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PLUTONIUM METALLOGRAPHY*

by

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ABSTRACT

An evaluation of the effectiveness of plutonium metallography reveals inadequacies in electrolysis preparation techniques. The probable causes and the approaches to the problems that have been proposed by the participating laboratories over the past two decades have been reviewed. A brief history of the metal is included.

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Perhaps no other material in history has had the concentrated attention, the dedication of financial resources, and the limited application that have been shared by plutonium and uranium. The groundwork for their elevation to such prominent positions was laid in 1919 by Rutherford's work on nuclear disintegration. The twenty years following his revelation that atomic nuclei are not indestructible saw first a relatively slow advance in physics and then rapid progress in the development of machines to accelerate charged particles and in understanding the reactions thus produced. Atom splitting became commonplace, fissioning of uranium-235 was observed and verified, and the magnitude of the energy released in the process became known. With regard to plutonium, the period culminated in the concept of radiative capture by Frisch and Meitner.

By 1940 the concept of the element that was to be called plutonium had been proposed by L. A. Turner and others. They conceived of the formation, by radiative capture, of a nucleus having $Z = 94$ and $A = 239$ and which would probably be fissionable in the manner of uranium-235. Moreover, it appeared that the element could be synthesized in quantity and, therefore, would not be limited in amount by its natural occurrence. Nor would recovery of the new element be complicated by the formidable isotopic separation of uranium-235 from 238, in which uranium-235 occurs only to the extent of 0.07 percent. Of course, military interest in the prospect of releasing energy through fission was well established and growing.

Governmental involvement in the field of nuclear energy, other than in the academic world, first took place in the United States in the fall of 1939 when the Advisory Committee on Uranium was formed by the president in the interest of national security. Governmental funding began in the spring of 1940 with the allocation of $6,000 for the purchase of graphite and uranium oxide to determine the absorption cross section of carbon. By August the need had risen to $40,000, and the first contract was awarded to Columbia University.

Early in 1941 other contracts were let to Princeton University and the University of Chicago to coordinate with Columbia in achieving a sustained chain reaction, and to the University of California to investigate the production of element 94 in particle accelerators. The first chain reaction was achieved in December and a source of plutonium, its position now assured, came into being. The first product of the pile, however, was the isotope 238. The first fissionable isotope, plutonium-239, came from the bombardment of uranium solutions in cyclotrons at the University of California and Washington University. By the end of 1942, microgram quantities of plutonium-238 had been produced, and plutonium was considered to be an element whose behavior was as well known as those of some other relatively obscure elements in the periodic table.

Now the phenomenal effort that was to be devoted to the new element as a source of nuclear energy for military use became apparent. In January, 1943, the decision to build the Hanford Engineer Works had been made, and construction began in April. Project Y to produce a nuclear device began at Los Alamos in March. A pile to produce plutonium and a pilot plant for its chemical separation were being built at Clinton, Tennessee. The Clinton pile was started in November. The pilot plant was started in December, and its first plutonium product, consisting of 190 milligrams, was obtained in February, 1944. Of more specific interest here, the first metallographic examination of plutonium was made late in 1943 by R. S. Rosenfels at the University of Chicago with cyclotron-produced material. This achievement took place less than four years after the concept of plutonium had first been proposed.

The Hanford Engineer Works began operation in 1944. Reduction of the metal in gram quantities began at Los Alamos in February, 1945, when the first shipment of the product of the Hanford reactors and separation plant was received. The Chemistry and Metallurgy Division was formed that year with the responsibility of fabricating a military device in the shortest possible time. Included in this Division was a Physical Metallurgy Group, under the leadership of G. L. Kehl, in which a systematic study of plutonium was to take place. The first observations, at Los Alamos, however appear to have been made in May, 1944, by A. U. Seybolt and his associates. It is not clear whether the material examined was a product of cyclotron irradiation or the Clinton pile. Examples of the early work with both alpha and stabilized delta phases are included here in plates 1 and 2. The microstructures show, in retrospect, that a great deal of skill and patience went into their preparation.

Metal in sufficient quantity for metallurgical investigation became available in England in 1951 and in France in 1956. The first account of work on plutonium in Russia was presented in 1955, the presumption being that the metal became available for investigation several years earlier. In all instances micrography played an early and important role in the burgeoning studies of plutonium. Numerous articles describing, or alluding to, metallographic practices appeared in the open literature after 1958, and presentations of phase diagrams were richly illustrated with photomicrographs. Metallography has continued to play an essential role in the accumulation of knowledge about this unusual element.

