residue upon drying and therefore requiring no cleaning of the foils before insertion into the microscope. Care was taken to never allow the sample to dry before it was ready to be loaded into the microscope.

Once the sample had been transfered to another hood located near the microscope, the specimen was taken out of the ethanol-filled container and allowed to dry. While drying, the specimen was loaded into a special microscope specimen holder which allowed the specimen to be retracted inside the holder after loading. This type of specimen holder is commercially available and was purchased from Gatan, Inc.. Retracting the specimen into the holder enclosed the specimen thereby minimizing the potential spread of contamination to areas outside the ventilation hoods, as well as decreasing the possibility of contamination to the microscope goniometer and objective lens regions. An additional measure was taken to ensure containment of all Pu, and involved the use of a transfer device which cradled the specimen holder and enclosed the end of the holder where the specimen was located (Figure 2). This transfer device was used when transporting the specimen holder to and from the microscope.

A JEOL 200B transmission electron microscope (TEM) and a JEOL 2000EX scanning transmission electron microscope (STEM) were used to examine the plutonium foils. Neither microscope was altered in any way to facilitate the observation of plutonium. The STEM was configured with a Tracor Northern x-ray microanalysis system and all foils were examined at an accelerating voltage of 200kV.

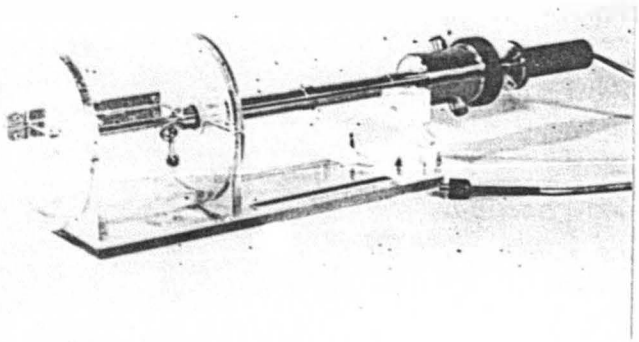

Figure 2. Transfer device for transporting TEM specimen wand with Pu specimen to and from the electron microscope.

RESULTS AND DISCUSSION

Using the conditions described above, preparation of plutonium foils with viewable thin regions was found to be quite reproducible, with one out of two foils typically having thin regions. Surface oxide was always present on the foils but did not interfere with general examination of the microstructures, or diffraction data from electron tranparent areas. Typical regions of the delta phase material were found to have a high density of

7 4 0 3 2 9

bend contours, probably from the weight and subsequent stress of the specimen in the thin regions. Figure 3 shows the accumulated radiation damage (voids) found distributed throughout the specimen. It is suspected the radiation damage occurs primarily from alpha decay. Observations of alpha phase plutonium revealed an interesting microstructure with irregular grain boundaries and possible twin formation (Figure 4).

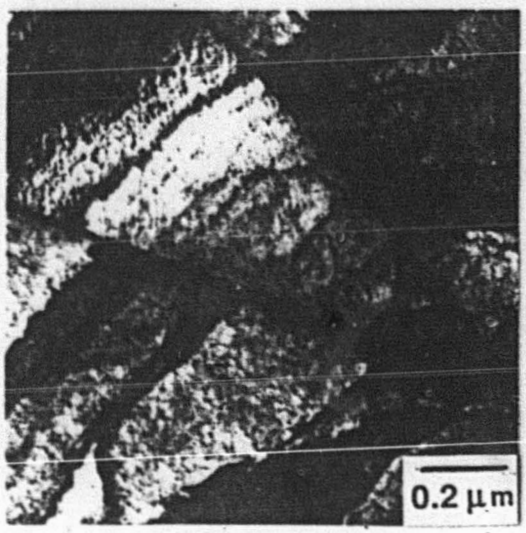

Figure 3. Microstructure of 21 year old delta Pu.

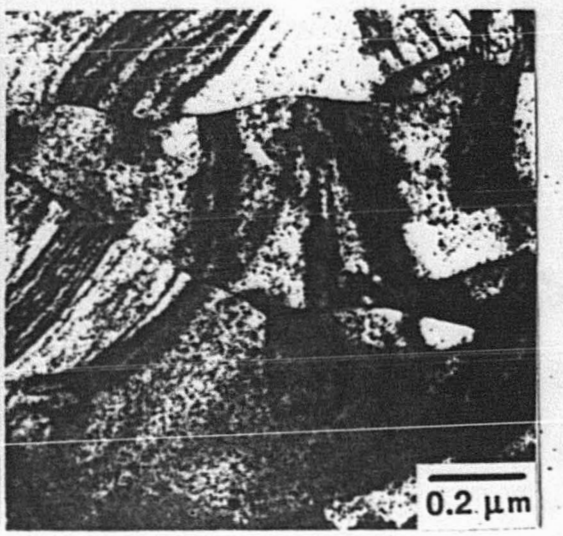

Figure 4. Microstructure of as-cast alpha phase Pu.

CONCLUSIONS

Reproducible sample preparation of plutonium for characterization using transmission electron microscopy has been successfully achieved under normal atmospheric conditions, without the use of elaborate inert atmosphere systems or devices. This allows higher specimen production, minimizing the tedious operation of typical glove box configurations, and also decreases the costs associated with such an operation. Oxidation problems normally associated with plutonium metal were eliminated by keeping all prepared TEM foils in essentially nonreactive solution environments. These included fresh ethanol and methanol which are clean and contain low quantities of oxygen and water.

Several electrolyes were found to polish plutonium although different solutions worked better for different phases. Further experiments will be performed in an attempt to establish a single electolyte which polishes multiple phase material.

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REFERENCES

1. D.L. Rohr and K.P. Staudhammer, J. Nucl. Mater. 144, 202 (1987).

2. D.L. Rohr, K.P. Staudhammer, K.A. Johnson, Los Alamos Report, LA-9965-MS (March 1984).

3. K.A. Johnson, K.P. Staudhammer, M.F. Stevens, Unpublished research.

4. A.W. Brewer and F.J. Fraikor, J. Nucl. Mater. 21, 345 (1967).

5. D.L. Douglass and S.E. Bronisz, J. Nucl. Mater. 23, 107 (1967).

6. L. Ekbom, U. Johansson, M. Tornquist, J. Nucl. Mater. 24, 230 (1967).

7. K. P. Staudhammer, K. A. Johnson, M. F. Stevens, and W. J. Medina 44th Proc. Ann. EMSA Meeting, edited by G. W. Bailey (San Francisco Press, 1986), p. 564.

8. M.A. Choudhry and A.G. Crocker, J. Nucl. Mater. 127, 119 (1985).

9. E.G. Zukas, S.S. Hecker, J.R. Morgan, R.A. Pereyra, Proc. Conf. Solid-Solid Phase Transformations, Edited by H. Aaronson (The Metallugical Society of AIME, 1982), pp. 1333-1337.

10. S.S. Hecker, E.G. Zukas, J.R. Morgan, R.A. Pereyra, ibid., pp. 1339-1343.

11. R.D. Baker, S.S. Hecker, D.A. Harbur, Los Alamos Science Winter/Spring 1983, 142

12. F.H. Ellinger, C.C. Land, V.O. Struebing, J. Nucl. Mater. 12, 226 (1964).

13. K.C. Thompson-Russell and J.W. Edington, Practical Electron Microscopy in Materials Science, Monograph 5, (The Macmillan Press Ltd., London, 1977).

14. L.E. Murr, Electron and Ion Microscopy and Microanalysis, (Marcel Dekker, Inc., New York, 1982), p. 686.

15. R.A. Pereyra, private communication.

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