

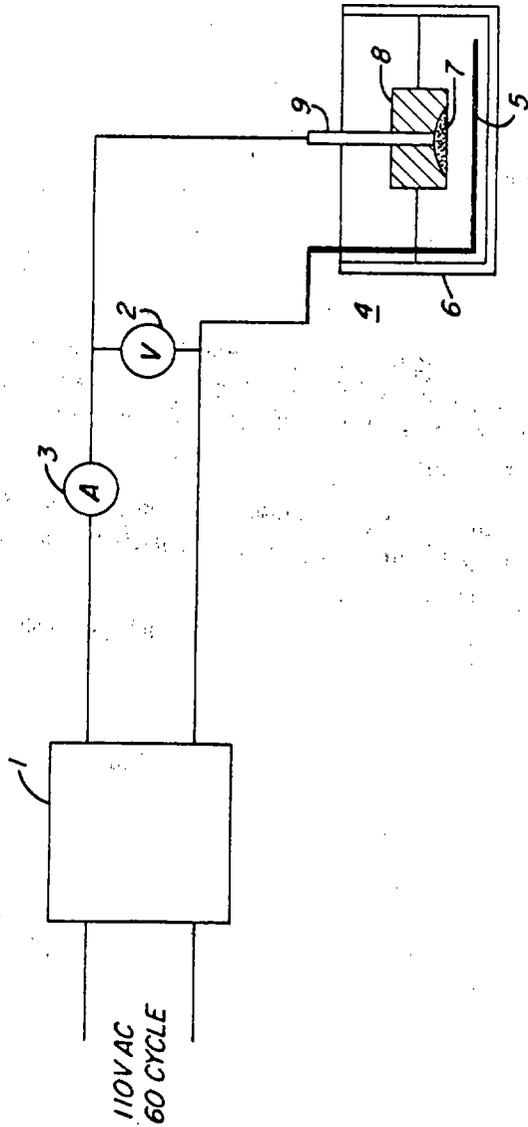
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A.C. ETCHING OF PLUTONIUM

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A.C. ETCHING OF PLUTONIUM

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ABSTRACT OF THE DISCLOSURE

A method of etching plutonium in which alternating current is passed through an electrolytic solution containing an inorganic acid, the said plutonium being one of the electrodes.

This invention relates to the electrolytic etching of metals and, more particularly, to the alternating current electro-etching of plutonium.

Plutonium metallographic samples have usually been etched by means of D.C. electrolytic techniques, with various solutions being used depending on which plutonium allotrope was under investigation and the particular metallographic features of interest. In the D.C. electrolytic etching of alpha plutonium, for example, the use of electrolytes base on orthophosphoric acid results in a polished (but unetched) surface which is active enough in polarized light to reveal grains fairly well. The use of chromic-acetic acid-based electrolytes on alpha plutonium reveals the structure by means of faint relief effects. The chromic-acetic acid electrolytes, however, do not provide consistently good results, and under even the best circumstances deposit spots of grey oxide on the surface and preferentially attack microcracks, which are a common feature of electrorefined high-purity alpha plutonium. Furthermore, the chromic-acetic acid-based electrolytes react quite strongly with alcohol and very violently with glycerine. The results of etching delta plutonium (stabilized at room temperature by alloying) by using D.C. techniques have in general also been variable.

A new method of etching, which involves A.C. rather than D.C. electrolysis, has been developed and is applicable to plutonium. This A.C. technique, again with different electrolytes depending on the material being studied and the effects desired, has been found to give dependable bright field delineation of plutonium microstructures without oxide deposition or preferential attack at the edges of microcracks or voids.

Accordingly, an object of the present invention is to provide a new method of etching of plutonium which will give dependable bright field delineation of plutonium microstructures without oxide deposition or preferential attack at the edges of microcracks or voids.

It is a further object of this invention to provide increased oxidation resistance ("passivation") to alpha plutonium.

It is another object of the invention to eliminate the staining caused by the formation of a flocculent layer on the surface of an etched specimen.

Other objects of the invention and particular procedural features will become apparent to those skilled in the art upon a review of the following specification with reference to the accompanying drawing, wherein:

The figure is a schematic diagram of the equipment utilized in the alternating current electrolytic polishing and etching.