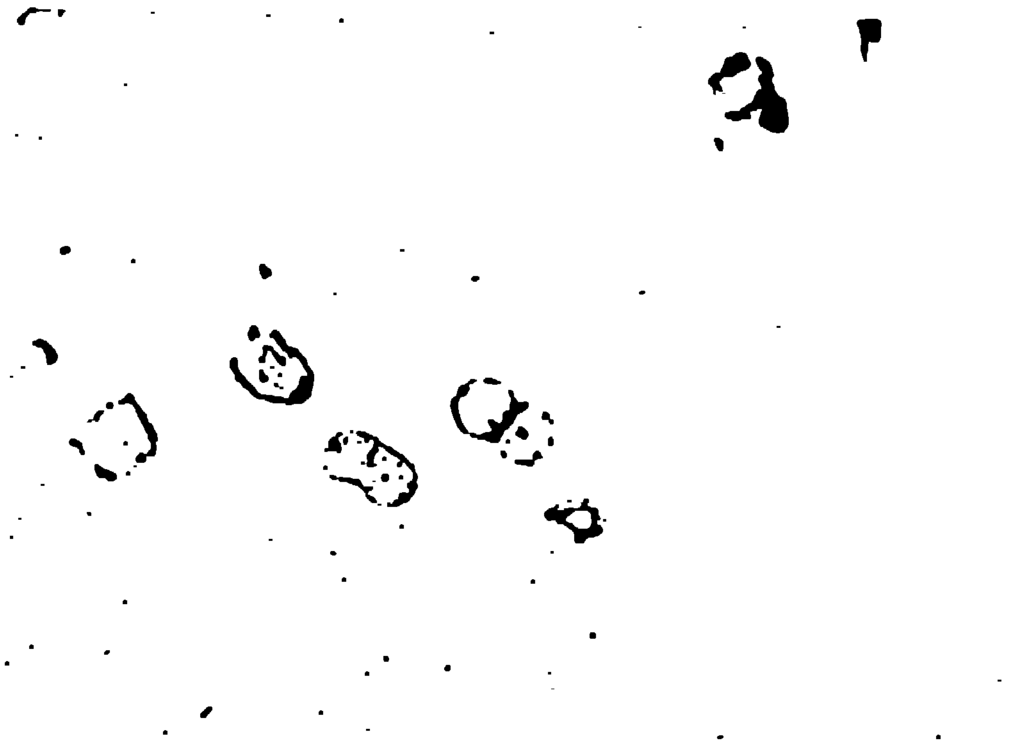

Plate 1. Plutonium metal. Mechanically polished with tin oxide and ethyl alcohol. X 500. (A. Gerds, July 27, 1944.) The inclusions can be identified as plutonium hydride.

