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THE METALLOGRAPHIC PREPARATION OF PLUTONIUM AND ITS ALLOYS AT LOS ALAMOS*

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The first metallographic examination of plutonium was achieved in 1943 at the University of Chicago when R. S. Rosenfels developed a technique for mounting microgram quantities of metal[1]. When gram quantities of the element became available in 1944, the major portion of the research on the metallurgy of plutonium was transferred to Los Alamos. Under the direction of Cyril Stanley Smith and Eric R. Jette, metallographic techniques that fulfilled the urgent needs of the war program were developed by George Kehl and his associates. As more plutonium metal became available the original procedures were refined, and as more was learned of its unusual properties, more effective metallographic techniques were evolved.

The metallographic preparation and examination of plutonium and plutonium alloys is complicated by the high toxicity of the metal, as well as by its unique behavior. The permissable total body-burden has been set at approximately 0.6 micrograms. It is the only known metal that has six allotropic forms, all of which occur in a temperature range from room temperature to 640°C, the melting point. A negative coefficient of thermal expansion is observed in delta, the face-centered-cubic phase which exists between 317 and 450°C. Thermodynamic considerations indicate plutonium has higher affinities for oxygen, nitrogen and hydrogen than has any other metal. The rate of reaction with oxygen in air is such that a nonadherent, powdery PuO_2 layer will form in a few hours, particularly

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in the presence of moisture. This loose oxide powder is a contributing factor to the health hazard.

Even though considerable quantities of relatively pure plutonium have been examined, the metallographic emphasis at Los Alamos has been on alloys pertaining to phase diagram studies. Some recent investigations are concerned with reactor problems, such as the behavior of fuel alloys and their compatibility with various reactor materials.

The handling of metallographic specimens of plutonium and its alloys at Los Alamos differs only in degree from techniques used at any other laboratory or for any other metal. Specimens are usually small, of the order of 0.1 to 0.2 cc or 2 to 4 grams. They are kept in closed containers and are mechanically prepared for examination in a train of gloveboxes because of the high health hazard encountered. The rapid deterioration of a polished surface by the formation of oxide necessitates that each specimen be prepared and examined rapidly. For this reason, the preparation and examination of a single specimen is completed before the preparation of another is begun. These additional requirements limit the number of specimens one metallographer can examine daily to five or less.

The primary purpose of the glovebox train is to protect personnel by confining alpha-active contamination, rather than to protect a specimen by maintaining an inert atmosphere. The boxes are only reasonably tight, but a slight negative pressure of about an inch of water is maintained, so that all air movement is into an exhaust system. Helium is provided, but used only when a particularly reactive or pyrophoric alloy is to be prepared, or when filings ignite. The box may then be isolated and flooded with helium to control rapid oxidation. The train consists of five gloveboxes plus an open-front box, all interconnected, with gasketed doors between each. One pair of neoprene, gauntlet-type gloves is fixed at ports on the front of each glovebox. The metallographer always wears a pair of surgeon's gloves for protection in the event a hole develops in a neoprene glove.

Operations which produce the largest amount of dust, such as filing and sectioning, are carried on in the box farthest from the hood. In each successive box, moving toward the hood and the open air, less and less dust is produced, so that the possibility of contamination of the laboratory air is minimized. A minimum of motor-driven equipment has been installed in the boxes both to facilitate cleaning of the boxes and for the safety of personnel. Because specimens are passed freely from box to box, the utmost cleanliness is required to confine alpha-active dust, and also to keep polishing wheels and cloths free of extraneous grit. All interior surfaces are kept wet with oil and are periodically wiped with an oily rag to remove the accumulation of fine dust. Where sawing and filing are a part of the operation, the dust and debris are gathered and stored in plastic screw-cap containers.

The usual practice is to examine a cross section of a specimen. New specimens are removed from the containers and taken into the glovebox train. If loose material is present, the container is also taken into the train before it is opened. The specimens are sectioned with a midget hack saw and filed flat in the box farthest from the hood. The use of a cut-off wheel or any similar equipment is avoided because sufficient heat may be generated to transform a plutonium-rich phase, and because excessive amounts of plutonium may be accumulated in a cooling medium.

