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METALLOGRAPHIC PREPARATION AND STRUCTURE OF PLUTONIUM AND SOME PLUTONIUM ALLOYS

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Abstract

The preparation of plutonium and plutonium-alloy specimens for metallographic study was investigated. Descriptions are given of the mechanics of mounting the specimens in plastic, of grinding, of polishing (both mechanical and electrolytic), and of etching. A table of data for electrolytic polishing of the specimens is included. Microstructures are described, and microphotographs given, for the following specimens: plutonium; one-atomic-percent-gallium plutonium alloy; three-atomic-percent-gallium plutonium alloy; ninety-atomic-percent-uranium plutonium alloy; and ninety-five-atomic-percent-uranium plutonium alloy.

THE METALLOGRAPHIC PREPARATION AND STRUCTURE OF PLUTONIUM AND PLUTONIUM ALLOYS

Introduction

In the preparation of plutonium and its alloys for metallographic examination, certain difficulties are encountered that necessitate a change in the procedure customarily followed in the handling of common metals.* Plutonium specimens are usually small in size, requiring a special mounting technique to facilitate grinding and polishing; the metal is attacked by water and certain oils, and to such a degree by short exposures, that the metallographic surface is ruined; and the radioactive nature of plutonium presents a serious health problem, which adds considerably to the preparation difficulties.

Specimen Mounting

The usual plastics used for mounting metallographic specimens, e.g. bakelite, Lucite, Tenite, etc., are not satisfactory for mounting specimens of plutonium because of the heat and pressure required for molding. Pure plutonium suffers phase changes at low temperatures, and the temperatures and pressures necessary for ordinary plastic mounting may radically change the original structure of the specimen.

Suitable room-temperature-casting plastics can be used for mounting purposes, and those materials after setting provide a sufficiently hard and desirable mount for the purpose intended. A commercial product, known as Catabond No. 700, to which is added about 25% by volume of Catabond accelerator No. 5 just before casting, has been found to be

*For previous reports on metallography of plutonium, see LA-70 and LA-79, and chapter IX of The Chemistry, Purification, and Metallurgy of Plutonium (C.A. Thomas and J.C. Warner, December, 1944.)

satisfactory, except for shrinkage. Shrinkage may be practically eliminated by the addition of a small amount of powdered bakelite added to the liquid plastic.

A methyl methacrylate casting plastic* has proven to be a more satisfactory mounting material than Catabond No. 700. A harder mount is obtained and, when properly cast, shrinkage of the mold during hardening is practically nil. The material is partially polymerized to about the viscosity of concentrated sulphuric acid and remains in this condition for approximately 30 days if stored at a temperature of about 15°C. When, however, the liquid plastic is raised to ordinary temperatures, the polymerization reaction will go to completion, forming a hard, durable, and acid resisting mass similar to thermo-setting Lucite. The polymerization process at ordinary temperature can be greatly accelerated by ultra violet light.

The mechanics of mounting a plutonium specimen in the plastics described above are as follows:

1. Because polishing and etching is generally carried out electrolytically, a platinum wire is attached to the specimen to provide electrical contact through the top of the mount.
2. The wired specimen is placed on a very slightly greased glass plate with the platinum wire pointing upward. A section of micarta tubing (approximately 1" long, 1" outside diameter, and 1/16" wall thickness) is placed on the plate and around the specimen.

*Preparation procedure described in LAMS 307.

Plastecene is packed around the junction of the micarta ring edge and the glass plate to prevent the plastic from escaping from within the mold.

3. Enough liquid plastic is cast into the micarta ring to form a layer 1/4" to 3/8" thick. The material is allowed to set undisturbed for about 15 minutes to enable air bubbles to be expelled, after which complete polymerization is hastened by means of ultra violet radiation (usually 3 to 4 hours).*

4. Layer casting as described in item 3 is continued until the mold is completely filled.

Metallographic Grinding:

Because of the health hazard associated in the handling of plutonium, it is essential that manual grinding of such specimens be carried out in a suitable dry box, and that the technician be fully protected from contamination by appropriate clothing and respirators.

The technique of grinding plutonium is essentially the same as applied to common metals and alloys. Four grades of emery paper of decreasing grit size are used (Behr-Manning or equivalent) - specifically Nos. 1, 1/0, 2/0 and 3/0 - each lubricated with a small amount of kerosene. Kerosene has been selected as an appropriate lubricant after trying a number of others, e.g. alcohols, castor oil, etc., all of which were found to be inferior for this purpose.

Because appropriately graded diamond dust is generally superior to emery for grinding metallographic specimens, diamond-dust grinding was tried

* The source of ultra violet radiation should be placed far enough from the mold so that the heat does not cause "boiling" of the liquid plastic resulting in porosity of the hardened mount.

on plutonium. After repeated trials, it was concluded that emery abrasive worked equally as well as diamond dust, and better from the standpoint of convenience in executing the grinding operation.

Metallographing Polishing - Mechanical Technique:

Mechanical polishing of plutonium and its alloys has never proved very successful in contrast to electrolytic polishing. Because of the health hazard involved, as in grinding, mechanical polishing must be carried out in a dry box to prevent contamination. Regardless of the care exercised in polishing, e.g. light pressures, a slowly rotating lap, hand polishing, etc., there is inevitably formed a smeared surface layer or stain that is not removed during etching. This false surface condition, an extreme example of which is shown in Fig. 1, prevents uniform etching and adds only to confusion in interpreting structures.

Various types of polishing cloths have been tried, e.g. Buehler Miracloth, Buehler Botany cloth, silk, and billiard cloth, with some difference in performance, but none entirely preventing the formation of this false surface. In addition, and in conjunction with these polishing cloths, different polishing media have been used - Baker's tin oxide, Merck's heavy magnesia, Wolff's Rite Tonerde Nos. 1 and 2, levigated alumina having an uncontrolled and a controlled pH of 7.2, all suspended in different vehicles such as alcohols and oils, and mixtures of these two. The results in producing a satisfactory metallographic surface varied considerably but none were to be considered excellent.

