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A BRIGHT-FIELD, GRAIN STRUCTURE ETCH FOR DELTA PHASE STABILIZED PLUTONIUM

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A BRIGHT-FIELD, GRAIN STRUCTURE ETCH
FOR DELTA PHASE STABILIZED PLUTONIUM

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February, 1966

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A BRIGHT FIELD GRAIN STRUCTURE ETCH FOR DELTA PHASE STABILIZED PLUTONIUM

INTRODUCTION

This paper describes the development of a bright-field, grain structure etch usable on delta phase, stabilized plutonium alloys regardless of their metallurgical condition.

Grain structure etchants in common usage for delta phase, stabilized plutonium alloys are based on the production of an adherent-surface, oxide layer to permit examination under polarized light. Attempts to use this method on cored delta phase stabilized alloys have not been successful, and only fair results have been obtained on homogenized alloys; therefore, a better etching technique for these alloys needed to be developed.

SUMMARY

An oxide-free surface delineating grain boundaries was produced in delta phase, stabilized plutonium alloys having a variety of metallurgical treatments. Zirconium stabilized alloys were etched with solutions based on orthophosphoric, tetraphosphoric or citric acid. Delta phase plutonium stabilized with aluminum or gallium could only be etched with 200 ml ethanol, 116 g citric acid and 10 ml of a solution of either potassium or sodium nitrate in 100 ml of water.

EXPERIMENTAL PROCEDURE

Equipment

The etching development was done with a Zeiss electro-polisher, which allows the metallographer to observe the metal surface at approximately 200X magnification during electro-polishing. This observation is highly desirable

because the metallographer can watch the microstructure develop during etching and can stop etching when the best structure is obtained. Viewing the sample surface during etching is also advantageous in etchant evaluation or development since corrosion or pitting of the surface is easily seen. The current density versus voltage for any electrolyte can easily be determined. The visual observation of the behavior of the metal surface at different portions of this curve makes etchant evaluation an easier job.

A cross-sectional sketch of this equipment and its interior design is illustrated in Figure 1.⁽¹⁾ The unique feature of this unit is the combination of an electrolytic cell and an incident light microscope. The sample (1) is held by a spring loaded stainless steel plunger (2) (which also serves as the anode of the electrolytic cell) against a small orifice (3). The electrolyte, contained in a small dish (4), is pumped by a plastic coated pump (5) to the front end of the unit and flows across the sample surface back to the dish. A stainless steel cup with a small window in the end (6) protects the microscope objective and also serves as the cathode connection for the electrolytic cell. The light for microscopic observation during etching passes through air, glass, and the electrolyte.

(1) F. Raemmele and K. Veit, "A New Polishing Concept from East Germany, *Metals Progress*, vol. 81, no. 1, January, -1962:

FIGURE 1. Cross Sectional Sketch of Zeiss Electroetcher

Most of the samples to be etched are mounted in a nonelectrical conducting, polyester resin; therefore, electrically conductive paint is used to make electrical contact between the stainless steel plunger (2, Figure 1) and the mounted sample. Figure 2 shows a painted, mounted sample in place and ready to etch.

The Zeiss etcher was placed in a small satellite glove box connected to

the metallographic glove box with a plastic sleeve. Figure 3 shows the etcher in operation.

Sample Preparation

Specimens are mounted in polyester resin in 3/4 in. ID teflon molds. After removal of the mounted samples from the molds, they are faced flat on a small lathe in successive increments of 0.010, 0.005, 0.002, 0.002, 0.001 and 0.001 in. to minimize surface

FIGURE 2. A Sample Ready for Etching in the Zeiss Electropolisher. E-5373

FIGURE 3. Glove Boxed Zeiss Electropolisher in Operation. E-5374

strain. The samples are then ground on 180, 320, and 600 mesh SiC grit cloths on 240 rpm lapping wheels, using carbon tetrachloride as a lubricant. Rough polishing was done, on a Syntron vibratory polisher, using a slurry of 6 μ aluminum oxide in carbon tetrachloride on silk. The final polishing, also on a Syntron vibratory

polisher, was on Microcloth, using a slurry of 0.3 μ aluminum oxide in carbon tetrachloride. Prior to etching, the mounted sample is painted with electrically conducting paint.

RESULTS AND DISCUSSION

A large number of etchant compositions were investigated in this study. Components of the various etches are shown in Table I.

Delta phase, stabilized plutonium-zirconium alloys were quite easy to etch. A bright-field, grain structure was produced on Pu-10, 15 and 20 wt. % Zr alloys in various metallurgical conditions, with etchants based on orthophosphoric acid, tetraphosphoric acid or citric acid. Figure 4 shows a homogenized Pu-15 wt.% Zr alloy etched in 30 ml water, 150 ml 2-ethoxyethanol, 20 ml tetraphosphoric acid for 2 min at 10 mA/cm².

Figures 5 and 6 illustrate two different heat treatments of Pu-10 wt.% Zr alloys etched in 110 ml ethanol, 50 ml ethylene glycol and 20 ml orthophosphoric acid for 1 min at 14 mA/cm².

The only etchant producing an oxide free surface that delineated grain boundaries in Pu-4 at.% Al or Pu-0.8, 1.0 and 1.3 wt.% Ga alloys was 200 ml ethanol, 116 g citric acid and 10 ml of a solution of 25 g of either KNO₃ or NaNO₃ in 100 ml of water. When used at 5-10 V an excellent grain boundary etch is produced in 2 to 3 min regardless of the thermal treatment. Additions of an equivalent amount of HNO₃ water solution did not yield results comparable to the KNO₃ or NaNO₃ water solution. Results obtained with calcium, nickel, copper or iron nitrates were also unsuitable.