All specimens are mounted in plastic to facilitate handling through two pairs of cumbersome gloves. The mount is made in the open-front box, using a lucite ring closed at one end with aluminum foil fiber tape. The specimen, wiped free of any loose particles with carbon tetrachloride and cheesecloth, is brought from the glovebox train and placed in the ring, flattened side down, against the adhesive side of the tape. A catalyzed liquid casting resin is poured over the specimen to the desired depth and, after polymerization has progressed sufficiently, the plastic is cured.[2] It is possible to obtain a cured mount in about thirty

minutes, but in general practice, the mounts are cast late in the day, allowed to stand overnight at room temperature and cured in the morning for ten to twenty minutes at about 50°C under an infrared lamp. This method produces a hard mount of convenient size and shape. Enclosed facilities for pressure mounting are also available, but they are rarely used. The enclosed space is inadequate and the gloves can readily be burned on the heating elements. More important, however, the heat and pressure involved could alter any plutonium-rich phases that may be present.

Each mounted specimen is kept in a closed, labeled container whenever it is outside of the glovebox train, until it is unmounted for storage or scrapping. Since only one specimen is metallographically prepared for examination at a time, no identification is necessary within the train.

In preparation for polishing, the mounted specimen is flattened by drawing it across a mill file. A hole is drilled in the back of the mount down to the metal for later electrical contact. The sample is then passed to the adjacent box for paper grinding.

The rough polishing is a manual operation using a sequence of papers, usually 320, 400 and 600 grit silicon carbide and 4/0 emery paper. The successive grades of paper are backed by a thick glass plate in order to retain specimen flatness. Carbon tetrachloride is used as a lubricant, as well as a cleaning or washing agent through all of the steps until the specimen has been electropolished or etched. It is relatively inert to plutonium and is nonflammable; it evaporates quickly thus causing no liquid disposal problem and leaves no residue. In contrast, water causes rapid formation of PuO_2 on a polished surface and therefore is never taken into the gloveboxes. Between each polishing step, the specimen is cleaned with carbon tetrachloride and wiped on all surfaces with cheesecloth. This results in some transfer of dust or grit, and causes the use of a greater number of papers

and polishing cloths than would otherwise be used. This procedure does eliminate what might become a fairly elaborate solvent system for more thorough cleaning.

When paper polishing is completed, the cleaned specimen is passed to the next glovebox (moving toward the hood) where polishing is continued on a rotating lap, using either 600-grit alundum on billiard cloth or 15-micron diamond paste on Microcloth, again with carbon tetrachloride as a lubricant. Final polishing is performed in the box next to the hood on a rotating wheel covered with Microcloth and charged with either one-micron diamond or Linde B alumina. After mechanical polishing, the specimen is thoroughly washed with carbon tetrachloride, wiped with cheesecloth and passed out of the glovebox into its container in the hood. At this time the specimen is examined with a bench microscope to evaluate polishing quality. If the alloy is unfamiliar, the general character of the specimen is of interest. The details of an interface are often visible in the mechanically polished state, but they may be obscured by the formation of an oxide during an otherwise successful electropolish or electroetch. Such surfaces are often photographed before electropolishing or electroetching. Where large variations in hardness cause relief during mechanical polishing, PuO_2 is apt to form at the surface discontinuities. This condition may develop with continued polishing to the extent that the plutonium is completely obscured by oxide, in which case the specimen must be returned to the abrasive papers and examined after an earlier stage of polishing.

The open-front box is used for etching, since water, acids and flammable solvents are often involved. Up to the present time, no effective means of chemically etching plutonium has been developed. Electrolytic polishing and etching, on the other hand, have been used successfully. The electrolytic cell is a three-inch crystallizing dish with a stainless steel gauze cathode at the bottom. The

specimen is made the anode of the cell through a stainless steel probe inserted into the drilled hole at the back of the mount to make contact with the metal. A banana plug arrangement on the end of the probe also supports the specimen during electrolysis.

By a process of elimination, two electrolytes have come into general use. The electrolyte most widely used contains varying proportions of tetraphosphoric acid, water, and 2-ethoxyethanol,[3] and it is useful over a wide range of cell potentials. A good polished surface can be produced on alpha plutonium and microstructural details can be delineated in most alloys. A common uranium etchant, composed of eight parts orthophosphoric acid, five parts ethanol, and five parts glycerol, has proven successful with many alloys, and to a degree, with delta plutonium. The best results have been obtained with a cell potential between five and ten volts and a current density between 40 and 200 ma/cm^2. If the voltage during electrolysis is excessive, or if electrical contact with the specimen fails before it touches the electrolyte, PuO_2 will be formed. This is a disappointing occurrence, because it means that the specimen must be returned to the glovebox train for repolishing. Nothing has yet been found that will remove visible PuO_2, except mechanical polishing. Considerable difficulty has been encountered in achieving a reproducible surface, particularly with pure plutonium. No specific cure for this problem has yet been found. The surfaces obtained with the tetraphosphoric acid electrolyte seem to be influenced by the plutonium ion concentration in the solution, evaporative losses, temperature, and age of the solution. More work is necessary to develop a reliable method of electropolishing and etching, and to understand the etching characteristics of plutonium and its alloys.