The equipment illustrated in the figure is simple and inexpensive, consisting essentially of a 110 v., 60 cycle A.C. source, a 10-amp capacity variable transformer 1,

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voltage meter 2, current meter 3, and an electrolytic cell 4. One electrode 5 of the electrolytic cell 4 is stainless steel mesh, placed in the bottom of a Pyrex crystallizing dish 6, containing the electrolyte; the other electrode is the polished surface of the specimen 7. Specimens are mounted in a plastic specimen mount 8, and a stainless steel probe 9 inserted through a hole in the plastic mount 8 touches the back of the specimen 7 to establish electrical continuity in the circuit. The specimen-to-electrode distance is nominally 0.5 cm. and unless noted differently under a specific procedure the electrolytes are not stirred.

Example 1.—Alpha plutonium

Alpha, the room temperature allotrope of pure plutonium, can be consistently and satisfactorily etched utilizing an electrolyte having the following composition by volume: 10 nitric acid, 90 methanol. The voltage utilized may vary (4 to 8 v. A.C.) with a current density of 0.7 to 0.9 amp/sq. cc. The time may vary from 10 to 30 sec. and a specimen is rinsed first with water and then with methanol. A blast of hot air is utilized to dry the specimen. In addition the electrolyte composition may be varied, the above electrolyte being suitable from about 3 to 30% by volume nitric acid, the remainder consisting of methanol.

Grain boundaries and twins in alpha plutonium are delineated due to the variations in the rate at which metal is removed from grains having different orientations. The A.C. etch does not preferentially remove the metal adjacent to the microcracks. The microstructure revealed by this method is essentially the same as that revealed by other techniques but is not obscured by gaping holes marking the location of former microcracks or by electrodeposited spots of grey oxide. Also, the microstructure may be seen without resorting to the use of polarized light. The A.C. method is much more reliable in producing satisfactory results than is the D.C. technique.

Another advantage of the A.C. method is the increased oxidation resistance imparted to alpha plutonium. This "passivation" allows extended examination and re-examination of samples without the necessity for reworking them. A photomicrograph of an alpha plutonium surface that had been exposed to normal laboratory air (about 50% relative humidity) for 10 days after being etched by means of the A.C. technique showed a surface which was somewhat discolored (gold shades) but no loose oxide had formed. On samples prepared by other methods significant formation of nonadherent oxide usually can be seen in less than 24 hours. On an A.C. etched sample that had been periodically examined during a 38-day period no loose oxide was evident though the color of the surface had changed from gold to red, to blue, and finally to white-speckled blue. At 60 days, loose oxide had definitely formed in the microcracks and on the surface in the speckled regions of the specimen.

The etching step forms a light golden-brown flocculent layer on the surface of the specimen. However, if the etched surface is rinsed with water as soon as it is removed from electrolyte A, the flocculent layer is easily washed away. This layer is removed much more cleanly, leaving no stain, if the stainless steel probe is used to "dope" the electrolyte previous to etching the specimen. Doping is accomplished by "etching" the probe for 30 sec. at 1 amp, or until there is a slight discoloration of the electrolyte.

Increasing the current density to about 1.5 amp/sq. cm., when etching alpha, yields a microstructure having considerable "faceting" of the grain surfaces. This faceting may indicate subgraining. The high current density that produces this microstructural faceting also produces a feature termed here as "edge attack." Edge attack, or

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excessive pitting at the specimen periphery, is consistently associated with high current density.

Example 2.—Alpha plutonium

Combined polishing and etching by A.C. electrolysis is possible on alpha plutonium samples prepared only through 600 grit paper. The specimens are polished (samples finished on 600 grit paper) and electroetched in an electrolyte as set forth in Example 1. A voltage of 50 v. (A.C.) and a time of 45 sec. were utilized and the rinsing and drying operations were the same as given above for etching.

The specimen should be tilted away from the stainless steel mesh electrode so that the evolving gas will easily rise and escape. To achieve a uniform polish-etch, the specimen should be rotated 90° every 10 or 12 sec. During the combined polishing and etching operation, however, microcracks are extensively attacked, whereas during the electrolytic etching of mechanically polished surfaces the microcracks retain their original shapes.