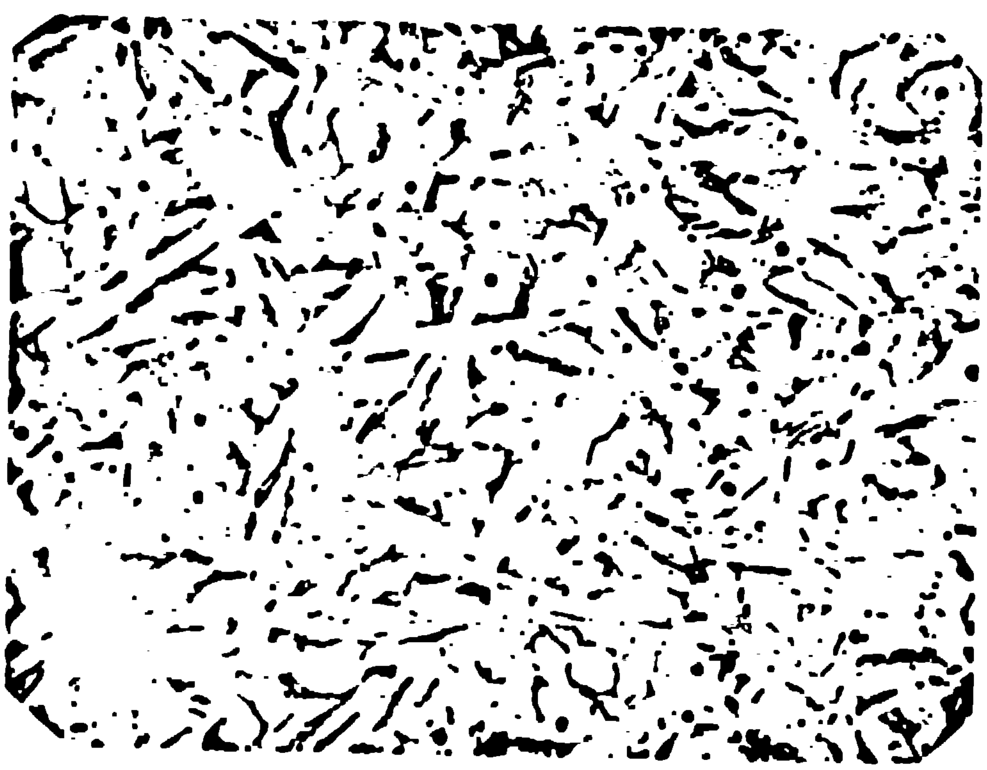

Plate 2. Plutonium-1 wt. percent gallium alloy, cast. X 500. (A. Gerds, August 28, 1945) This cored specimen was electroetched in a solution of 6 parts orthophosphoric acid, 5 parts glycol, and 9 parts water.

Expansion of laboratory facilities for studying plutonium continued through the 1950's, but not with the single-mindedness of purpose nor the intensity that had prevailed in the immediately preceding decade. At Los Alamos the military applications effort continued, and was joined by similar efforts at the Hanford Laboratories and the Rocky Flats Plant. Battelle Memorial Institute became involved on a contract basis. The Lawrence Livermore Laboratory, a late comer, committed its metallographic facility to plutonium in 1962.

In peaceful uses, Los Alamos began a study of applicable binary alloy systems in 1948. The Argonne National Laboratory, which supplanted the Metallurgical Laboratory of the University of Chicago, began work with plutonium in 1954 in connection with reactor development. The Mound Laboratory joined in this effort in 1956. The Savannah River Plant, the most recent, has been engaged primarily in the production of nuclear fuels.

With this prestigious background, what have we metallographers accomplished with plutonium? Do the results of our efforts compare favorably with those of our contemporaries who have worked in less restricted fields? There seems little doubt that, with respect to the state of the art, our workmanship and instrumentation compares favorably with those prevailing in the ferrous and nonferrous fields. The technical elegance of our microstructures, however, is not comparable. They are not as crisply defined. Photomicrographs of plutonium and its stabilized phases continue to exhibit characteristics of electropolished and weakly etched specimens. Methods of specimen preparation that will consistently produce comparable results are yet to come, and they will come only with greater effort than was initially expended in preparing the metals.

The difficulties occur almost entirely in the electrochemical stage of preparation. Plutonium, in all of its commonly encountered phases, responds well to mechanical grinding and polishing. Conventional abrasives and practices work well if nonaqueous lubricants are used. Carbon tetrachloride has had the widest acceptance but kerosene, glycol, trichloroethylene, and methyl chloroform have also been used. The alpha phase, being the hardest, is also the easiest to polish, and a polished surface suitable for photography readily achievable. The delta phase presents a greater problem. Being relatively soft, it is subject to galling; however, the careful use of clean, sharp abrasive papers and clean laps makes the preparation of delta surfaces suitable for etching not a difficult task.

It happens infrequently that a mechanically prepared delta surface will be photographed. It is quite reactive, as are all the plutonium phases, and the rate of metal removal in the polishing process must be rapid, otherwise the rate of oxidation and corrosion by moisture-bearing lubricants will overtake polishing.

Being softer, the surface of polished delta has a higher energy than does polished alpha and initial oxidation occurs extremely rapidly. Consequently, fine scratches that usually can be overcome optically stand out in a distressing manner. The disturbed surface layer, however, may be readily removed electrolytically.

It is in this final stage of preparation that problems arise. Plutonium's activity and tendency to form insoluble compounds with strong acids have precluded chemical etching. The same characteristics have also limited the time it may be exposed to aqueous electrolytes. Thus the selection of suitable electrolytes consist essentially of nonaqueous solutions in which ethylene glycol, glycerine, ethyl and methyl alcohols, and 2-ethoxy ethanol are the common diluents in combination with tetraphosphoric, orthophosphoric, citric, nitric, acetic, or lactic acids. Achieving distinct polishing or etching conditions with these electrolytes is difficult. Their polishing curves of potential versus current do not exhibit the desired plateau which indicates optimum conditions for polishing, but are generally only slightly inflected. The result appears to be an overlapping of the two processes wherein one or the other can only be emphasized.

The metal is inherently in a state of stress as a consequence of perpetual damage from self irradiation. In additon, phase transformation may have occurred at a relatively low temperature. This state contributes to masking normal stress concentrations at structural discontinuities that are the basis for the selective solution that makes grain boundaries visible in reflected light.