It is still a matter for debate whether alpha grain boundaries have been developed. An anodized surface will respond readily to polarized light, showing

large grains or grain colonies, however, X-ray diffraction powder patterns indicate that alpha plutonium has a very fine grain size. Delta plutonium, on the other hand, can be etched to develop a well-delineated grain structure. The beta allotrope has been stabilized to room temperature, and its grain structure can be obtained by electroetching; it also responds well to polarized light. The gamma phase has not yet been observed at room temperature as a single phase. It is usually found to coexist with alpha or with alpha and delta, apparently as a metastable phase. Mechanical polishing may transform a metastable phase through any of the intervening phases to alpha plutonium as a result of cold work. An extremely long electropolish will remove the cold-worked layer to reveal the true structure, but will also remove inclusions and develop large surface irregularities. Plutonium becomes relatively passive to water after electropolishing or etching, and specimens may be rinsed with distilled water and dried with a blast of hot air.

Since an etched specimen is free of any loose alpha-active particles, it can now be handled outside an enclosure for a limited time; however, loosely adherent PuO_2 will begin to form on the surface in a matter of hours. The sample is never touched with the hands, but is transferred with tongs, the tips of which become contaminated. All of the instruments, bench microscopes, metallographs and hardness tester, are equipped with disposable plastic stages so the specimen mount never comes in contact with any part of the instrument, except, of course, the diamond indenter of the hardness tester. As a precaution against the spread of contamination, a pair of tongs is kept in a receptacle near each instrument. Should an accident occur, for example should a microscope stage be lowered instead of raised and a specimen or mount touch an objective lens, a thorough scrubbing will, in most cases, remove the contamination.

The specimen is now examined, analyzed, and photographed in the normal manner. General structure and any microstructural details that are considered important are recorded. Every specimen is photographed, because, unlike an ordinary metallographic specimen, a polished surface of plutonium cannot be stored for future reference. Every effort is made to obtain as much information as possible from each specimen. Hardness measurements are useful as a means of identification and therefore are made on all constituents massive enough to accept a diamond-pyramid indentation at loads of ten or twenty-five grams. The plutonium allotropes, for example, have diamond-pyramid hardness numbers of approximately 250 for alpha, 130 for beta, 90 for gamma and 50 for delta at 25-gram loads. (Epsilon and delta prime have never been identified at room temperature.) X-ray diffractometer patterns are made, using a Philips diffraction unit, to further substantiate metallographic identification. The goniometer is protected from contamination by wrapping the metallographic specimen in a thin plastic film.

After all of the information has been obtained, the sample is returned to the glovebox train for unmounting. The metal is then sealed in evacuated capsules for heat treatment, if such a treatment seems desirable, or for storage.

The results of the techniques described are illustrated in the following photomicrographs. Examples of several plutonium allotropes are shown, as well as some identifiable inclusions. Microstructures resulting from eutectic, eutectoid and peritectoid reactions are also included. Binary alloys of plutonium with fifty-two elements, including rare-earth metals, alkaline-earth metals, noble metals, and most of the more common elements, have been metallographically prepared and examined. The procedures described have been demonstrated to be practical, relatively simple, fast, safe, and effective for plutonium and its alloys.

References:

1. Coffinberry, A. S. and Waldron, M. B., Progress in Nuclear Energy, Volume 1, Series V (1956).

2. Casting resin - Selectron 5026, Pittsburgh Plate Glass Co., Pittsburgh, Pa. Catalyst - Lupersol DDM - Lucidol Div., Novadel-Agene Corp., Buffalo 5, N. Y.

3. Electrolyte compositions

Solution No. 1 - 8 parts H_3PO_4 + 5 parts ethanol + 5 parts glycerol.