Example 3.—Delta plutonium

Delta-stabilized plutonium can be etched satisfactorily by a twostep procedure involving both A.C. and D.C. To perform the step utilizing direct current a D.C. power supply of 0 to 50 v. and D.C. meters replace the 110 v., 60 cycle A.C. source and A.C. meters. In the first step (A.C.) an electrolyte of 90 parts by volume lactic acid, 15 parts by volume water and 6 parts by volume sulphuric acid is used. 18–20 v. A.C. is used for cored delta (50 v. for equilibrated delta) and times of 5–10 sec. for cored delta (20 sec. to 1 min. for equilibrated delta). The specimen is then rinsed very promptly. If rinsed quickly enough the second step (D.C.) may be avoided. In the second step the PuO₂ layer is removed by electrolyzing in a solution of 8 parts volume sulphuric acid, 5 parts by volume ethanol and 5 parts by volume glycerin. Utilizing the specimen as the anode the voltage of 35 v. D.C. is applied for 1 sec. The specimen is first rinsed with water and then with methanol. In this method as in the above-described method the electrolyte composition may vary within certain limits, e.g., water volume may vary between about 5 and 30 parts and the sulphuric acid volume between 1 and 10 parts as compared to 90 parts by volume lactic acid.

The cored structures often show small amounts of alpha plutonium between the delta dendrites. The problem encountered with A.C. etching of delta alloys is that the electrolyte reacts with delta plutonium to form on the specimen surface a thin and very adherent coating of what X-ray diffractometry indicates is PuO₂. If the specimen, after being removed from the bath, is rinsed very quickly with water, this layer will be too thin to obscure the microstructure. An etched specimen having a thick layer can be cleaned by Step 2, through X-ray diffractometry will even then indicate that some PuO₂ is still present on the etched surface. Step 2 etching times longer than 1 sec. will decrease the amount of PuO₂ remaining but will also polish away the A.C. etched surface.

Example 4.—Beta plutonium

In etching beta plutonium alloys an electrolyte as set

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forth in Example 3 may be used at 50 v. for 10 sec. The specimen is rinsed with water as soon as possible after removing the specimen from the electrolyte, then with methanol and dried with a blast of hot air. The A.C. etching of beta plutonium will not reveal twins or grain boundaries as well as does the chromic-acetic acid based D.C. etch, but it does reveal coring more clearly.

Since certain changes may be made in the above invention without departing from the scope thereof it is intended that the invention should not be limited by the above disclosure but only by the following appended claims.

What is claimed is:

1. The method of etching alpha plutonium comprising passing an alternating current through an electrolytic solution which contains alpha plutonium as one electrode, said electrolytic solution being from about 3 to 30% by volume nitric acid, the remainder comprising methanol.

2. A method as in claim 1 wherein electrolyte contains a small amount of stainless steel introduced into the solution by the previous etching of stainless steel.

3. A method as in claim 2 wherein the stainless steel is etched until there is a slight discoloration of the electrolyte.

4. The method of claim 1 wherein the electrolytic solution is about 10% by volume nitric acid, the remainder consisting of methanol and a small amount of stainless steel introduced into the solution by the previous etching of stainless steel.

5. The method of etching delta plutonium comprising passing an alternating current through an electrolytic solution which contains delta plutonium as an electrode, said electrolytic solution being about 90 parts by volume lactic acid, 5 to 30 parts by volume water and 1 to 10 parts by volume sulphuric acid.

6. The method of claim 5 wherein the delta plutonium specimen is immediately washed with water after electrolysis.

7. The method as in claim 5 wherein the delta plutonium dioxide layer is eliminated by electrolyzing the delta plutonium specimen in an electrolyte, said electrolyte being 8 parts by volume sulphuric acid, 5 parts by volume ethanol and 5 parts by volume glycerin for about 1 sec. at 35 v. D.C.

8. The method of etching beta plutonium comprising passing an alternating current through an electrolytic solution which contains beta plutonium as an electrode, said electrolytic solution being about 90 parts by volume lactic acid, 5 to 30 parts by volume water and 1 to 10 parts by volume sulphuric acid.

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