Metallographic Polishing - Electrolytic Technique:

Electrolytic polishing of metallographic specimens is ideally

suited for producing surfaces free from cold work and in the case of plutonium, free from the false surface (Fig.1), although inclusions are generally removed in this process, and the surface is somewhat undulated, which, however, is not objectionable even at low magnifications. The most satisfactory results in the polishing of plutonium and its alloys have been obtained by electrolytic methods, although the kind and concentration of the electrolyte is determined by the composition of the plutonium alloy. Conventional electrolytic polishing cell arrangements have been found to be satisfactory, with a source of direct current being supplied by either a rectifier or a direct-current generator.

For any electrolytic polishing solution, the proper current for successful polishing is in that range of currents where a change in applied voltage does not change the current. This "plateau" of a current-voltage curve is found by experimentation, and for the most part the current densities shown in Table I were so determined.

The electrolytic polishing data given in Table I were derived experimentally. It should be noted that the composition of the electrolyte, and the conditions of the procedure differ depending upon the kind and alloy content of the plutonium specimen.

Etching:

In general, the etching of plutonium and its alloys is a rather difficult procedure and to date no satisfactory reagent has been found that will etch successfully by immersion or by swabbing techniques. Our experience indicates that satisfactory etching can be obtained by electrolytic methods, using the same electrolyte as is appropriate for polishing, but at a lower current density. The exact current density and time required for etching, when using the reagents given in Table I, is difficult to recommend and is best determined by trial.

Interpretation of Microstructures:

Plutonium

The microstructure of cast, nominally pure, plutonium at four different magnifications is shown in Fig. 2. The photomicrographs suggest the presence of two or perhaps three metallic phases - hence a lack of equilibrium - and a rather nonuniform distribution of these phases, as is so clearly shown in Fig. 2A. The density of this specimen is not known with certainty, although it has been reported as being of intermediate density. The acicular phase is certainly different from the matrix, since after repeated electrolytic polishings, it always remained in relief. The gray - and white-etching areas constituting the matrix, distinctly shown in Fig. 2C, were always revealed in the same distribution and pattern after the specimen had been repeatedly repolished and etched, and hence are definitely not staining effects. They may be either two phases, or differently orientated grains of one phase. The acicular phase (alpha?) seems to form or grow in an identical manner, save for direction, in both.

One Atomic Percent Gallium-Plutonium Alloy

The structure of this alloy, after homogenizing the "as cast" structure by annealing at 450°C for 16 hours, is rather difficult to interpret. The photomicrographs shown in Fig. 3 suggest the presence of two metallic phases and a minor intermetallic or non-metallic constituent.

Three Atomic Percent Gallium-Plutonium Alloy

The "as cast" structure of this alloy at four magnifications is shown in Fig. 4. The structure is typical of "as cast" solid solution alloys e.g. alpha brass and shows in this case a rather marked tendency towards coring.

Homogenization secured by annealing at 550°C for 19 hours produces

equi-axed grains, as shown in Fig. 5, and eliminates, as would be expected, the original "as cast" structure.

The lamellar structure, most clearly shown in Fig. 5 D, is probably not real, but is the result of electrolytic polishing and etching with tetra phosphoric acid. Depending upon the time of etching with this reagent either a few or all of the grains exhibit this lamellar condition. In part, this apparent structure may be attributed to grain orientation of the plane of sectioning with respect to the attack of this particular etchant. This circumstance is in part supported by the observation that when etching the alloy in the "as cast" condition with tetra phosphoric acid, a faint lamellar pattern is observed in the matrix. However, no evidence of this structure is apparent when ortho phosphoric acid is used as the etchant. Because the homogenized specimen of this alloy (Fig. 5) could not be satisfactorily etched with ortho phosphoric acid or other reagents, definite conclusions as to the validity of the above reasoning cannot be made.

Ninety Atomic Percent Uranium-Plutonium Alloy

The annealed structure of this alloy (500°C for 4 hours) shown in Fig. 6, suggests the existence of two phases, one as a matrix, the other as a grain boundary phase. It is probable that the grain boundary phase is intermetallic in nature. Alloys containing 75 and 80 atomic percent uranium respectively completely crumble into powder when handled, after some ageing (?atmospheric corrosion) at room temperatures.

Ninety-Five Atomic Percent Uranium-Plutonium Alloy

The behavior of this alloy during electrolytic polishing and etching is similar to that of uranium. The annealing treatment (500°C for 4 hours) produced an equi-axed grain structure, and as shown in Fig. 7D, the amount of grain-boundary constituent is, as expected, less than observed in the 90%

uranium alloy (Fig. 6).

TABLE I - ELECTROLYTIC POLISHING DATA FOR PLUTONIUM AND PLUTONIUM ALLOYS

Electrolyte	Conditions	Composition of Specimen	Remarks
12 p. H_3PO_4 - 85% 18 p. H_2O 5 p. $C_2H_6O_2$	1" between electrodes 54°C. Current Density investigated 4.25 to 5.25 amperes per square inch. *	Pure plutonium (as cast)	Specimen does not etch satisfactorily.
8 p. H_3PO_4 - 85% 12 p. H_2O 7 p. $C_2H_6O_2$	Horizontal and vertical electrode positions investigated. 3/4" to 1" between electrodes 54°C Current Density investigated 5.5 to 9 amperes per square inch. *	Pure plutonium (as cast)	Current density appears to be very critical for polis
1 p. H_3PO_4 - 85% 1 p. H_2O 2 p. $C_2H_6O_2$	1" between electrodes 24° to 50°C investigated Current Density investigated 0.75 to 2.5 amperes per square inch. *	3% gallium alloy of plutonium (cast and annealed)	Polishes fair but surface wavy. Does not etch specimen pro
1 p. H_3PO_4 - 85% 2 p. H_2O 2 p. $C_2H_6O_2$	3/4 to 1" between electrodes 24° to 50°C investigated Current Density investigated 0.5 to 3.25 amperes per square inch. *	3% gallium alloy of plutonium (cast and annealed)	Polishes fairly well. Does not etch satisfactorily
6 p. H_3PO_4 - 85% 9 p. H_2O 5 p. isopropyl alcohol	3/4" between electrodes. Room temperature - 24°C. Current Density investigated 2.25 to 2.75 amperes per square inch. *	Pure plutonium (as cast)	Polishes quite slowly. Will etch.
6 p. H_3PO_4 - 85% 9 p. H_2O 5 p. isopropyl alcohol	3/4" between electrodes Room temperature to 50°C investigated. Current Density investigated 0.5 to 6 amperes per square inch. *	3% gallium alloy of plutonium (cast and annealed)	Specimen polishes and etch fairly well. Wavy surface produced.