Solution No. 2 - 7 parts $H_6P_4O_{13}$ + 36 parts H_2O + 57 parts 2-ethoxyethanol.

Solution No. 3 - 2 parts $H_6P_4O_{13}$ + 3 parts H_2O + 5 parts 2-ethoxyethanol.

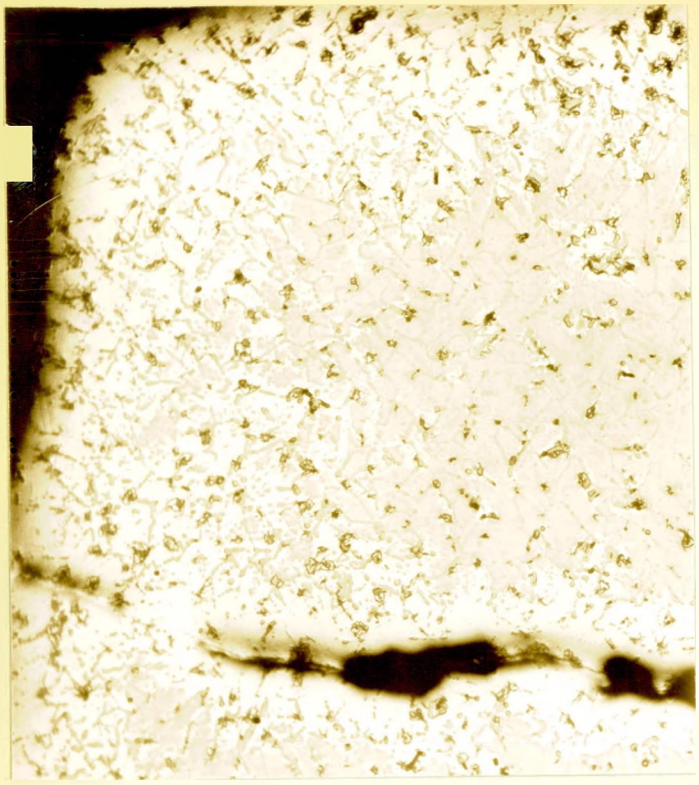

Fig. 1 PuO_2 surface film on cast alpha plutonium. Unetched. Briefly polished with Linde B suspended in water to develop PuO_2 film. 100X

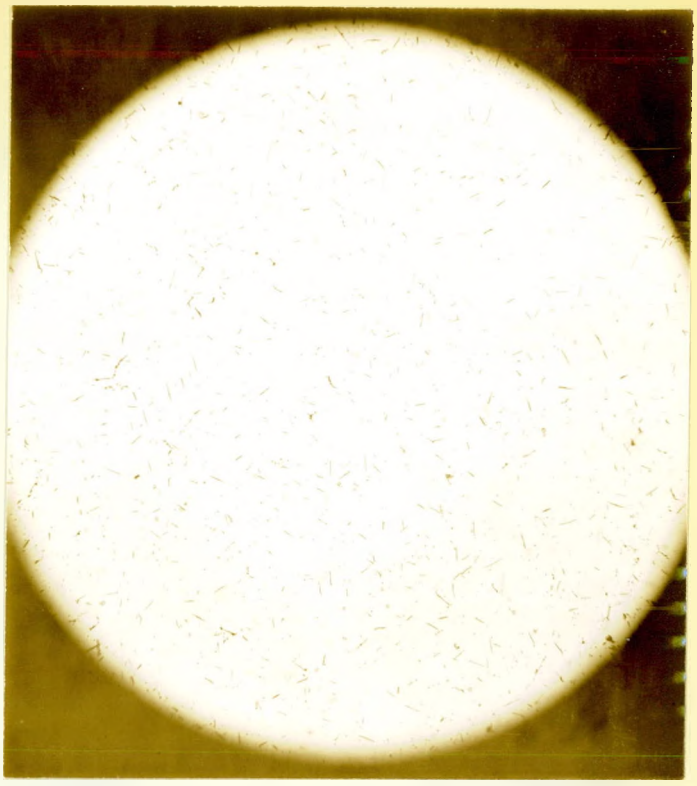

Fig. 2 Cast alpha plutonium. Electropolished 30 sec at 18 V in Sol. 2 (3). Typical α plutonium microstructure with average amount of unidentified inclusions. 100X