TABLE I
COMPONENTS FOR ETCHANT EVALUATION FOR STABILIZED
DELTA PHASE PLUTONIUM ALLOYS

<u>Acids</u>	<u>Solvents</u>	<u>Other</u>
Nitric	Ethanol	Halide salts
Orthophosphoric	Methanol	Nitrate salts
Tetraphosphoric	2-ethoxyethanol	
Sulfuric	Hydrogen peroxide	
Acetic	Ethylene glycol	
Chromic	Water	
Citric		
Oxalic

FIGURE 4. Homogenized Pu-15 wt% Zr.
Etched. R-5976 500X.

FIGURE 5. Pu-10 wt% Zr Alloy Heat
Treated 8 hr at 230 °C. Etched. 500X.
R-6426

FIGURE 6. Pu-10 wt% Zr Alloy Heat
Treated 2 hr at 500 °C and 16 hr at
230 °C. Etched. 500X. R-6414

Figure 7 illustrates the microstructure of as-cast Pu-4 at. % Al alloy. Note that although the coring has caused a difference in etching rate, which produces surface relief, excellent grain structure is obtained. Figure 8 shows the same alloy after cold working and homogenization for 150 hr at 450 °C.

Figures 9, 10, and 11 are of homogenized Pu-0.8, 1.0 and 1.5 wt. % Ga alloys etched with the citric acid, ethanol, nitrate solution at 5 to 10 V for 1 to 2 min.

Figures 12, 13, and 14 are as-polished and etched structures of Pu-1 wt. % Ga samples with different cooling rates. The sample in Figure 12 has been cooled at 1 °C/min from 775 °C to 640 °C (epsilon portion of equilibrium diagram) and quenched to room temperature. The sample in Figure 13 was cooled from 775 °C at 15 °C/min to 640 °C and quenched to room temperature. Large core clusters can be seen in the as-polished structure as a result of the 15 °C/min through the liquid plus epsilon region of the Pu-Ga equilibrium phase diagram. After etching, these large core clusters consist of similarly oriented fine

FIGURE 7. As-cast. Pu-4 at.% Al Alloy. Etched. 150X. R-6093

FIGURE 8. Cold Worked and Homogenized Pu-4 at.% Al Alloy. Etched. 250X. R-6334

FIGURE 9. Pu-0.8 wt% Ga Alloy Homogenized 150 hr at 450 °C. Etched. 250X. R-6345

FIGURE 10. Pu-1.0 wt% Ga Alloy Homogenized 150 hr at 450 °C. Etched. 250X. R-6348

FIGURE 11. Pu-1.3 wt% Ga Alloy Homogenized 150 hr at 450 °C. Etched. 250X. R-6350

A. As-polished. 250X. R-6455

B. Etched. 250X. R-6456.

*FIGURE 12. Pu-1 wt% Ga Alloy Cooled
at 1 °C/min from 775 °C to 640 °C and
Quenched*

A. As-polished. 250X. R-6453.

B. Etched. 250X. R-6457.

*FIGURE 13. Pu-1 wt% Ga Alloy Cooled
at 15 °C/min from 775 °C to 640 °C and
Quenched*

A. As-polished. 250X. R-6454.

B. Etched. 250X. R-6458.

*FIGURE 14. Pu-1 wt% Ga Alloy Cooled
at 15 °C/min from 775 °C to 640 °C
Held at 640 °C for 15 min and Quenched*

grains. The rest of the structure results from the quench from 640 °C and is similar to the grain structure in Figure 12. The sample in Figure 14 was cooled from 775 °C at 15 °C/min to 640 °C, held at 640 °C for 15 min, and then quenched to room temperature. During the 15 min hold at 640 °C, the large core clusters have disappeared because of homogenization. (2)

Figure 15 is the etched microstructure of a Pu-1 wt.% Ga alloy cast into a 625 °C mold, cooled at approximately 3 to 5 °C/min to 425 °C, held for about 1 hr at 425 °C, and slow cooled to room temperature. Sharp grain boundaries are evident even though the grains are cored.

FIGURE 15. Pu-1 wt% Ga Alloy Cast into a 625 °C Mold, Cooled at Approx. 3 to 5 °C/min to 425 °C, Held at 425 °C for 1 hr and Furnace Cooled to Room Temperature. 250X. R-6520

CONCLUSIONS

Excellent bright-field, grain structure delineation on delta phase plutonium stabilized with zirconium

was obtained by using any of the following etchants:

- (1) 30 ml water,
150 ml 2-ethoxyethanol,
20 ml tetraphosphoric acid;
- (2) 110 ml ethanol,
50 ml ethylene glycol,
20 ml orthophosphoric acid;
- (3) 200 ml ethanol,
116 g citric acid,
10 ml of a solution of 25 g
potassium or sodium nitrate
per 100 ml of water.

Bright field, grain structure delineation on delta phase plutonium stabilized with aluminum or gallium was obtained only with etch number 3.

ACKNOWLEDGMENTS

The author wishes to thank D. G. Rencken for his help in developing this technique.

(2) H. R. Gardner. *Physical and Mechanical Metallurgy Studies on Delta Stabilized Plutonium-Gallium Alloys*, BNWL-13. April, 1965.

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