* Stainless-steel cathodes used for all electrolytes.

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Electrolyte	Conditions	Composition of Specimen	Remarks
4 p. H_3PO_4 - 85% 6 p. H_2O	3/8" to 3/4" between electrodes Room temperature - 24°C. Current Density investigated 2.0 to 4.25 amperes per square inch. *	Pure plutonium (as cast)	Current Density appears to be quite critical for polishing specimen. Will etch readily.
4 p. H_3PO_4 - 85% 6 p. H_2O	1" between electrodes 23°C to 50°C investigated. *	90% uranium alloy of plutonium (cast and annealed)	Polishes and etches quite well.
6 p. H_3PO_4 - 85% 9 p. H_2O 5 p. $C_2H_6O_2$	1" between electrodes 50°C. Current Density - 1 to 17 amperes per square inch. *	95% uranium alloy of plutonium.	Polishes well.
6 p. H_3PO_4 - 85% 9 p. H_2O 5 p. $C_2H_6O_2$	3/4" between electrodes 54°C. Current Density investigated 2 to 4 amperes per square inch. *	3% gallium alloy of plutonium (as cast)	Smoothly polished surface. Will also etch specimen.
6 p. H_3PO_4 - 85% 9 p. H_2O 5 p. $C_2H_6O_2$	Anode lower - 1" between electrodes 54°C. Current Density investigated - 2 to 7 amperes per square inch. Perforated platinum cathode.	Pure plutonium (as cast)	Polishes and etches well.
6 p. H_3PO_4 - 85% 9 p. H_2O 5 p. $C_2H_6O_2$	1" between electrodes Investigated with anode lower and upper horizontally and also with electrodes placed vertically. Current Density investigated 4 to 6 amperes per square inch. Perforated platinum cathode.	3% gallium alloy of plutonium (cast and annealed).	Specimen difficult to etch properly. Current Density seems critical. Polishes but with a wavy surface.

* Stainless-steel cathodes used for all electrolytes.

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Electrolyte	Conditions	Composition of Specimen	Remarks
6 p. H_3PO_4 - 85% 9 p. H_2O 5 p. isopropyl alcohol	3/4" between electrodes 24°C. Current Density investigated 1 to 2 amperes per square inch. *	1% gallium alloy of plutonium (as cast).	Specimen pitted while polishing.
5 p. H_3PO_4 - 85% 5 p. $C_2H_6O_2$ 8 p. isopropyl alcohol	1" between electrodes 50°C. Current Density investigated 0.5 to 2.75 amperes per square inch. *	1% gallium alloy of plutonium (as cast).	Specimen polished surface finely pitted. Does etch specimen.
5 p. H_3PO_4 - 85% 9 p. $C_2H_6O_2$ 8 p. isopropyl alcohol	1" between electrodes 50°C. Current Density investigated 0.5 to 2.5 amperes per square inch. *	1% gallium alloy of plutonium (as cast).	Polishes slowly does no etch well.
5 p. H_3PO_4 - 85% 10 p. H_2O 8 p. isopropyl alcohol	7/8" between electrodes 35° to 50°C. Current Density investigated 0.5 to 2.75 amperes per square inch. *	3% gallium alloy of plutonium (cast and annealed).	Current density quite critical for polishing.
1 p. tetra phosphoric acid 1 p. H_2O 1 p. $C_2H_6O_2$	1" between electrodes 50°C. Current Density investigated 1.25 to 5.5 amperes per square inch. Current Density Investigated 0.2 to 0.5 amperes per square inch. *	3% gallium alloy of plutonium (cast and annealed). 95% uranium alloy of plutonium (cast and Annealed).	Does not etch readily. Polishes well. Does not etch readily. Polishes well - wavy su
1 p. tetra phosphoric acid 10 p. H_2O 20 p. $C_2H_6O_2$	50°C. 1" between electrodes. Current Density investigated 3.0 to 4.75 amperes per square inch. Current Density investigated - 1.5 to 3.5 amperes per square inch. *	3% gallium alloy of plutonium (cast and annealed). 1% gallium alloy of plutonium (as cast).	Polishes well at about amperes per square inch. Etches at about 1.00 am per sq. inch. Fine bub like marks on surface. C.D. appears quite crit for polishing. Stains when etched.

* Stainless-steel cathodes used for all electrolytes.

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Electrolyte	Conditions	Composition of Specimen	Remarks
1 p. tetra phosphoric acid 10 p. H_2O 15 p. $C_2H_6O_2$	1" between electrodes 50°C. Current Density Investigated 2.5 to 3.5 amperes per square inch. *	3% gallium alloy of plutonium (cast and annealed).	Polishes at 3.5 amperes per square inch. Etches at 0.5 amperes per square inch. Fine bubble-like marks on surface.
3 p. tetra phosphoric acid 20 p. H_2O 50 p. $C_2H_6O_2$	7/8" between electrodes 50°C. Current Density investigated 2.0 to 3.0 amperes per square inch. *	3% gallium alloy of plutonium (cast and annealed).	Current Density quite critical for satisfactory polishing.
3 p. tetra phosphoric acid 20 p. H_2O 50 p. $C_2H_6O_2$	3/8 to 3/4" between electrodes 24°C. Current Density investigated 1.5 to 2.0 amperes per square inch. *	3% gallium alloy of plutonium (as cast).	Specimen stained badly and polished only in parts. May polish at higher current densities.
1 p. tetra phosphoric acid 4 p. H_2O 10 p. alcohol	½" between electrodes *	3% gallium alloy of plutonium.	
4 p. tetra phosphoric acid 1 p. H_2O	½" between electrodes 23°C. No agitation *	3% gallium alloy of plutonium.	Etched but did not polish.
4 p. tetra phosphoric acid 1 p. H_2O 1 p. alcohol	½" between electrodes *		
1 p. tetra phosphoric acid 40 p. H_2O 100 p. alcohol	*		

* Stainless-steel cathodes used for all electrolytes.