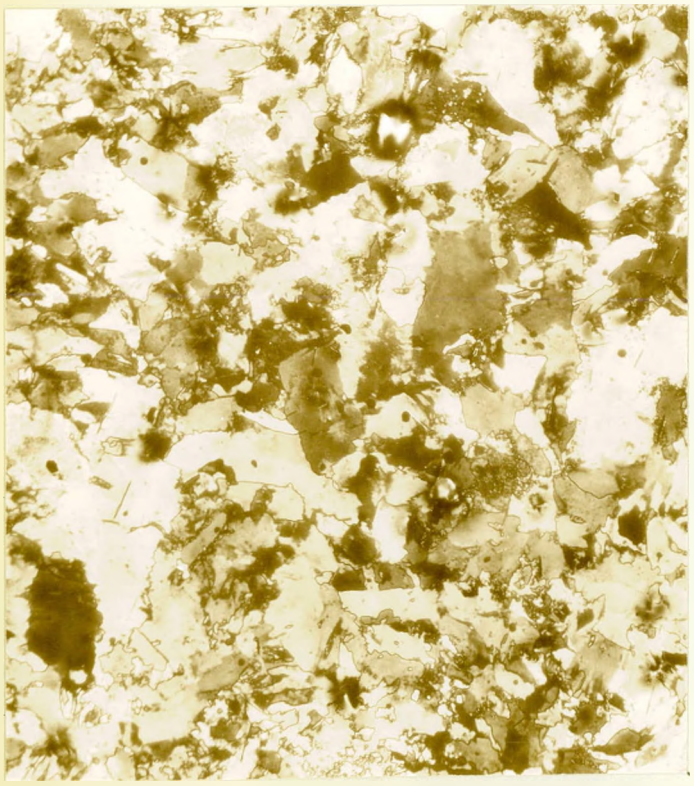

Fig. 3 Same specimen as Fig. 2 Electropolished 3 min at 16 V in Sol 3 Photographed using polarized light. Apparent α grain "colonies" can be observed 100X

Fig. 4 Pu 10 a/o U. Heat treated in the beta range and water quenched. Electroetched 6 min at 6 V in Sol. 1. The alloy appears to be beta plutonium solid solution. 100X

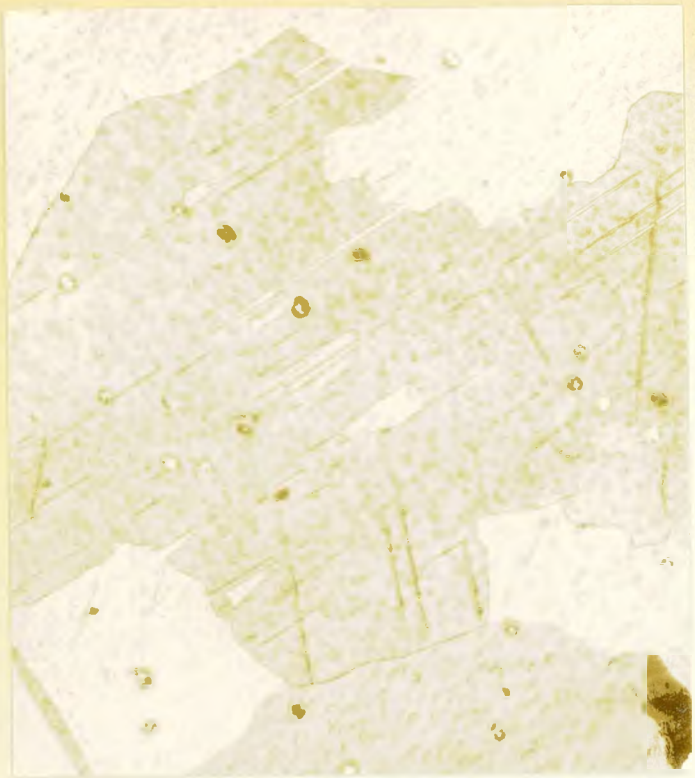

Fig. 5 Same specimen as Fig. 4. Electro-etched 20 min at 14 V plus 2 min at 6 V in Sol. 3 and photographed using polarized light. Fine detail and sharp delineation of grains is shown. 250X