The response of plutonium to etching does not seem to be particularly sensitive to isotopic composition, but mechanical and thermal histories and impurities are important in this respect. This characteristic may account to some extent for our inability to achieve consistent results, but it falls short of explaining an exasperating unpredictability that occurs from day to day or from environment to environment.

Current practices appear to be the result of continued probing by individuals who are unsatisfied with their own methods and who are disappointed when they try to adopt procedures that are used at other laboratories. This may be due to personal preferences, although having been unsuccessful in transferring procedures from Los Alamos to the Livermore Laboratory, I find this explanation inadequate. Phosphate electrolyte recipes that were part of well-established routines at Los Alamos failed to give comparable results at Livermore. For example, the tetraphosphate solutions were discarded completely. The orthophosphate solutions continued to be used with both alpha and delta plutonium although they gave satisfactory results only under widely different conditions. Instead of a short etch time at 6 to 8 volts in the familiar 8-5-5 formulation of orthphosphoric acid, glycerine, and alcohol, it was necessary to limit the potential to the range of 2-1/2 to 4 volts and to extend the time manyfold, sometimes to as much as hours. The microstructures, however, were of better quality and satisfied a more exacting demand. One of the tetraphosphate solutions was replaced with the citric acid-based etchant introduced as Batelle Northwest Laboratories[6] as a routine reagent for delta.

Relative humidity has been mentioned as a factor contributing to the success or failure of preparation techniques, but this, too, seems inadequate since humidity is often comparable at Los Alamos and Livermore. Perhaps air pollution is a factor, although no correlation was observed with the widely variable degree of pollution at Livermore. At any rate, it seems that the unpredictability of plutonium is a somewhat baffling reality and each metallographer must develop his own way of coping with it.

Vibratory polishing and electropolishing techniques have been adopted to replace, or supplement, the conventional methods of mechanical preparation. Most of the effort, however, has been expended in researching the electroetching processes. At Los Alamos in 1964 an alternating current technique was introduced that gave a somewhat wider selection of electrolytes and improved the quality of alpha surfaces.

Early efforts in France[4] were directed toward developing an epitaxial oxide on alpha plutonium to permit examination under polarized light in the manner of uranium. (For many years this was the only mode in which the structure of alpha could be observed.) Electrolytes consisting of phosphoric,[8] sulfuric, or nitric acids in combination with nonaqueous diluents were explored. One of these, a solution of nitric acid in glycol, frequently modified, has been used extensively as a bright field etchant in the United States.

A method of electroetching alpha in a nitrate solution was introduced at the Battelle Memorial Institute.[7] Their method involved the use of nitric acid, alcohol, and water and successfully produced structures for examination under bright field illumination. A similar etchant was adopted at the Battelle Northwest Laboratory and at Los Alamos where it is used in the alternating current mode.

At the Battelle Nortnwest Laboratory a visual method of observing and controlling the etching process was introduced in 1966[6] and applied to both alpha and delta plutonium. This adaptation seems to offer one of the best solutions to the problems encountered in the use of low conductivity electrolytes. Phosphoric, citric, and nitric acid-based electrolytes are recommended for the method.

The effectiveness of low conductivity electrolytes was improved at the Rocky Flats Plant[5] by swabbing with heated electrolytes containing varying proportions of orthophosphoric acid in glycerine and alcohol. The heated solution is applied to the specimen with a hand held swab through which the solution is forced by an external pump. The swab also acts as the anode in the cell.

An ion etcher was frequently used at the Livermore Laboratory to prepare samples for bright field examination in preference to etching in nitrate solutions. Adequate cooling for small specimens of alpha was accomplished with a conductive mount containing iron powder. Following etching, a cleaning step to remove loose particles of plutonium was required and noticeably degraded the etched surface. An ion etcher, however, is a desirable tool. In this regard, one that is presently used at Los Alamos[10] to etch thoria appears capable of alleviating the heating problem. In principle, the ion beam is drawn from a glow discharge that is maintained within a hollow-anode ion gun. The energy of the beam is continuously controllable and it can be focused, or restricted, to minimize the energy imparted to the specimen. The effectiveness of the design with regard to plutonium has not yet been determined.

These innovative techniques have helped to overcome some of the inadequacies that have been apparent in plutonium metallography during the past two decades. Since we are aware of the inadequacies in our method, more answers will be sought and found by those who have chosen this restricted but rewarding field. The descriptions of techniques and processes included here have deliberately been made very brief since each would be considered a complete article in the technical literature.

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