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Electrolyte	Conditions	Composition of Specimen	Remarks
3 p. tetra phosphoric acid 20 p. H_2O 50 p. alcohol	*		
5 p. tetra phosphoric acid 20 p. H_2O 50 p. isopropyl alcohol	$\frac{1}{4}$" between electrodes Temperature from 23°C. to 40°C. Current Density investigated 0.5 to 1.25 amperes per square inch. *	3% gallium alloy of plutonium	Very little polishing or etching action.
5 p. tetra phosphoric acid 5 p. $C_2H_6O_2$ 8 p. isopropyl alcohol 1 p. H_2O	7/8" between electrodes 50°C. Current Density investigated 0.5 to 4.0 amperes per square inch. *	3% gallium alloy of plutonium.	Polishes and etches with properly regulated current density.
2 p. H_3PO_4 - 85% 3 p. H_2O	1" between electrodes Room Temperature *	95% uranium-plutonium alloy.	Wavy surface produced. Does not etch well.
3 p. tetra phosphoric acid 47 p. H_2O	1" between electrodes Room Temperature 23°C. *	1% gallium alloy of plutonium	Polishes at 2 amperes per square inch. Etches at 1 ampere per square inch. Polishes and etches well.
3 p. tetra phosphoric acid 17 p. H_2O	1" between electrodes Room temperature 23°C. *	95% uranium alloy of plutonium.	Polishes at 1 amper per square inch. Etches at 0.2 to 0.4 ampere per square inch. Surface somewhat wavy.
2 p. H_3PO_4 - 85% 3 p. H_2O	1" between electrodes Room Temperature 23°C to 25°C. *	90% uranium alloy of plutonium.	Etches at 0.5 ampere per square inch. Polishes at about 1 ampere per square inch. Current Density appears quite critical.

* Stainless-steel cathodes used for all electrolytes.

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Electrolyte	Conditions	Composition of Specimen	Remarks
3 p. tetra phosphoric acid 47 p. H_2O	1" between electrodes Room Temperature 23°C. *	3% gallium alloy of plutonium.	Polishes at about 2 amperes per square inch. Etches at about 0.5 amperes per square inch.

* Stainless-steel cathodes used for all electrolytes.

p. - Parts by volume.

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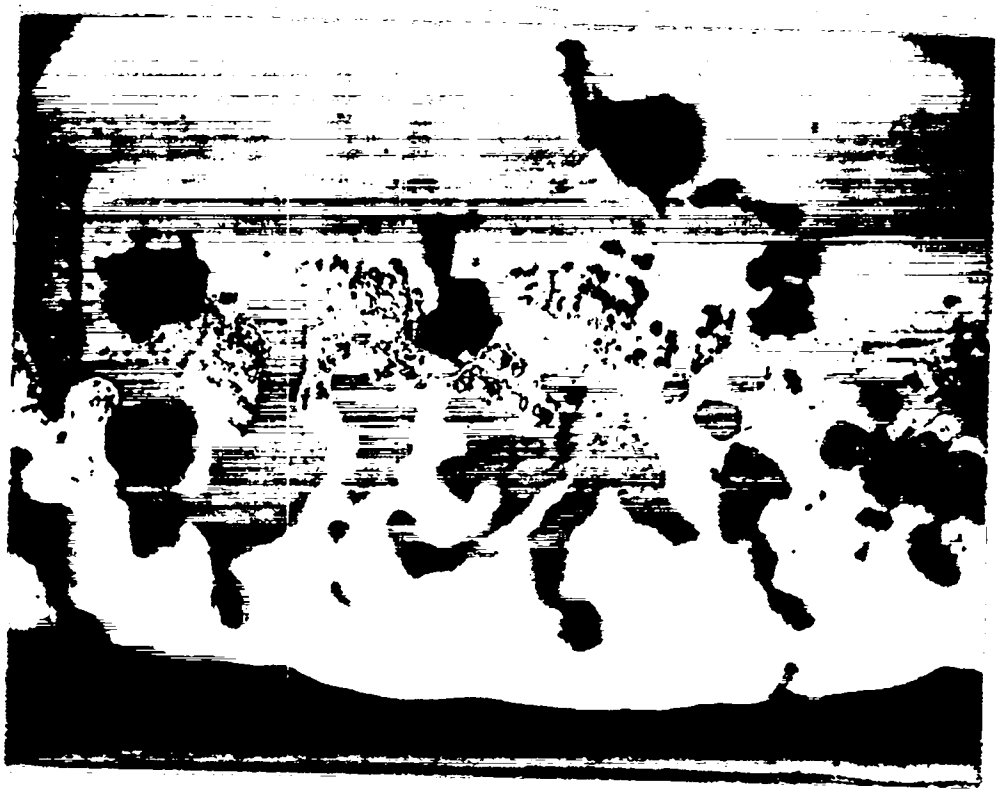


Fig. 1. Illustrating the false surface (grey areas) produced on the surface of plutonium by mechanical polishing.

No. 4072-3A Unetched 1000x

[redacted]