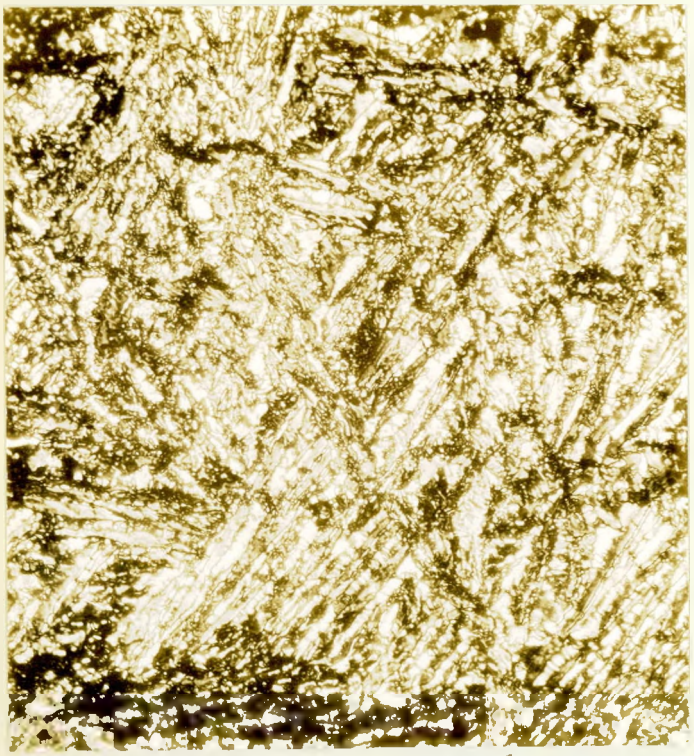

Fig. 7 Same specimen as Fig. 6. Electro-etched 2 min at 16 V in Sol. 3. Intimate mixture of two phases is shown. Photo-graphed using polarized light. 250X

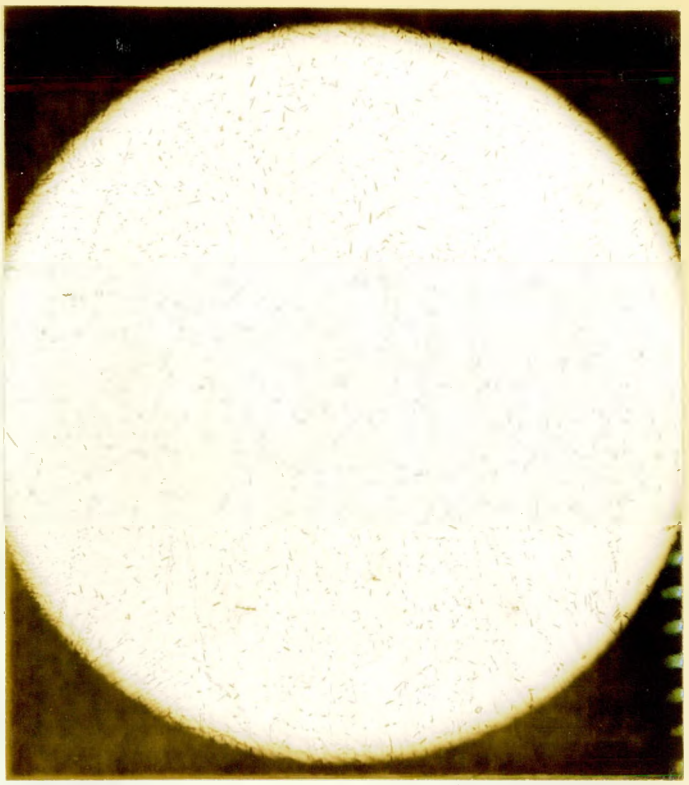

Fig. 6 Cast Pu plus 0.2 a/o Si, 0.2 a/o Al. Electroetched 5 min at 9 V in Sol. 2. Faint structure can be seen as well as usual acicular inclusions. The alloy was found to be gamma solid solution plus alpha Pu. 100X

Fig. 8. Cast Pu + 8 a/o Al. Etched by cathodic bombardment. Cast structure of delta plutonium. 500X

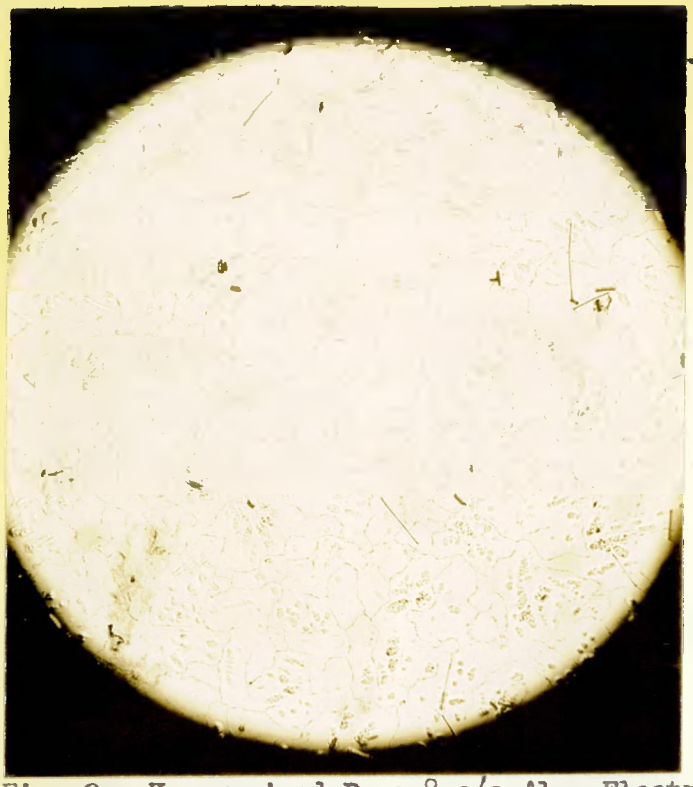

Fig. 9. Homogenized Pu + 8 a/o Al. Electro-etched 1 min at 16 V in Sol. 2. Well delineated delta plutonium structure. 100X

Fig. 10 Plutonium melted in contact with powdered MgO. As mechanically polished. Acicular Pu_2O_3 in an alpha-plutonium matrix is shown. 500X

Fig. 11 Plutonium held 30 hours at 1000°C in tungsten-coated tantalum crucible. The surface is as mechanically polished. Massive Pu_2O_3 particles are shown (dark gray) as well as surface PuO_2 surrounding the Pu between the Ta grains. 1000X

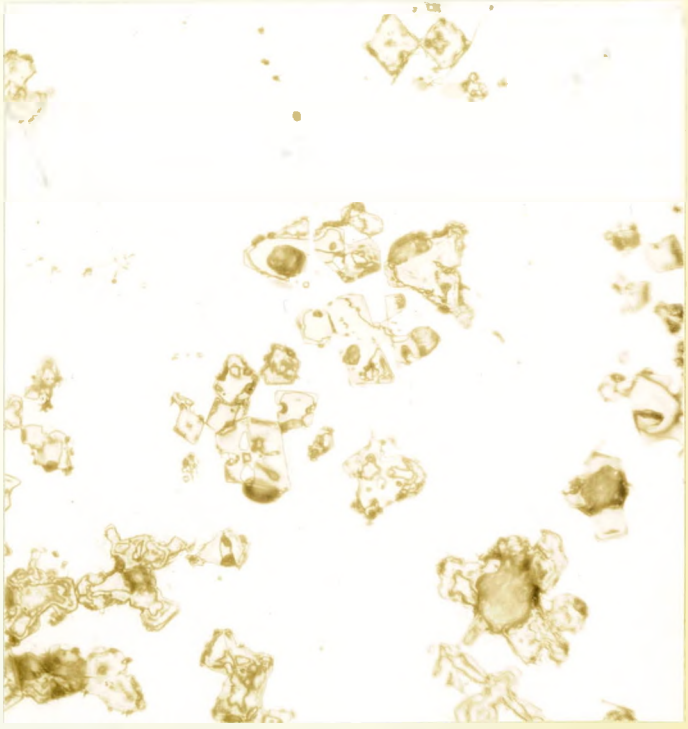

Fig. 12. PuN in alpha plutonium. As mechanically polished. The angular, massive inclusions have been visually identified as PuN. 500X

Fig. 13 Plutonium saturated with H_2 at 500°C and pressure of 0.36 mm of Hg. Electropolished 20 sec at 9 V in Sol. 2. Inclusions are PuH_2, partially masked with PuO_2, in alpha plutonium. 500X

Fig. 14 Plutonium + 5 a/o C. Electropolished 20 sec at 12 V in Sol. 2. Massive PuC in alpha plutonium is shown. 500X

Fig. 15 Plutonium + 5 a/o C. Same specimen as Fig. 14, but a different area. Same electropolish. Some PuC present, but acicular compound presumed to be a complex compound in an alpha Pu matrix. 500X