A. 100x
No. 4406-1

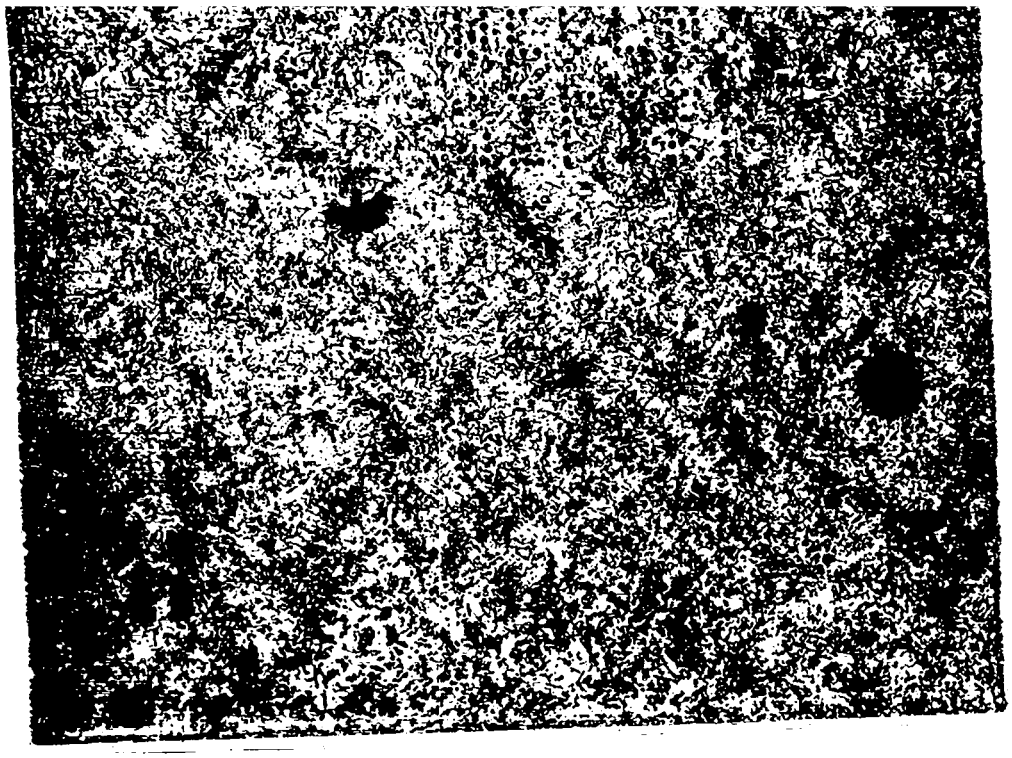
B. 250x
No. 4406-2

Fig. 2. Photomicrographs of nominally pure plutonium, remelted in MgO crucibles after reduction and then cast. Etchant: electrolytically in 50cc H_3PO_4 (85%), 90cc H_2O, 50cc C_2H_5OH.

C. 500x
No. 4406-3

D. 1000x
No. 4406-4

Fig. 2. Photomicrographs of nominally pure plutonium, remelted in MgO crucibles after reduction and then cast. Etchant: electrolytically in 50cc H_3PO_4 (85%) 90cc H_2O, 50cc C_2H_5OH.



A. 100x
No. 4979-8

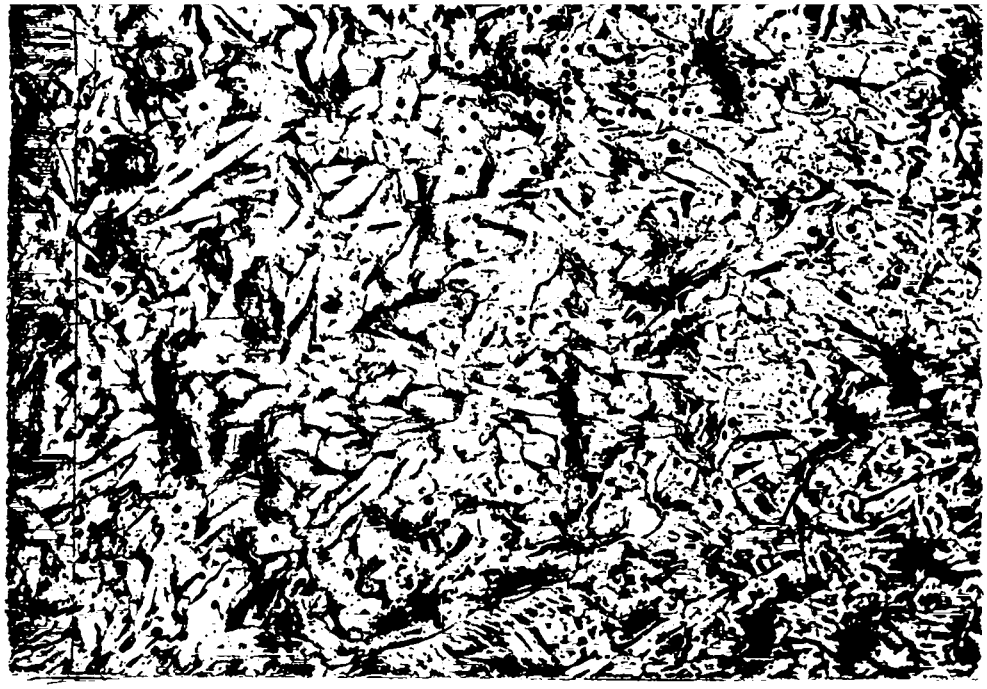
B. 250x
No. 4979-9

Fig. 3. Photomicrographs of 1% gallium alloy of plutonium cast and heated at 450°C for 16 hours. Density 17.57 g./cc. Etchant: electrolytically in 3 parts tetra phosphoric acid, 47 parts H_2O.

C. 500x
No. 4979-10

D. 1000x
No. 4979-11

Fig. 3c Photomicrographs of 1% gallium alloy of plutonium cast and heated at 450°C for 16 hours. Density 17.57g./cc. Etching electrolytically in 3 parts tetra phosphoric acid, 47 parts H_2O.



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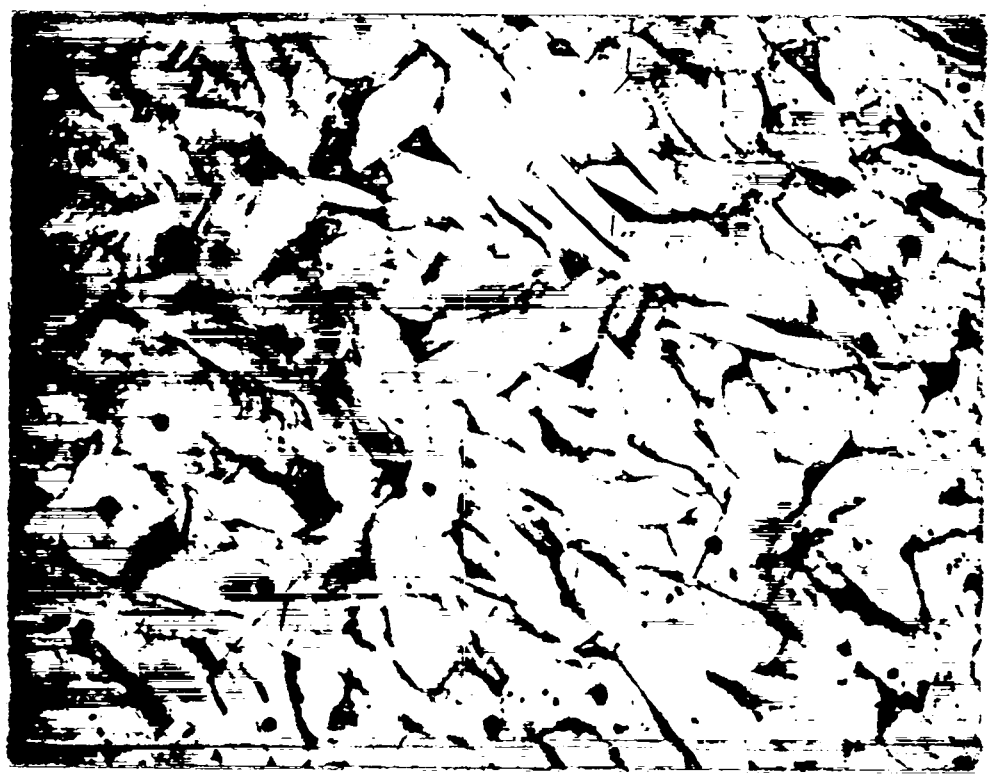
No. 4977-7



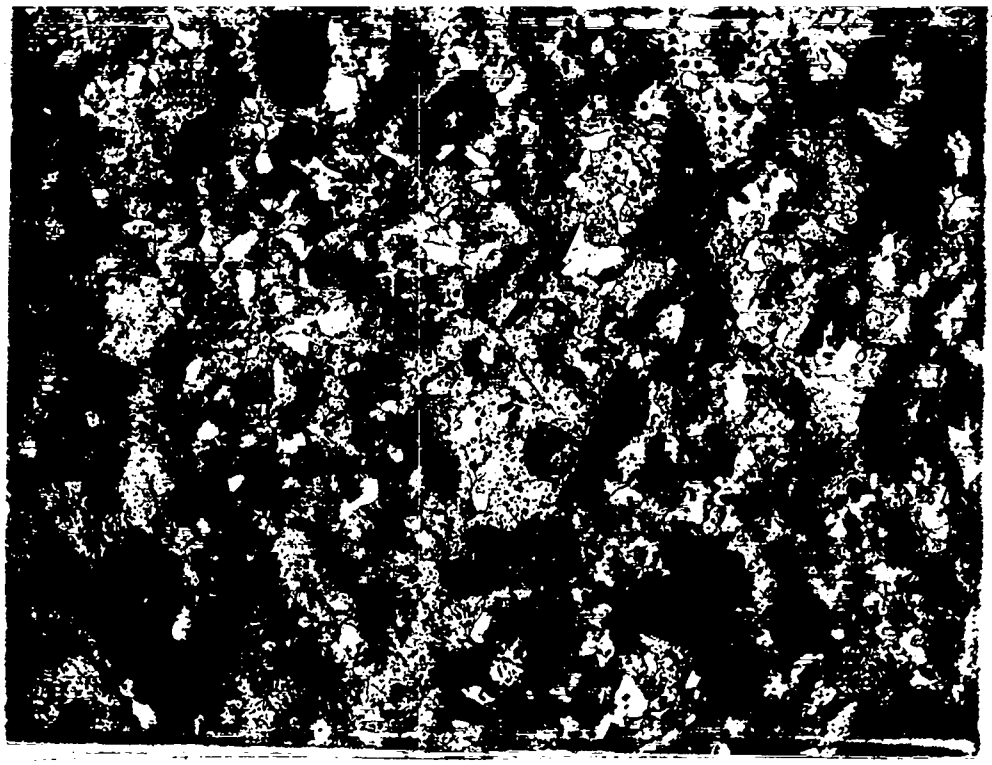
B. 250x
No. 4977-8

Fig. 4. Photomicrographs of 3% gallium alloy of plutonium as cast. Etchant: electrolytically in 6 parts H_3PO_4 - 85% - 9 parts H_2O - 5 parts $C_2H_6O_2$.

C. 500x
No. 4977-9

D. 1000x
No. 4977-10

Fig. 4. Photomicrographs of 3% gallium alloy of plutonium as cast. Etchant: electrolytically in 6 parts H_3PO_4 - 85%, 9 parts H_2O, - 5 parts $C_2H_6O_2$.