Fig. 16 Inclusions in Delta Pu. Electropolished 20 min at 12 V in Sol. 3. Inclusions tentatively identified as Pu_2O_3. 500X

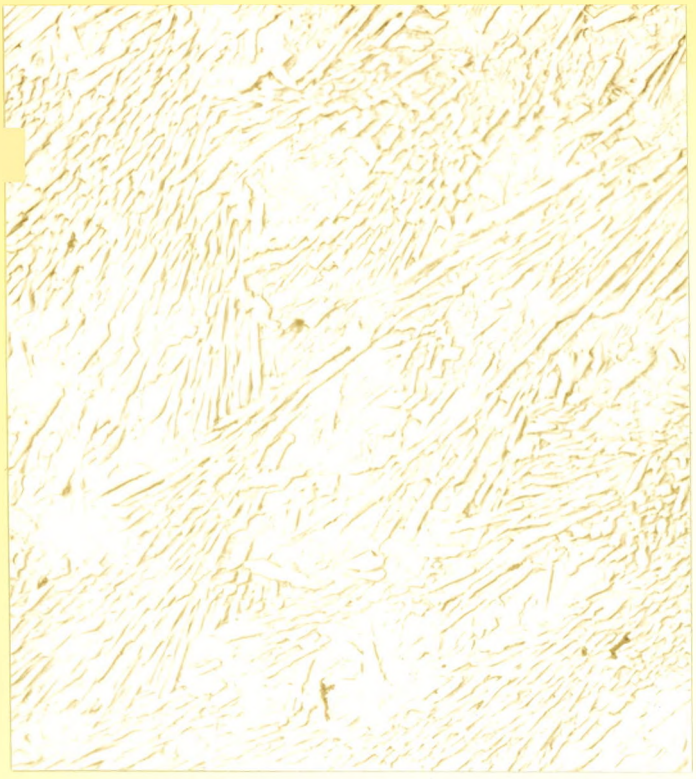

Fig. 17 Plutonium + 10 a/o Ru. Electro-etched 10 sec at 8 V in Sol. 1. The eutectic microstructure consists of Pu_3Ru in alpha plutonium. 500X

Fig. 18 Plutonium + 5 a/o Ru. Electro-etched 20 sec at 8 V in Sol. 2 plus 20 sec at 20 V in Sol 3. The eutectoid microstructure consists of a fine mixture of $Pu_{19}Ru$ in alpha plutonium. 1000X

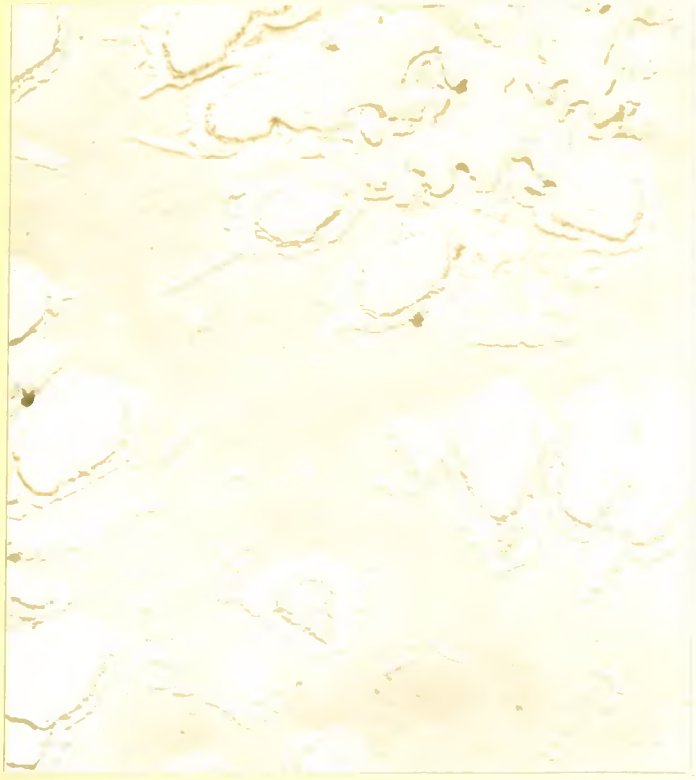

Fig. 19 Pu + 20 a/o Th. Cast. Electro-tched 20 sec at 10 V in Sol. 1 The micro-tructure shows primary Th-rich solid solution, surrounded by peritectoid Pu_2Th in a delta solid-solution matrix. 1000X