A. 100x
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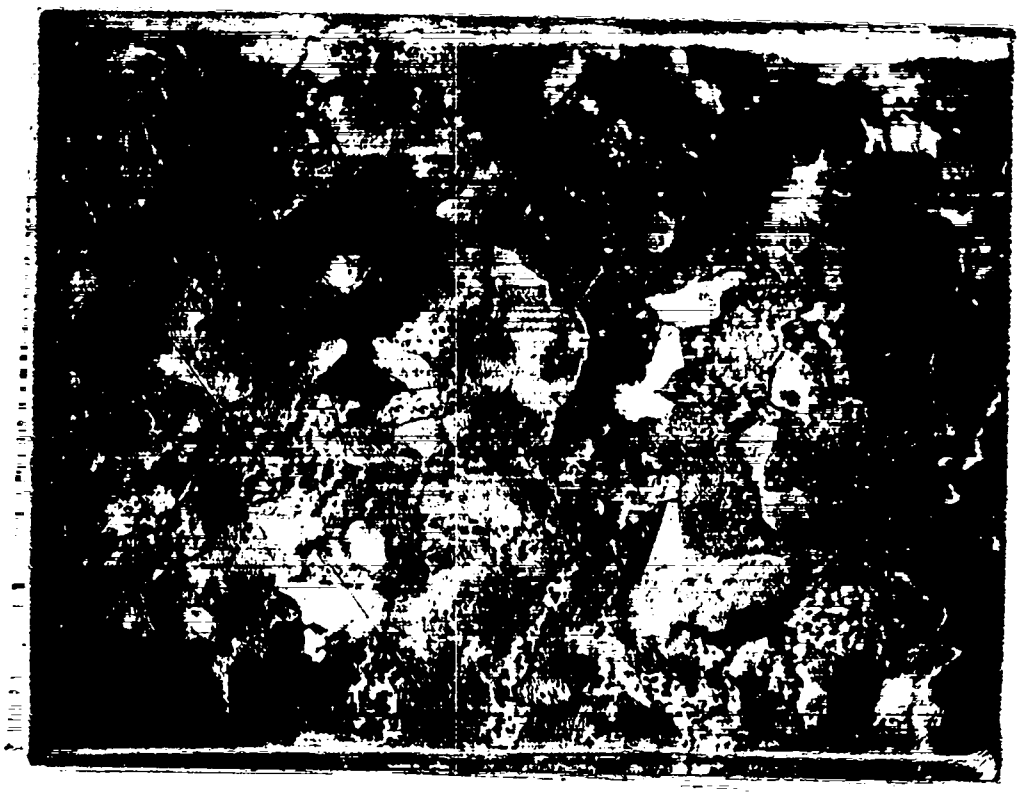


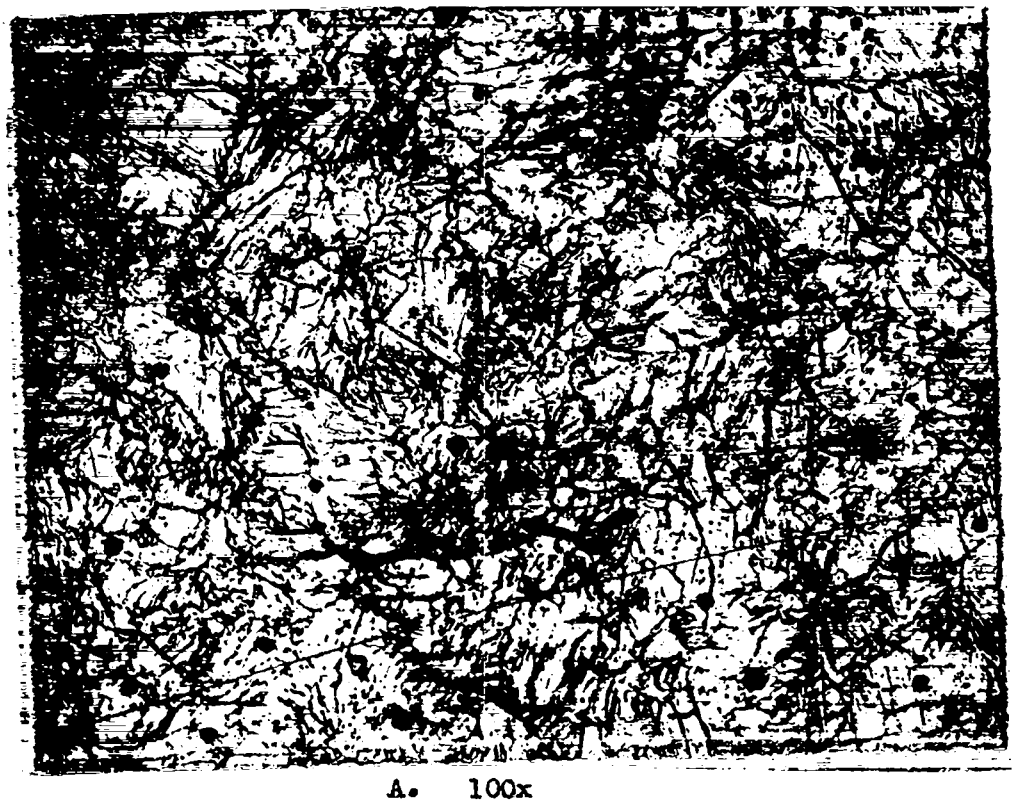
B. 250x
No. 4981-6

Fig. 5. Photomicrographs of 3% gallium alloy of plutonium cast and annealed at 550°C for 19 hrs. Etchant: electrolytically in 5 parts tetra phosphoric acid, 47 parts H_2O.

C. 500x
No. 4981-7

D. 1000x
No. 4981-13

Fig. 5. Photomicrographs of 3% gallium alloy of plutonium cast and annealed at 550°C for 19 hrs. Etchant: electrolytically in 3 parts tetra phosphoric acid, 47 parts H_2O.



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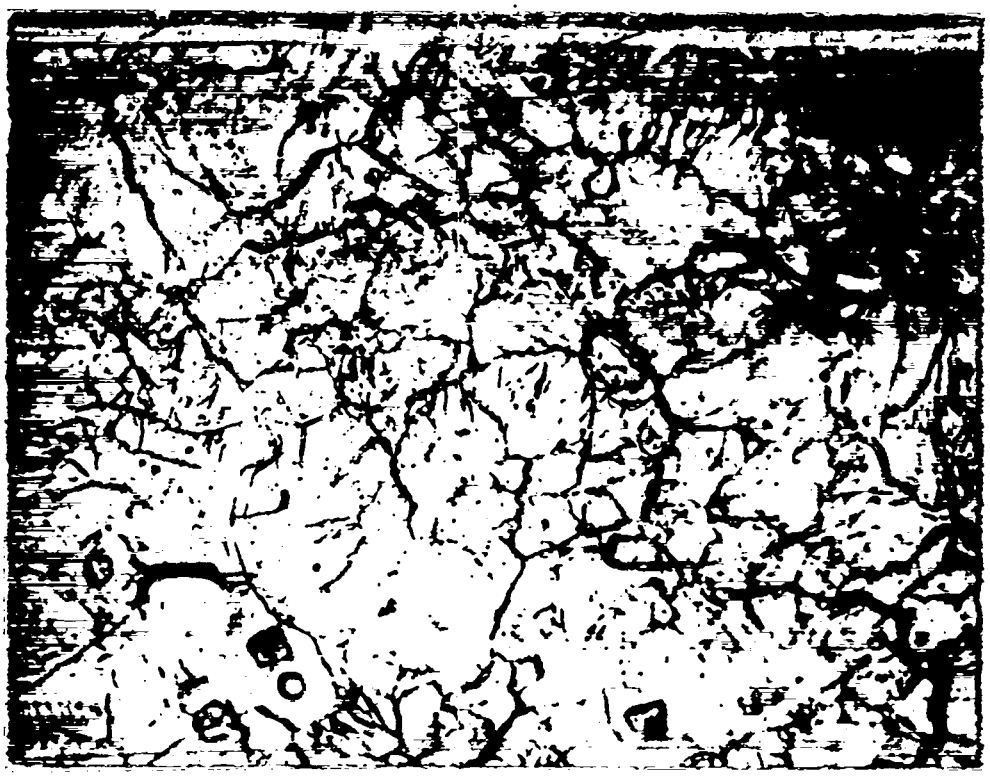

B. 250x
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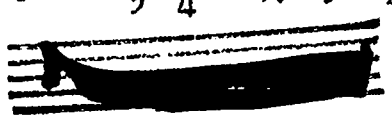
Fig. 6. Photomicrographs of 90% uranium, 10% plutonium alloy cast and annealed at 500° C for 4 hrs. Etchant: electrolytically in 4 parts H_3PO_4 - 85% , 6 parts H_2O.

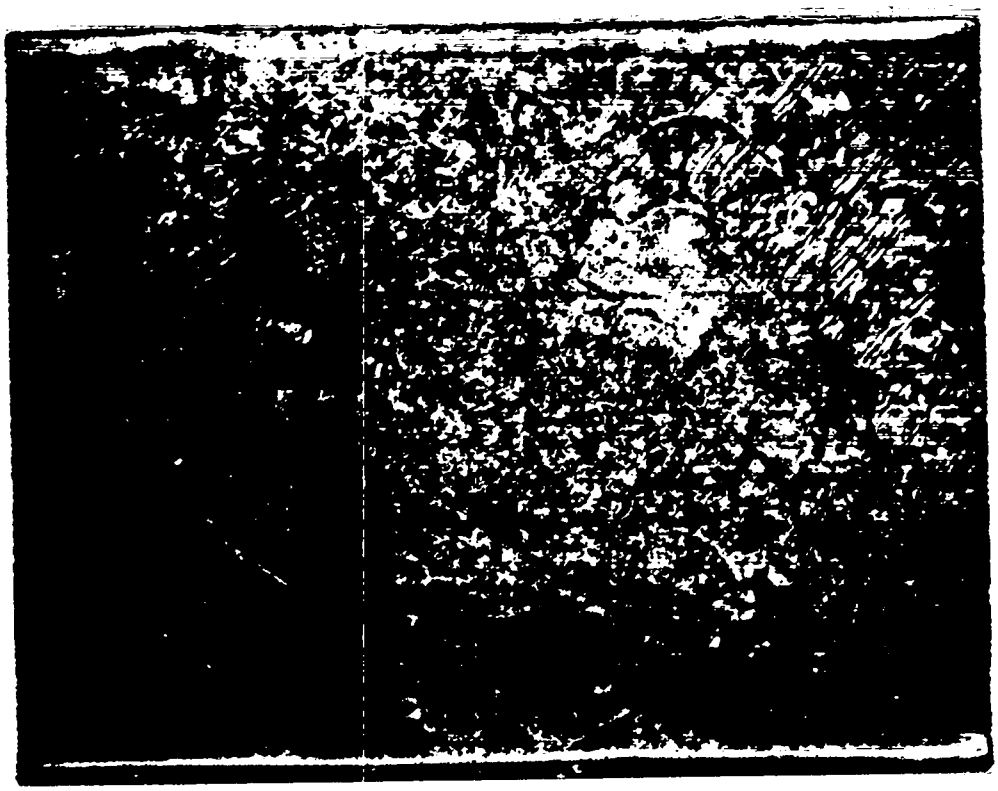


C. 500x
No. 4983-3

D. 1000x
No. 4983-4

Fig. 6. Photomicrographs of 90% uranium, 10% plutonium alloy cast and annealed at 500°C for 4 hrs. Etchant: electrolytically in 4 parts H_3PO_4 - 85%, 6 parts H_2O

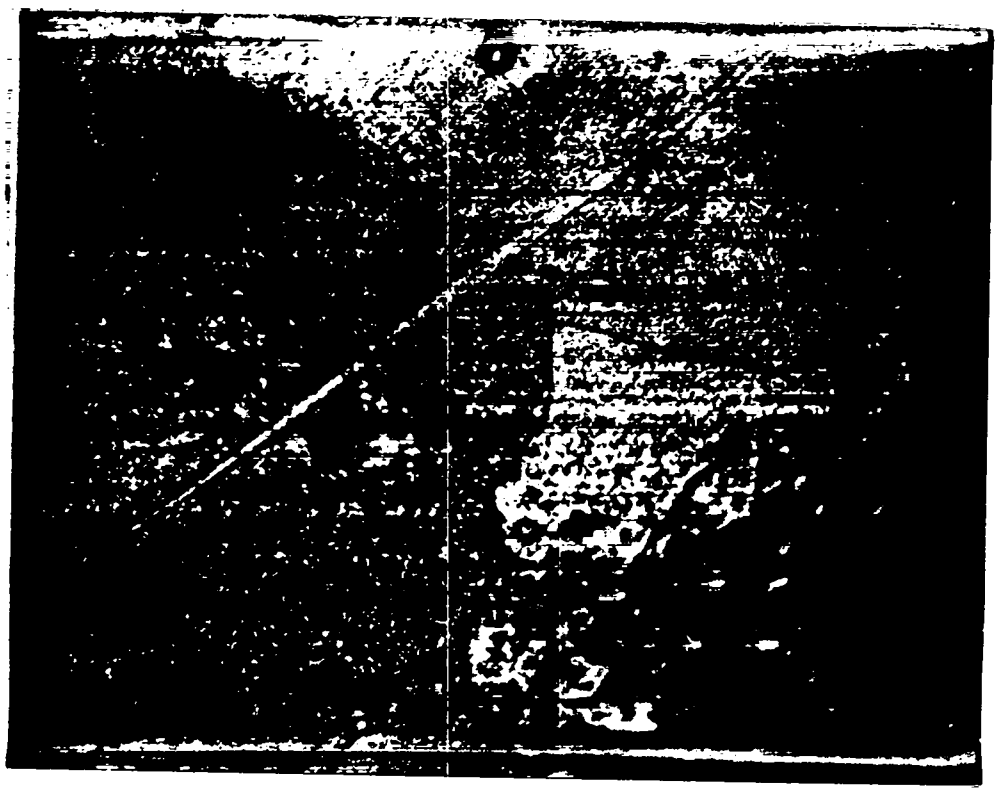
A. 100x
No. 4982-1



B. 250x
No. 4982-2

Fig. 7. Photomicrographs of 95% uranium 5% plutonium alloy cast and annealed at 500° C for 4 hrs. Etchant: electrolytically 15 ml. tetra phosphoric acid 85 ml H_2O.

C. 500x
No. 4982-3



D. 1000x
No. 4982-4

Fig. 7. Photomicrographs of 95% uranium 5% plutonium alloy cast and annealed at 500° C for 4 hrs. Etchant: electrolytically 15 ml tetra phosphoric acid - 85 ml H_2O.